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# Non-conventional bonding between organic molecules. The "halogen bond" in crystalline systems

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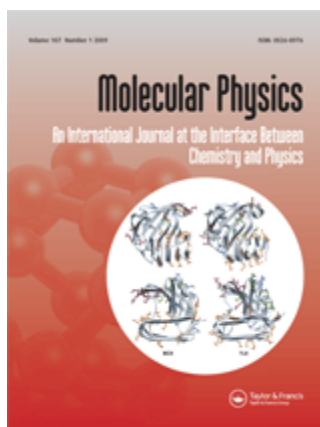
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**Non-conventional bonding between organic molecules. The "halogen bond" in crystalline systems**

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10 **Non-conventional bonding between organic molecules. The "halogen bond" in**  
11 **crystalline systems**  
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28 **APPENDIX I**  
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5 Consider a molecule (A) with nuclei of charge  $Z_j$  at points  $(j) = [x_j y_j z_j]$ . Let  $\rho_k$  be the  
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7 electron density in an elementary volume  $V_k$  centered at point  $(k) = [x_k y_k z_k]$ .  $\rho_k$  is derived  
8  
9 from MP2/6-31G\*\* wavefunctions. Each e-pixel has charge  $q_k = \rho_k V_k$ . In an usual MO  
10  
11 calculation for a medium size organic molecule, with typical steps of  $0.08 \text{ \AA}$ , one has some  
12  
13  $10^6$  pixels, too many for practical use; the distribution is then contracted into  $n \times n \times n$   
14  
15 super-pixels,  $n$  being called the condensation level. Each pixel is assigned to a particular  
16  
17 atom in the molecule, as follows. Let  $p$  be the number of atoms for which the nucleus-pixel  
18  
19 distance is smaller than the atomic radius. If  $p=1$ , the pixel is assigned to that atom. If  $p >$   
20  
21  $1$ , the pixel is assigned to the atom from which the distance is the smallest fraction of the  
22  
23 atomic radius. If  $p = 0$ , the pixel is assigned to the atom whose atomic surface is nearest.

24  
25 Consider now a second molecule, B with nuclei of charge  $Z_m$  at points  $(m) = [x_m y_m$   
26  
27  $z_m]$ , and whose e-pixels of charge  $q_i = \rho_i V_i$  are at positions  $(i) = [x_i y_i z_i]$ . Let  $R_{ln}$  be  
28  
29 the distance between any two centers of pixels or nuclear positions  $l$  and  $n$ ; the  
30  
31 electrostatic potential  $\Phi_i$  generated by molecule A at point  $(i)$  of the charge density of  
32  
33 molecule B and that generated by molecule A at nucleus  $m$  of molecule B,  $\Phi_m$ , with  
34  
35 the corresponding Coulombic potential energies  $E_i$  and  $E_m$ , are respectively:

$$36$$

$$37 \Phi_i = 1/(4\pi\epsilon_0) [ \sum_k q_k / R_{ik} + \sum_j Z_j / R_{ij} ]; \quad E_i = q_i \Phi_i \quad (1)$$

$$38$$

$$39 \Phi_m = 1/(4\pi\epsilon_0) [ \sum_k q_k / R_{km} + \sum_j Z_j / R_{jm} ] \quad E_m = Z_m \Phi_m \quad (2)$$

$$40$$

$$41 E_{\text{Coul,AB}} = \sum_i E_i + \sum_m E_m \quad (3)$$

42  
43  
44 When e-pixels of two approaching molecules overlap, besides the un-physical aspect  
45  
46 of the matter, numerical singularities in the  $R^{-1}$  dependence may result for very short  
47  
48 pixel-pixel distances; all pixel-pixel distances shorter than half the stepsize of the  
49  
50 pixel mesh are reset at half the stepsize (the 'collision avoidance' procedure).

51  
52 Let  $\epsilon_i$  be the total electric field exerted by surrounding molecules at pixel  $i$ ,  $\alpha_i$  the  
53  
54 polarizability at pixel  $i$ , and  $\mu_i$  the dipole induced at pixel  $i$  by that field. The linear  
55  
56 polarization energy is:

$$57$$

$$58$$

$$59 E_{\text{Pol},i} = -1/2 \mu_i \epsilon_i = -1/2 \alpha_i \epsilon_i^2 \quad (4)$$

$\alpha_i$  is approximated in the PIXEL scheme as  $\alpha_i = (q_i/Z_{\text{atom}}) \alpha_{\text{atom}}$ , where  $Z_{\text{atom}}$  and  $\alpha_{\text{atom}}$  are the atomic charge and polarizability of the atom to whose basin the pixel belongs (from standard repertories). The sum of  $\alpha_i$  's is equal to the total volume polarizability of the molecule.

As before, when e-pixels of two molecules overlap pixel-pixel distances are subjected to the 'collision avoidance' scheme (see above); then, the polarization energy at pixel  $i$  is damped as:

$$E_{\text{Pol},i} = -1/2 \alpha_i [\varepsilon_i d_i]^2 \quad \text{for } \varepsilon < \varepsilon_{\text{max}}, d_i = \exp(-\varepsilon_i / (\varepsilon_{\text{max}} - \varepsilon_i)) \quad (5)$$

and  $E_{\text{Pol},i} = 0$  for  $\varepsilon > \varepsilon_{\text{max}}$ .  $\varepsilon_{\text{max}}$ , the limiting field, is an adjustable empirical parameter in the formulation. The total polarization energy at a molecule is the sum of polarization energies at each of its electron density pixels,  $E_{\text{Pol,TOT}} = \sum E_{\text{Pol},i}$ .

Dispersion energies are calculated as a sum of pixel-pixel terms in a London-type expression:

$$E_{\text{Disp,AB}} = (-3/4) \sum_{i,A} \sum_{j,B} E_{\text{OS}} f(R) \alpha_i \alpha_j / [(4\pi\varepsilon^0)^2 (R_{ij})^6] \quad (6)$$

$$f(R) = \exp[-(D/R_{ij} - 1)^2] \quad (\text{for } R_{ij} < D) \quad (7)$$

where  $D$  is an adjustable empirical parameter.  $E_{\text{OS}}$  (the 'oscillator strength') can be taken in a first approximation as the energy of the highest occupied molecular orbital (HOMO), or, in a more refined approach, by considering each pixel as a separate oscillator, with a formal ionization potential  $I_i$ , which in turn is a function of the ionization potential,  $I^\circ$  of the atom to whose basin the pixel belongs, and of the distance between the pixel and the atomic nucleus,  $R_i$ :

$$E_{\text{OS}} = (I_i I_j)^{1/2}; \quad I_i = I^\circ \exp(-\beta R_i) \quad (8)$$

The empirical parameter  $\beta$  is a function of the atom type (see Table).

For the repulsion energy, the total charge density overlap integral between molecules A and B calculated over the original uncontracted charge densities is subdivided into contributions from pairs of atomic species  $m$  and  $n$ ,  $S_{mn}$ . The expressions are:

$$S_{AB} = \sum_{i,A} \sum_{j,B} [\rho_i(A) \rho_j(B)] V \quad (9)$$

$$E_{Rep,mn} = (K_1 - K_2 \Delta\chi_{mn}) S_{mn} \quad (10)$$

where  $\Delta\chi_{mn}$  is the corresponding difference in Pauling electronegativity.  $K_1$  and  $K_2$  are positive disposable parameters. For atoms with  $Z > 30$  (in this case Br and I) the presence of the  $d$ -electrons in the valence shell produces larger overlap and hence a slight (8%) decrease in  $K_1$  is introduced. The total repulsion energy is the sum over all  $m$ - $n$  pairs.

The total intermolecular Pixel interaction energy is:

$$E_{Tot} = E_{Coul} + E_{Pol} + E_{Disp} + E_{Rep} \quad (11)$$

The empirical parameters in the Pixel formulation were optimized considering 1) the agreement between calculated lattice energies and experimental heats of sublimation for organic crystals, 2) interaction energies between molecular dimers in comparison with ab initio calculations, and 3) qualitative agreement between Pixel partitioned energies and Intermolecular Perturbation Theory (IMPT) partitioned energies. The numbers are  $\epsilon_{max} = 150 \cdot 10^{10} \text{ V m}^{-1}$  in eq. (5),  $D = 3.0 \text{ \AA}$  in eq. (7),  $K_1 = 4800$  and  $K_2 = 1200$  in eq. (10) for energies in  $\text{kJ mol}^{-1}$  with electron densities in  $\text{electrons \AA}^{-3}$ . While these are suggested as universal parameters, very minor adjustments can be made to fit any desired thermochemical or structural property of the particular system under investigation, without substantial loss of physical realism.

The PIXEL computer code and documentation, OPiX package, are downloadable under the conditions stated from the author's site: <http://users.unimi.it/gavezzot>

**Table** Physical properties of atoms in the Pixel formulation

atom	atomic radius, Å	atomic polarizability, Å <sup>3</sup>	electronegativity	ionization potential, au	
				I°	β
H	1.10	0.39	2.1	0.500	0.4
C aliphatic	1.77	1.05	2.5	0.414	0.8
C aromatic	1.77	1.35	2.5	0.414	0.9
C aromatic bridge	1.77	1.90	2.5	0.414	1.05
N	1.64	0.95	3.0	0.534	0.5
O	1.58	0.75	3.5	0.500	0.4
F	1.46	0.50	4.0	0.640	0.0
Cl	1.76	2.30	3.0	0.477	0.35
S	1.81	3.00	2.5	0.381	0.4
Br	1.87	3.27	2.80	0.434	0.1
I	2.03	5.50	2.50	0.384	0.1

A.Gavezzotti, Molecular Aggregation, Oxford University Press, Oxford 2007, pp.304ff.

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27 **APPENDIX II**  
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Atomic coordinates for all the molecule involved in the calculations

## iodoisopropane

I	0.0000	0.0000	0.0000
C	0.0000	0.0000	-2.1500
C	1.2574	-0.7259	-2.6633
C	-1.2574	-0.7259	-2.6633
H	0.0000	1.0182	-2.5100
H	2.1392	-0.2167	-2.3033
H	1.2574	-0.7259	-3.7433
H	1.2574	-1.7441	-2.3033
H	-2.1392	-0.2167	-2.3033
H	-1.2574	-0.7259	-3.7433
H	-1.2574	-1.7441	-2.3033

## bromoisopropane

BR	0.0000	0.0000	0.0000
C	0.0000	0.0000	-1.9500
C	1.2574	-0.7259	-2.4633
C	-1.2574	-0.7259	-2.4633
H	0.0000	1.0182	-2.3100
H	2.1392	-0.2167	-2.1033
H	1.2574	-0.7259	-3.5433
H	1.2574	-1.7441	-2.1033
H	-2.1392	-0.2167	-2.1033
H	-1.2574	-0.7259	-3.5433
H	-1.2574	-1.7441	-2.1033

## benzonitrile

N	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.138000
C	0.000000	0.000000	-2.538600
C	0.000000	-1.214600	-3.235800
C	0.000000	-1.213600	-4.606700
C	0.000000	-0.000000	-5.320100
C	0.000000	1.213600	-4.606700
C	0.000000	1.214600	-3.235800
H	0.000000	-2.149400	-2.695000
H	0.000000	-2.150800	-5.143400
H	0.000000	0.000000	-6.400100
H	0.000000	2.150800	-5.143400
H	0.000000	2.149400	-2.695000

## benzonitrile pentafluoro

N	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.143100
C	-0.000001	-0.000001	-2.576000
C	-0.000001	-1.193701	-3.288400
C	-0.000001	-1.198301	-4.666100
C	-0.000001	-0.000001	-5.350900
C	-0.000001	1.198299	-4.666100
C	-0.000001	1.193699	-3.288400
F	-0.000001	-2.349700	-2.630300
F	-0.000001	-2.348201	-5.347400
F	-0.000001	-0.000001	-6.680700
F	-0.000001	2.348199	-5.347400
F	-0.000001	2.349699	-2.630300

## benzoquinone

O	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.222000
C	0.000000	1.264300	-1.981700
C	-0.000001	1.264299	-3.311700
C	-0.000001	-0.000001	-4.071400
O	-0.000001	-0.000001	-5.293400
C	-0.000001	-1.264301	-3.311700
C	0.000000	-1.264300	-1.981700
H	0.000000	2.204300	-1.449900
H	-0.000001	2.204299	-3.843500
H	-0.000001	-2.204301	-3.843500
H	0.000000	-2.204300	-1.449900

## chlorobenzene

CL	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.740000
C	0.000000	1.199450	-2.432500
C	-0.000000	1.199450	-3.817500
C	-0.000000	-0.000000	-4.510000
C	-0.000000	-1.199450	-3.817500
C	0.000000	-1.199450	-2.432500
H	0.000000	2.134800	-1.892500
H	-0.000000	2.134800	-4.357500
H	-0.000000	-0.000000	-5.590000
H	-0.000000	-2.134800	-4.357500
H	0.000000	-2.134800	-1.892500

## bromobenzene

BR	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.900000
C	-0.000000	1.199450	-2.592500
C	-0.000000	1.199450	-3.977500
C	-0.000000	-0.000000	-4.670000
C	-0.000000	-1.199450	-3.977500
C	-0.000000	-1.199450	-2.592500
H	0.000000	2.134800	-2.052500
H	-0.000000	2.134800	-4.517500
H	-0.000000	-0.000000	-5.750000
H	-0.000000	-2.134800	-4.517500
H	0.000000	-2.134800	-2.052500

## iodobenzene

I	0.000000	0.000000	0.000000
C	0.000000	0.000000	-2.100000
C	-0.000000	1.199450	-2.792500
C	-0.000000	1.199450	-4.177500
C	-0.000000	-0.000000	-4.870000
C	-0.000000	-1.199450	-4.177500
C	-0.000000	-1.199450	-2.792500
H	0.000000	2.134800	-2.252500
H	-0.000000	2.134800	-4.717500
H	-0.000000	-0.000000	-5.950000
H	-0.000000	-2.134800	-4.717500
H	0.000000	-2.134800	-2.252500

## chlorobenzene pentafluoro

CL	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.740000
C	0.000000	1.199399	-2.432500
C	-0.000001	1.199399	-3.817500
C	-0.000001	-0.000001	-4.510000
C	-0.000001	-1.199401	-3.817500
C	0.000000	-1.199400	-2.432500
F	0.000000	2.359900	-1.762500
F	-0.000001	2.359899	-4.487500
F	-0.000001	-0.000001	-5.850000
F	-0.000001	-2.359901	-4.487500
F	0.000000	-2.359900	-1.762500

## bromobenzene pentafluoro

BR	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.900000
C	-0.000001	1.199399	-2.592500
C	-0.000001	1.199399	-3.977500
C	-0.000001	-0.000001	-4.670000
C	-0.000001	-1.199401	-3.977500
C	-0.000001	-1.199400	-2.592500
F	0.000000	2.359900	-1.922500
F	-0.000001	2.359899	-4.647500
F	-0.000001	-0.000001	-6.010000
F	-0.000001	-2.359901	-4.647500
F	0.000000	-2.359900	-1.922500

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## iodobenzene pentafluoro

I	0.000000	0.000000	0.000000
C	0.000000	0.000000	-2.100000
C	-0.000001	1.199399	-2.792500
C	-0.000001	1.199399	-4.177500
C	-0.000001	-0.000001	-4.870000
C	-0.000001	-1.199401	-4.177500
C	-0.000001	-1.199401	-2.792500
F	0.000000	2.359900	-2.122500
F	-0.000001	2.359899	-4.847500
F	-0.000001	-0.000001	-6.210000
F	-0.000001	-2.359901	-4.847500
F	0.000000	-2.359900	-2.122500

## furan

O	0.000000	0.000000	0.000000
C	0.000000	1.093300	-0.823900
C	0.000000	0.713400	-2.090100
C	0.000000	-0.713400	-2.090100
C	0.000000	-1.093300	-0.823900
H	0.000000	2.119600	-0.487500
H	-0.000001	1.358099	-2.956600
H	-0.000001	-1.358101	-2.956600
H	0.000000	-2.119600	-0.487500

## pyridine

N	0.000000	0.000000	0.000000
C	0.000000	1.142540	-0.700150
C	0.000000	1.190700	-2.079310
C	-0.000001	-0.000001	-2.779000
C	0.000000	-1.190700	-2.079310
C	0.000000	-1.142540	-0.700150
H	0.000000	2.075500	-0.156100
H	-0.000001	2.137300	-2.599300
H	-0.000001	-0.000001	-3.859000
H	-0.000001	-2.137300	-2.599300
H	0.000000	-2.075500	-0.156100

## pyridine pentafluoro

N	0.000000	0.000000	0.000000
C	0.000000	1.108430	-0.679250
C	0.000000	1.168620	-2.057940
C	-0.000001	-0.000001	-2.789000
C	0.000000	-1.168620	-2.057940
C	0.000000	-1.108430	-0.679250
F	0.000000	2.263000	0.000800
F	-0.000001	2.354700	-2.681600
F	-0.000001	-0.000001	-4.129000
F	-0.000001	-2.354701	-2.681600
F	0.000000	-2.263000	0.000800

## 4-COOH bromobenzene

BR	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.900000
C	-0.000001	1.199399	-2.592500
C	-0.000001	1.199399	-3.977500
C	-0.000001	-0.000001	-4.670000
C	-0.000001	-1.199401	-3.977500
C	-0.000001	-1.199400	-2.592500
H	0.000000	2.134799	-2.052500
H	-0.000001	2.134799	-4.517500
H	-0.000001	-2.134801	-4.517500
H	0.000000	-2.134800	-2.052500
C	-0.000001	-0.000001	-6.150000
O	-0.000001	1.039229	-6.750000
O	-0.000001	-1.169131	-6.825000
H	-0.000002	-1.169132	-7.825000

## 4-CN bromobenzene

BR	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.900000
C	-0.000001	1.199399	-2.592500
C	-0.000001	1.199399	-3.977500
C	-0.000001	-0.000001	-4.670000
C	-0.000001	-1.199401	-3.977500
C	-0.000001	-1.199400	-2.592500
H	0.000000	2.134799	-2.052500
H	-0.000001	2.134799	-4.517500
H	-0.000001	-2.134801	-4.517500
H	0.000000	-2.134800	-2.052500
C	-0.000001	-0.000001	-6.110000
N	-0.000001	-0.000001	-7.250000

## 4-aminobromobenzene

BR	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.900000
C	-0.000001	1.199399	-2.592500
C	-0.000001	1.199399	-3.977500
C	-0.000001	-0.000001	-4.670000
C	-0.000001	-1.199401	-3.977500
C	-0.000001	-1.199400	-2.592500
H	0.000000	2.134799	-2.052500
H	-0.000001	2.134799	-4.517500
H	-0.000001	-2.134801	-4.517500
H	0.000000	-2.134800	-2.052500
N	-0.000001	-0.000001	-6.050000
H	-0.000001	0.866029	-6.550000
H	-0.000001	-0.866031	-6.550000

## 4-nitrobromobenzene

BR	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.900000
C	-0.000001	1.199399	-2.592500
C	-0.000001	1.199399	-3.977500
C	-0.000001	-0.000001	-4.670000
C	-0.000001	-1.199401	-3.977500
C	-0.000001	-1.199400	-2.592500
H	0.000000	2.134799	-2.052500
H	-0.000001	2.134799	-4.517500
H	-0.000001	-2.134801	-4.517500
H	0.000000	-2.134800	-2.052500
N	-0.000001	-0.000001	-6.140000
O	-0.000001	1.056549	-6.750000
O	-0.000001	-1.056551	-6.750000

## 4-hydroxy bromobenzene

BR	0.000000	0.000000	0.000000
C	0.000000	0.000000	-1.900000
C	-0.000001	1.199399	-2.592500
C	-0.000001	1.199399	-3.977500
C	-0.000001	-0.000001	-4.670000
C	-0.000001	-1.199401	-3.977500
C	-0.000001	-1.199400	-2.592500
H	0.000000	2.134799	-2.052500
H	-0.000001	2.134799	-4.517500
H	-0.000001	-2.134801	-4.517500
H	0.000000	-2.134800	-2.052500
O	-0.000001	-0.000001	-6.030000
H	-0.000001	0.939689	-6.373020

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Atomic coordinates for some dimer calculations

TITL	bromopropane	benzoquinone	Br...O 3.6
ATOM	BR	0.0000	0.0000 0.0000
ATOM	C	0.0000	0.0000 -1.9500
ATOM	C	1.2574	-0.7259 -2.4633
ATOM	C	-1.2574	-0.7259 -2.4633
ATOM	H	0.0000	1.0182 -2.3100
ATOM	H	2.1392	-0.2167 -2.1033
ATOM	H	1.2574	-0.7259 -3.5433
ATOM	H	1.2574	-1.7441 -2.1033
ATOM	H	-2.1392	-0.2167 -2.1033
ATOM	H	-1.2574	-0.7259 -3.5433
ATOM	H	-1.2574	-1.7441 -2.1033
ATOM	O	0.0000	0.0000 3.6000
ATOM	C	0.0000	0.0000 4.8220
ATOM	C	0.0000	-1.2643 5.5817
ATOM	C	0.0000	-1.2643 6.9117
ATOM	C	0.0000	0.0000 7.6713
ATOM	O	0.0000	0.0000 8.8933
ATOM	C	0.0000	1.2643 6.9117
ATOM	C	0.0000	1.2643 5.5817
ATOM	H	0.0000	-2.2043 5.0499
ATOM	H	0.0000	-2.2043 7.4434
ATOM	H	0.0000	2.2043 7.4434
ATOM	H	0.0000	2.2043 5.0499

TITL	iodopropane	pyridine	I...N 3.6
ATOM	I	0.0000	0.0000 0.0000
ATOM	C	0.0000	0.0000 -2.1500
ATOM	C	1.2574	-0.7259 -2.6633
ATOM	C	-1.2574	-0.7259 -2.6633
ATOM	H	0.0000	1.0182 -2.5100
ATOM	H	2.1392	-0.2167 -2.3033
ATOM	H	1.2574	-0.7259 -3.7432
ATOM	H	1.2574	-1.7441 -2.3033
ATOM	H	-2.1392	-0.2167 -2.3033
ATOM	H	-1.2574	-0.7259 -3.7432
ATOM	H	-1.2574	-1.7441 -2.3033
ATOM	N	0.0000	0.0000 3.6000
ATOM	C	0.0000	-1.1425 4.3001
ATOM	C	0.0000	-1.1907 5.6793
ATOM	C	0.0000	0.0000 6.3790
ATOM	C	0.0000	1.1907 5.6793
ATOM	C	0.0000	1.1425 4.3001
ATOM	H	0.0000	-2.0755 3.7561
ATOM	H	0.0000	-2.1373 6.1993
ATOM	H	0.0000	0.0000 7.4589
ATOM	H	0.0000	2.1373 6.1993
ATOM	H	0.0000	2.0755 3.7561

chlorobenzene	benzoquinone	Cl...O 3.4
CL	0.0000	0.0000 0.0000 1
C	0.0000	0.0000 -1.7400 1
C	0.0000	1.1994 -2.4325 1
C	0.0000	1.1994 -3.8174 1
C	0.0000	0.0000 -4.5099 1
C	0.0000	-1.1994 -3.8174 1
C	0.0000	-1.1994 -2.4325 1
H	0.0000	2.1348 -1.8925 1
H	0.0000	2.1348 -4.3574 1
H	0.0000	0.0000 -5.5899 1
H	0.0000	-2.1348 -4.3574 1
H	0.0000	-2.1348 -1.8925 1
O	0.0000	0.0000 3.4000 2
C	0.0000	0.0000 4.6220 2
C	0.0000	-1.2643 5.3817 2
C	0.0000	-1.2643 6.7117 2
C	0.0000	0.0000 7.4713 2
O	0.0000	0.0000 8.6933 2
C	0.0000	1.2643 6.7117 2

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C	0.0000	1.2643	5.3817	2
H	0.0000	-2.2043	4.8499	2
H	0.0000	-2.2043	7.2434	2
H	0.0000	2.2043	7.2434	2
H	0.0000	2.2043	4.8499	2

TITL bromobenzene furan Br...O 3.4

ATOM	BR	0.0000	0.0000	0.0000
ATOM	C	0.0000	0.0000	-1.9000
ATOM	C	0.0000	1.1994	-2.5925
ATOM	C	0.0000	1.1994	-3.9774
ATOM	C	0.0000	0.0000	-4.6699
ATOM	C	0.0000	-1.1994	-3.9774
ATOM	C	0.0000	-1.1994	-2.5925
ATOM	H	0.0000	2.1348	-2.0525
ATOM	H	0.0000	2.1348	-4.5174
ATOM	H	0.0000	0.0000	-5.7499
ATOM	H	0.0000	-2.1348	-4.5174
ATOM	H	0.0000	-2.1348	-2.0525
ATOM	O	0.0000	0.0000	3.4000
ATOM	C	0.0000	-1.0933	4.2239
ATOM	C	0.0000	-0.7134	5.4901
ATOM	C	0.0000	0.7134	5.4901
ATOM	C	0.0000	1.0933	4.2239
ATOM	H	0.0000	-2.1196	3.8875
ATOM	H	0.0000	-1.3581	6.3566
ATOM	H	0.0000	1.3581	6.3566
ATOM	H	0.0000	2.1196	3.8875

END

TITL iodobenzene benzonitrile I...N 3.4

ATOM	I	0.0000	0.0000	0.0000
ATOM	C	0.0000	0.0000	-2.1000
ATOM	C	0.0000	1.1994	-2.7925
ATOM	C	0.0000	1.1994	-4.1774
ATOM	C	0.0000	0.0000	-4.8699
ATOM	C	0.0000	-1.1994	-4.1774
ATOM	C	0.0000	-1.1994	-2.7925
ATOM	H	0.0000	2.1348	-2.2525
ATOM	H	0.0000	2.1348	-4.7174
ATOM	H	0.0000	0.0000	-5.9499
ATOM	H	0.0000	-2.1348	-4.7174
ATOM	H	0.0000	-2.1348	-2.2525
ATOM	N	0.0000	0.0000	3.4000
ATOM	C	0.0000	0.0000	4.5380
ATOM	C	0.0000	0.0000	5.9386
ATOM	C	0.0000	1.2146	6.6358
ATOM	C	0.0000	1.2136	8.0066
ATOM	C	0.0000	0.0000	8.7200
ATOM	C	0.0000	-1.2136	8.0066
ATOM	C	0.0000	-1.2146	6.6358
ATOM	H	0.0000	2.1494	6.0950
ATOM	H	0.0000	2.1508	8.5433
ATOM	H	0.0000	0.0000	9.8000
ATOM	H	0.0000	-2.1508	8.5433
ATOM	H	0.0000	-2.1494	6.0950

END

TITL bromobenzene pentafluoro + furan Br...O 3.4

ATOM	BR	0.0000	0.0000	0.0000
ATOM	C	0.0000	0.0000	-1.9000
ATOM	C	0.0000	1.1994	-2.5925
ATOM	C	0.0000	1.1994	-3.9774
ATOM	C	0.0000	0.0000	-4.6699
ATOM	C	0.0000	-1.1994	-3.9774
ATOM	C	0.0000	-1.1994	-2.5925
ATOM	F	0.0000	2.3599	-1.9225
ATOM	F	0.0000	2.3599	-4.6474
ATOM	F	0.0000	0.0000	-6.0099
ATOM	F	0.0000	-2.3599	-4.6474
ATOM	F	0.0000	-2.3599	-1.9225
ATOM	O	0.0000	0.0000	3.4000
ATOM	C	0.0000	-1.0933	4.2239
ATOM	C	0.0000	-0.7134	5.4901

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ATOM C 0.0000 0.7134 5.4901
ATOM C 0.0000 1.0933 4.2239
ATOM H 0.0000 -2.1196 3.8875
ATOM H 0.0000 -1.3581 6.3566
ATOM H 0.0000 1.3581 6.3566
ATOM H 0.0000 2.1196 3.8875
END
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TITL iodobenzenepentafluoro + benzonitrile I...N 3.4
ATOM I 0.0000 0.0000 0.0000
ATOM C 0.0000 0.0000 -2.1000
ATOM C 0.0000 1.1994 -2.7925
ATOM C 0.0000 1.1994 -4.1774
ATOM C 0.0000 0.0000 -4.8699
ATOM C 0.0000 -1.1994 -4.1774
ATOM C 0.0000 -1.1994 -2.7925
ATOM F 0.0000 2.3599 -2.1225
ATOM F 0.0000 2.3599 -4.8474
ATOM F 0.0000 0.0000 -6.2099
ATOM F 0.0000 -2.3599 -4.8474
ATOM F 0.0000 -2.3599 -2.1225
ATOM N 0.0000 0.0000 3.4000
ATOM C 0.0000 0.0000 4.5380
ATOM C 0.0000 0.0000 5.9386
ATOM C 0.0000 1.2146 6.6358
ATOM C 0.0000 1.2136 8.0066
ATOM C 0.0000 0.0000 8.7200
ATOM C 0.0000 -1.2136 8.0066
ATOM C 0.0000 -1.2146 6.6358
ATOM H 0.0000 2.1494 6.0950
ATOM H 0.0000 2.1508 8.5433
ATOM H 0.0000 0.0000 9.8000
ATOM H 0.0000 -2.1508 8.5433
ATOM H 0.0000 -2.1494 6.0950
END
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9 **Non-conventional bonding between organic molecules. The "halogen bond" in crystalline**  
10 **systems**  
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14 A. GAVEZZOTTI

15 Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, Milano,  
16 Italy  
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27 **APPENDIX III**  
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list of Cl...N contacts in ascending order  
structures with N(atom) < 50

acceptor code:

23 =N-  
4 C=N nitrile  
19,20 NHR amino or amide

refcode	Cl...N	C-Cl-N	acceptor	chemical environment
DESKER01	2.954	163.7	23	C=O)-CCl=CCl-CH=N-NH
CCACEN	2.984	178.3	4	chlorocyanoacetylene
CIMTAT	2.996	157.4	23	pyrimidin-purine N
WORTUS	3.003	153.6	4	
PCLPYR	3.014	180.0	23	pentachloropyridine
ROFHUP	3.026	170.1	4	
BAFJOH	3.031	177.5	4	
ROKCAV	3.037	174.2	4	
MAGZIE	3.041	165.4	23	
JUSTIA	3.044	161.0	4	
BAWMUH	3.045	164.4	4	
UMILOR	3.047	159.1	23	
QEKDIT	3.047	171.2	23	
MOCCEM	3.048	158.5	4	
SAKGUG	3.059	179.4	4	
ZUGPOI	3.060	172.3	4	
YOSHOD10	3.061	169.2	4	
BAWMUH	3.061	169.2	4	
BAWNIW	3.070	176.6	4	
MOCCEM	3.083	155.8	4	
MAGZIE	3.088	167.6	23	
BIHNEL	3.091	173.1	23	
NABZAS	3.092	170.1	23	
HUFXUB	3.093	166.8	23	
ADILUV	3.093	158.5	23	
QEKDAL	3.095	174.6	4	
UDEPEY	3.096	166.2	23	
PIJBOO	3.097	168.5	23	
ZERPOB	3.098	165.9	23	
YOSHOD10	3.099	176.5	4	
VUGSIZ10	3.100	180.0	23	
LAGMOV	3.101	158.9	4	
UHAPIC	3.104	173.3	23	
BAWNOC	3.106	168.8	4	
FARQAR	3.109	175.4	23	
QEKDIT01	3.111	174.7	23	
VUGSIZ10	3.112	172.9	23	
VUGSIZ02	3.120	180.0	23	
DESKER	3.122	177.0	23	
TAJCEM	3.125	166.6	23	
KADPAG	3.126	160.5	23	
ADULEQ03	3.127	161.6	4	
TEGYAF	3.128	170.7	23	
FARQAR	3.134	165.4	23	
BAWNIW	3.137	167.1	4	
IFULUQ04	3.138	158.3	23	
WIBYUB	3.140	174.6	23	
UHAPIC	3.143	175.2	23	
VAFMEU	3.145	172.6	23	
VUGSIZ02	3.146	173.1	23	
PUCJAY	3.146	142.2	4	
LAXZOA	3.147	176.6	4	
BAWMUH	3.147	162.1	4	
CLTRZL01	3.148	169.1	23	
VITRUL	3.149	179.2	23	
IPCLTZ10	3.149	177.4	23	
FOCBAB	3.151	174.5	4	
CEXOXP	3.151	156.7	23	
YITKOB	3.153	157.5	4	
WARYAQ	3.153	170.1	23	
CLBECN03	3.153	176.1	4	
LUHLOP	3.156	157.5	23	
WARYAQ	3.158	173.1	23	
HCPYIN	3.158	174.6	23	
JIYVUI	3.162	176.8	4	
WAFYIL	3.163	179.4	23	
RAXSAL	3.165	152.0	4	
BEDZPN10	3.168	153.0	23	

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3	ZEGCUJ	3.173	155.2	23
4	HOQBEU	3.175	175.9	4
5	QAPJOG	3.176	170.1	23
6	CLTRZL	3.177	169.0	23
7	DCMPHN10	3.179	174.7	23
8	SAZDEC	3.180	177.7	23
9	LAXZAM	3.180	170.6	23
10	RUPYOQ	3.183	167.2	23
11	PEJLOF	3.185	165.4	4
12	MCPYZF	3.185	174.4	23
13	JUSTIA	3.185	168.6	4
14	SAXCID	3.186	168.8	23
15	HCTDPY	3.186	150.1	23
16	TAHCEK	3.187	163.8	4
17	DEPFUZ	3.189	154.0	23
18	DCPYZO01	3.190	174.2	23
19	AFECUJ01	3.191	156.3	23
20	RATFUO	3.193	164.9	23
21	DIAZOX	3.196	175.1	23
22	AJAGIB	3.199	102.7	19
23	QOBJUM	3.201	139.6	23
24	CAVYIH	3.202	160.8	23
25	DCPYZO	3.203	174.5	23
26	PUGJEG	3.205	168.1	23
27	PIJBIT	3.207	177.1	23
28	FOSGID	3.207	170.5	20
29	CLCYBQ	3.207	166.0	4
30	ZIZMAW	3.208	160.1	4
31	BOTRUX	3.215	171.4	4
32	CASMAL	3.217	139.0	23
33	WANQAE	3.218	153.9	23
34	WANQAE	3.218	153.9	23
35	TAGVEC	3.220	155.6	4
36	REMDIW	3.220	134.4	23
37	TUXDEV	3.221	160.0	4
38	AJIGOP	3.222	139.7	23
39	WALXIR	3.225	158.2	4
40	FOMWIN	3.232	166.2	4
41	LEBMUB	3.236	156.2	23
42	EDUHOA	3.237	156.8	23
43	UFEROM	3.238	150.2	23
44	SIBDAI	3.238	137.3	23
45	MAFZEZ	3.238	169.6	23
46	YEDNAX	3.240	149.2	23
47	NEGJIS	3.240	126.1	23
48	LUSPEU	3.240	159.3	23
49	HUFXUB	3.240	154.1	23
50	YOSHOD10	3.241	168.3	4
51	LEBWUL	3.242	130.7	19
52	WETMAJ	3.246	174.2	23
53	ISUQIW	3.248	168.3	4
54	TAGVEC	3.250	159.8	4
55	JEHYIF	3.250	155.5	23
56	WETMEN	3.251	174.1	23
57	PEPQIK	3.251	169.8	23
58	OCAKOT	3.251	170.2	23
59	GALDON	3.252	157.7	23
60	AYEFIT	3.252	172.5	23
	UMETAH	3.253	168.1	23
	QEKDAL	3.253	177.1	4
	WAFYIL	3.254	156.8	23
	TEHCAL	3.255	170.0	4
	QEKDIT	3.255	161.3	23
	DCPYZO01	3.261	151.0	19
	GAKNEL	3.262	158.3	23
	CPTZTR	3.262	166.6	23
	YUZGUV	3.263	160.9	23
	WITLUG	3.263	168.5	4
	UDENAS	3.264	130.5	23
	OGEWIG	3.265	148.3	23
	MAYTOW	3.266	175.0	4
	TAHFIR	3.267	105.6	4
	UHAHIU	3.270	158.6	4
	LAXJAW	3.270	151.9	4
	DCPYZO	3.270	150.9	19
	YOSHOD10	3.271	166.4	4
	REMDIW	3.271	178.0	23
	NOKDAS	3.274	163.8	4

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3	ROKCAV	3.277	115.3	23
4	KEQGES	3.279	165.3	4
5	RUPYIK	3.280	160.9	23
6	FOHGAL	3.280	175.1	23
7	QOBJUM	3.283	163.4	23
8	CLPCPN	3.283	169.3	4
9	PIJBOZ	3.284	150.5	23
10	QEKDAL	3.286	152.8	4
11	GEDHEC	3.287	158.8	23
12	FELPIV	3.288	148.9	23
13	JELGEM	3.289	162.0	4
14	BUNJID	3.292	163.2	23
15	SAXCID	3.295	165.6	23
16	CMTBZN	3.295	172.3	4
17	TAHFIR01	3.298	105.6	4
18	BZPCBQ	3.298	140.6	4
19	LEBMIP	3.300	171.1	23
20	FEVNUP	3.300	128.9	19
21	ATOXUC	3.300	132.9	23
22	ZAMWAL	3.301	156.6	4
23	NANDUB	3.301	163.5	23
24	TUKROG	3.302	119.6	23
25	MCPYDO	3.302	150.0	23
26	CPTZTR	3.303	169.3	23
27	LAPBEK	3.304	172.3	23
28	IQIMAW	3.306	154.1	23
29	HEXPEF	3.306	152.5	23
30	MAPPAV	3.307	160.3	23
31	OLAMAP	3.309	157.4	23
32	ILUTAK	3.311	164.9	23
33	PIPPUZ	3.314	134.8	23
34	PAHBWU	3.314	164.5	23
35	MOSTIX	3.314	150.6	23
36	JEFCEC	3.314	151.7	4
37	MENMIB01	3.315	160.5	23
38	BAFJOH	3.315	156.7	4
39	PALQAV	3.316	168.8	23
40	LUPZUR	3.316	147.8	23
41	ISOFOL	3.320	155.2	4
42	LEBMIP	3.321	122.5	23
43	YAVRUI	3.323	146.9	4
44	YITKOB	3.324	166.6	4
45	PAHBWU01	3.325	164.3	23
46	APCLBT	3.325	156.5	23
47	WOCXAN	3.326	122.2	20
48	WAKJAU	3.328	162.6	23
49	NUNKUC	3.329	178.6	23
50	ZAMVUE	3.330	152.1	4
51	UHAPOI	3.330	147.6	19
52	PIJBIT	3.331	162.8	23
53	JAWBAL	3.333	113.4	23
54	YOWWUC	3.336	133.7	23
55	VAYVAT	3.336	145.9	23
56	NURQAS	3.338	129.7	23
57	GAKXAS	3.338	168.2	23
58	FUDQUQ	3.339	163.5	23
59	FELPIV	3.340	160.7	23
60	PIJBOZ	3.341	166.4	23
	NEFRIA	3.344	158.1	4
	TOZKEY	3.345	134.9	23
	QEKDIT01	3.347	163.1	23
	HEYKEB	3.347	174.8	4
	GETFOA	3.349	120.2	4
	FOMWIN	3.349	103.3	23
	FAYMEX	3.352	142.6	4
	FARQAR	3.352	100.5	23
	NAHVUO	3.353	174.8	19
	WANQAE	3.355	134.4	23
	WEMDUN	3.356	165.6	23
	PEKLIA	3.356	139.7	4
	WANQAE	3.357	134.4	23
	QEKDAL	3.357	134.1	4
	TAHFIR	3.358	104.0	4
	SAKHUH	3.358	104.1	23
	PIZYEC	3.358	149.5	4
	WOKHEJ	3.359	163.1	4
	CLVINA	3.359	122.2	23

1				
2				
3	RADGAF	3.360	115.3	23
4	QAHSIB	3.361	146.9	4
5	BEHGEB	3.361	102.0	23
6	XACGEO	3.362	115.2	19
7	ILUTAK01	3.362	165.4	23
8	FAGDOG	3.362	104.4	23
9	XAYYEC	3.364	157.1	23
10	KECSUG	3.364	127.2	23
11	MEDZOK	3.365	165.8	4
12	OJEQAV	3.366	161.6	23
13	CPYBZT	3.366	103.7	23
14	AHUQID	3.366	131.5	23
15	YAVRUI	3.367	133.4	23
16	UFEROM	3.367	120.3	23
17	BERSAS	3.367	107.9	23
18	JOFLAR	3.368	162.6	23
19	WAWPAM	3.369	135.4	4
20	XAZJUE	3.370	178.4	23
21	HEBKII	3.370	163.1	23
22	CLBZNT05	3.370	168.3	4
23	HEFWIZ	3.371	113.2	23
24	FELPIV	3.371	163.1	23
25	EBIDAV	3.372	166.9	23
26	CASBOO	3.372	121.1	23
27	AABHTZ	3.372	165.2	23
28	WALXIR	3.373	163.8	4
29	KUMTER	3.373	134.5	23
30	COMLEV	3.374	106.3	23
31	VOTPID	3.375	143.6	23
32	NUWGUH	3.375	154.5	4
33	PUZXAJ	3.376	158.3	23
34	MEGWIF	3.376	157.3	23
35	ZILDED	3.377	153.6	4
36	BULLID	3.379	154.6	23
37	XATTOC	3.380	161.5	23
38	BAWMUH	3.381	147.5	4
39	AHUMUL	3.381	119.0	23
40	JORFIF	3.383	156.5	23
41	XAYBEF	3.384	131.7	23
42	MENMTB01	3.384	152.6	23
43	QIZHIQ01	3.385	148.8	23
44	WEVLIS	3.386	111.0	19
45	LATFER	3.387	134.9	20
46	IFULUQ01	3.387	105.3	23
47	CMTBZN	3.387	175.0	4
48	PAMQUQ	3.388	160.5	23
49	WERSER	3.389	177.0	4
50	YUXMIN	3.390	120.1	23
51	BAWNIW	3.391	134.3	4
52	UGEGIW	3.392	139.6	23
53	TAJCEM	3.392	143.7	23
54	ETOHUQ	3.392	141.1	23
55	CAHXQX	3.393	128.6	19
56	TAHFIR01	3.394	103.9	4
57	NOGBUG	3.394	131.8	23
58	KECSUG	3.394	111.8	23
59	NOPBAV	3.395	103.2	23
60	CEKQOY	3.395	105.9	19
	VUXDAT	3.397	130.1	23
	EBICEY	3.397	127.6	23
	CLPTAZ	3.397	168.8	23
	LINNAX	3.398	161.9	4
	FOBYEB	3.398	133.0	4
	KIDDAC	3.399	111.7	23
	HAXCAK	3.399	101.6	23
	-----sum of intermolecular atomic radii			

list of Cl...O contacts in ascending order  
structures with N(atom) < 50

acceptor code:

17 C=O carbonyl or S=O  
5 -O-  
16 OH oxygen  
22 NO2 oxygen

refcode	Cl...O	C-Cl-O	acceptor	chemical environment
EDUJOC	2.793	165.8	22	NO2
KAJDAB	2.800	172.0	17	CCl3...SO2
EDUHUG	2.810	166.2	22	NO2
YAFFEQ	2.825	158.4	17	CCl3...OC
BEGPEJ	2.863	173.9	17	NO2
UHUHAG	2.875	168.8	17	CCl3
POBBEN	2.882	166.5	17	CCl3...SO2
BAQTUI	2.888	148.8	17	CCl3
WAMNOO	2.891	171.5	17	C6Cl4
JAJVOG	2.899	177.9	17	
EVIHIA	2.901	163.6	17	
WAMNOO	2.904	176.2	17	
SOMRIV	2.904	147.0	17	
CIKSIY	2.921	160.7	5	
NAMQIC	2.923	165.1	17	
ASUXUH	2.927	160.2	17	
FUPTUF	2.934	153.3	22	
FOHXUV	2.936	176.7	17	
JENTEB	2.942	171.1	17	
FIZGEA	2.943	172.4	17	
YISGIQ	2.946	171.6	17	
FIZGOK	2.946	168.3	17	
BAYKIW	2.946	152.1	22	
JORFIF	2.951	153.3	22	
CABXUZ	2.952	170.3	16	
KAJDAB	2.954	172.5	17	
UCAQUM	2.956	174.2	17	
VAPKOM	2.957	175.0	17	
MAYXAL	2.958	169.7	17	
HAXVOR	2.960	169.4	22	
XZCVIN10	2.961	179.0	5	
PEPFUL	2.962	170.0	22	
UMIMAE	2.964	159.0	5	
HEXPEF	2.965	167.9	22	
XAVRIV	2.967	177.7	17	
SEYRIX	2.968	169.8	17	
FIZGOK	2.968	161.8	17	
YASSUH	2.970	157.9	17	
IBIZID	2.971	160.4	22	
RESVIU	2.976	160.6	22	
XEHNUU	2.977	168.4	17	
SANVAF	2.981	173.4	17	
SAMDAL	2.981	163.3	17	
PHOXNA10	2.982	152.3	16	
TUDTUH	2.983	163.6	17	
EREQAT	2.983	160.0	17	
DCETSY10	2.983	160.3	17	
TOCPIM	2.985	167.9	17	
FILMUI	2.986	173.1	5	
FUPTUF	2.988	174.3	22	
ERESAV	2.989	173.0	5	
ECHNYL	2.989	167.6	16	
ZIYMOJ	2.990	168.7	17	
WANLAY	2.992	171.6	17	
RBFRPZ10	2.992	157.4	16	
KACJII	2.992	170.5	17	
ZEGCOD	2.994	156.7	22	
JEHSUL	2.994	160.2	22	
NOPREP	2.995	166.3	17	
YOHDI	2.996	171.9	17	
HAXWUY	2.996	173.5	17	
DCPYZO01	2.996	144.6	16	
VAVZAT	2.999	169.1	22	
NOQJIM	3.000	169.9	22	
DCPYZO	3.001	144.4	16	
GEXWUB	3.002	177.5	17	
HEVMOK	3.003	160.3	17	

1				
2				
3	GAHJIJ	3.005	161.2	17
4	DCLBZQ20	3.006	164.8	17
5	MOWDIL	3.007	159.9	22
6	EKEXAT	3.008	157.6	5
7	JUNFUT	3.010	177.9	17
8	UMILUX	3.011	163.2	16
9	AFECUJ01	3.011	157.8	22
10	XEBGER	3.014	173.0	17
11	HUZBIN	3.015	162.0	22
12	CLPYTZ	3.015	157.0	17
13	NAXDEV	3.016	167.6	22
14	HIPNOJ	3.017	163.6	17
15	TEWJEK	3.019	171.8	22
16	DELNEN	3.019	164.6	17
17	IFESOB	3.020	169.9	17
18	FILMUI	3.022	160.0	5
19	PAJKIV	3.023	173.1	5
20	HILMOE	3.023	167.5	17
21	DIMYON10	3.023	154.6	22
22	TICMAT	3.024	174.9	17
23	SEYRIX01	3.024	169.8	17
24	PENVOT	3.025	172.3	22
25	VOFCEY	3.026	173.2	17
26	RIHJOH	3.026	156.9	17
27	CMPYTO	3.027	148.0	17
28	BYMCPH	3.027	152.5	17
29	TCACAD01	3.029	155.4	17
30	DEZXEL	3.029	173.3	17
31	LAPGOY	3.031	163.4	17
32	RIHKOI	3.032	177.9	17
33	BEGPIN	3.033	150.6	17
34	BEFREJ	3.033	169.2	17
35	AJAKUR	3.033	158.9	22
36	KEJBIK	3.034	165.3	17
37	DIHWOG	3.035	173.6	17
38	BIKLEN	3.035	170.3	16
39	LUHJIH	3.037	166.1	17
40	KAJCOO	3.037	170.9	17
41	EKEXAT	3.037	160.6	5
42	YEWNET	3.038	175.2	17
43	NASMEA	3.038	160.4	5
44	BEFREJ	3.038	175.1	17
45	NATKID	3.039	160.4	5
46	ADUPOE	3.040	154.7	17
47	TCPXAD	3.041	143.7	17
48	EBEZIU	3.041	165.4	17
49	SAMDAL	3.042	165.9	17
50	MCMOXO	3.042	165.0	22
51	BEXSUS	3.043	178.3	17
52	NEGGOV	3.045	176.0	17
53	GERDIQ	3.045	151.1	17
54	ECEJOM	3.045	176.9	17
55	ASOKUO	3.045	168.6	17
56	CORDUI	3.047	169.8	17
57	VAHWUW	3.048	170.3	22
58	MAYTUC	3.048	172.3	17
59	MODHIW	3.049	166.3	17
60	JEMXUU	3.049	153.8	5
	WABYON	3.050	168.9	17
	HIBWIY	3.050	168.7	22
	JUNFUT	3.052	173.2	17
	JUNHUV	3.053	129.6	17
	HODSUO	3.053	173.5	17
	HATTOM	3.053	159.3	17
	KEYYII	3.054	158.5	17
	HIBWOE	3.054	170.9	22
	FEWRUV	3.054	175.7	17
	CDNPOL	3.054	169.6	22
	GARQIZ	3.055	146.9	17
	MOGROP	3.056	177.8	17
	EFAXAK	3.056	169.0	17
	BUTRAJ	3.056	160.2	17
	QIHPAY	3.058	150.4	17
	MIYLEL	3.059	163.3	16
	KEFTOF	3.059	167.8	17
	LAKGAF	3.060	172.9	17
	IREWIL	3.060	167.4	17
	HAXWIM	3.060	163.1	22

1				
2				
3	GESSAY	3.062	164.3	17
4	IWUHEN	3.063	164.4	5
5	DEFDUN	3.063	165.7	22
6	THTOXC	3.064	168.2	17
7	IRORIQ	3.064	169.7	22
8	OBEQAN	3.065	152.3	22
9	SATNAD	3.066	158.9	17
10	LETHIB	3.066	169.8	17
11	TUDTUH	3.068	166.4	18
12	GERDIQ	3.068	148.5	17
13	JORFEB	3.069	168.5	22
14	CAPLAH	3.069	166.1	17
15	ULAREE	3.070	145.8	22
16	QAPROP	3.070	165.9	17
17	ZERKOW	3.071	166.1	16
18	VEXYUS	3.071	142.8	17
19	KUNMUB	3.071	162.1	17
20	KAHQAM	3.072	145.9	17
21	GACZUF	3.073	158.5	17
22	DEFDUN01	3.073	163.4	22
23	CLNAPU	3.074	171.5	17
24	OBIDOS	3.075	170.5	22
25	IROREM	3.075	157.3	17
26	NIGFIS	3.076	165.3	5
27	JUNFUT	3.076	157.3	17
28	TUWXUE	3.077	169.7	17
29	TIJTIP	3.077	166.4	22
30	JORFEB	3.077	163.4	22
31	TEVJOT	3.078	152.8	17
32	XEDZUC	3.079	168.3	17
33	WEGPIH	3.079	131.0	22
34	GERDIQ	3.079	153.7	5
35	RATHAW	3.080	164.9	22
36	NEFRIA	3.080	156.4	16
37	MEBCAY	3.080	162.9	5
38	LUNNAJ	3.080	169.1	17
39	FIPRIF	3.080	163.3	17
40	ACAYOS	3.080	151.5	22
41	YASXOG	3.081	151.5	17
42	CESHAJ	3.081	163.2	5
43	BICXIU	3.082	154.3	22
44	DUVNAJ	3.083	172.5	5
45	TIENLC	3.084	174.6	17
46	FICFED	3.085	167.7	17
47	TSCPIP	3.086	163.1	5
48	IQAPAR	3.088	163.0	17
49	DACQOO	3.088	160.0	17
50	VENJED	3.089	177.9	17
51	ODEBIJ	3.090	171.4	17
52	DUWKUB	3.090	158.3	5
53	CUVYAT	3.091	165.2	22
54	FIBKAC	3.092	144.5	22
55	FACJAV	3.092	168.8	17
56	NUCDAQ	3.093	164.6	5
57	IDIVUN	3.093	161.9	17
58	LAGMUB	3.094	161.6	16
59	JOPFID	3.094	178.9	17
60	TEVJEJ	3.095	151.4	17
	TCACAD02	3.095	154.7	17
	SAZQOZ	3.095	172.9	17
	JIFRUL	3.095	156.1	22
	HAXCAK	3.095	160.2	22
	CORDOC	3.095	164.3	17
	CAGPUV	3.095	164.6	22
	ZATVEV	3.096	168.2	5
	MSCMDS	3.097	148.0	17
	GIKNUJ	3.097	167.5	17
	ETYCNP	3.097	147.4	22
	XUXHUT	3.098	167.7	17
	QIPVIU	3.098	166.8	17
	JUNFUT	3.098	151.2	17
	CHORLH01	3.098	159.1	16
	TRMNBE	3.099	164.6	5
	LEZGUS	3.099	138.4	22
	HIBWOE	3.099	156.5	22
	CUGGOA	3.099	151.6	17
	TECLPH01	3.100	174.0	17
	DELNEN	3.101	161.0	17

1				
2				
3	BZQDCL10	3.101	164.7	17
4	ZIYMOJ	3.102	164.1	18
5	NUKTIW	3.102	171.7	17
6	JUNFUT	3.102	162.6	17
7	JAXZUE	3.102	148.0	17
8	CEKWAQ	3.102	172.5	17
9	CABXAF	3.102	166.5	17
10	BUTREN	3.102	172.4	17
11	TAPNAA	3.103	171.0	22
12	GICYIA	3.103	168.0	16
13	DOYGIH01	3.103	164.7	17
14	EVINIG	3.104	134.1	17
15	BEMMEL	3.104	162.2	17
16	UBIKEV	3.105	163.7	17
17	MODHIW	3.105	161.3	17
18	EOCNON10	3.105	168.3	5
19	COFPAO10	3.105	160.9	17
20	PANHES	3.106	151.8	17
21	JORFIF	3.106	162.8	22
22	GARVIE	3.108	145.0	5
23	ERERIC	3.108	155.0	17
24	REMTEI	3.109	160.9	17
25	ODANUD	3.109	171.1	17
26	GANDII	3.109	165.2	17
27	SOJMUZ	3.110	172.3	17
28	IZONOA	3.110	163.1	17
29	DOXWIW	3.110	172.2	22
30	CLNODL	3.110	163.8	22
31	BEQBUU	3.110	164.3	5
32	WANLAY	3.111	159.8	17
33	CLNOBE02	3.111	156.5	22
34	CACPXL	3.111	165.5	17
35	ADENON	3.111	170.3	22
36	POBBEN	3.112	141.7	17
37	DICFOK10	3.112	169.7	17
38	DICFOK	3.112	169.7	17
39	TSCPIP	3.113	156.7	17
40	CODYEZ10	3.113	173.5	17
41	MEDNOZ	3.115	161.8	18
42	XUDCII	3.117	178.1	17
43	NUNGOS	3.117	143.9	16
44	FEQYIK	3.118	167.5	5
45	WATXAQ	3.119	167.7	17
46	IDIQUI	3.119	175.9	17
47	DUZSUM	3.119	147.5	17
48	CHLRLD	3.119	164.3	17
49	PCMALA01	3.120	155.6	18
50	ADILUV	3.120	136.8	5
51	CEZBOY	3.122	171.1	17
52	VAYVAT	3.124	167.9	18
53	VAVZAT	3.124	163.1	22
54	TITMUE	3.124	157.8	17
55	IDIQUI	3.124	165.9	17
56	TRIMCA10	3.125	169.3	17
57	LAKGAF	3.125	145.5	17
58	KAJCOO	3.125	137.6	17
59	EXICIX01	3.125	168.2	17
60	PANCYQ	3.126	164.8	17
	OKOBEV	3.127	175.7	17
	NETKEC	3.127	164.8	17
	CHLRLD01	3.127	164.0	17
	CACWIN	3.127	148.5	17
	DALNUA	3.128	158.8	17
	YEDPAZ	3.129	154.3	22
	TITQAO	3.129	135.6	5
	AZIRAC	3.129	173.3	22
	GAXLEW01	3.130	165.6	17
	FIFXIB	3.130	164.9	22
	EQONAZ	3.130	163.9	17
	CNCHAL	3.130	170.2	17
	VUGCUV	3.131	165.9	17
	SAVFOK	3.131	113.1	17
	TELQUW	3.132	149.7	18
	JIFRUL	3.132	136.0	5
	ZUDREV	3.134	176.2	5
	ROBYIQ	3.134	158.1	17
	NAXDEV	3.134	134.3	22
	FEVNUF	3.134	142.4	17



1				
2				
3	HIBWIY	3.135	157.0	22
4	GEDSUD	3.135	154.1	22
5	XAPWOA	3.136	166.7	18
6	JIWNAE	3.137	151.7	22
7	YOPTEC	3.138	158.0	5
8	VORVED	3.138	168.1	22
9	YITMET	3.139	169.6	17
10	TEVJOT	3.139	173.0	17
11	SEGKAQ	3.139	159.2	17
12	JASLAR	3.139	165.7	22
13	VODROV	3.141	161.5	17
14	PABBAV	3.141	175.3	17
15	MOGLAV	3.141	161.4	17
16	LIFCAE	3.141	153.7	17
17	CLETHZ	3.141	152.7	17
18	ZILJOT	3.142	167.5	17
19	VAFBOT	3.142	168.5	22
20	KADZOE	3.142	162.3	17
21	IWUTID	3.142	154.0	17
22	FUHGUK	3.142	178.1	22
23	BUTREN	3.142	150.6	22
24	DUZGOU	3.143	151.9	5
25	QIBVOM	3.144	155.9	17
26	OMORAJ	3.144	173.0	22
27	GAVDAI	3.144	150.3	17
28	CAGRAD	3.144	171.6	17
29	RDCPLB01	3.145	164.7	17
30	LIFCEI	3.146	157.0	17
31	JIGKEP	3.146	123.7	17
32	OBIDOS	3.147	173.9	22
33	VELJAX	3.148	157.5	17
34	UFECUD	3.148	148.0	17
35	QUDSUD	3.148	143.7	5
36	LESYUD	3.148	149.1	17
37	FIZGOK	3.148	139.2	5
38	WABYIH	3.149	165.0	17
39	PORXAV	3.149	171.3	17
40	HIJBOR	3.149	111.2	17
41	FAVSOK	3.149	165.7	16
42	XIKCOJ01	3.150	174.4	17
43	TECLPH01	3.150	155.0	5
44	QIWZIF	3.150	166.0	22
45	FIHTIA	3.150	173.5	17
46	AJAGIB	3.150	156.6	17
47	TEDXOP	3.151	173.4	17
48	PUDRIP	3.151	166.8	16
49	PCHSAN01	3.151	104.9	16
50	IJEPOC	3.151	161.1	17
51	GARVIE	3.151	143.8	5
52	BNITRB10	3.151	164.7	22
53	UCAREV	3.152	153.5	17
54	FAQPAO	3.152	153.6	5
55	CMODOD	3.152	159.9	5
56	BUTPUB	3.152	142.8	17
57	POBBEN	3.153	148.2	17
58	GERDIQ	3.153	138.8	17
59	DOXWIW	3.153	158.8	22
60	AWOPII	3.153	144.7	5
	XUDCII	3.154	167.1	16
	PIQPOU	3.154	130.4	17
	OHIBOW02	3.154	165.5	17
	NUHTEP	3.154	145.2	17
	NEFQUL	3.154	163.5	17
	HIBWOE	3.154	162.4	22
	ZIYMOJ	3.155	110.1	17
	NEGKEP	3.155	178.1	17
	LAPHOZ	3.155	158.5	17
	EBIZUL	3.155	172.2	22
	YICHAT	3.157	162.7	16
	KUVZIK	3.157	159.2	17
	PORXAV	3.159	172.4	17
	DUWKUB	3.159	160.4	5
	DCLNAP01	3.159	168.0	17
	CATMOZ	3.159	160.3	17
	GANQAO	3.160	162.9	22
	SEJCOZ	3.161	167.3	22
	LIFCEI	3.161	163.4	5
	KEJBEG	3.161	167.1	17

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2				
3	FIZGOK	3.161	146.5	17
4	DCPHER	3.161	159.0	5
5	UCECAG	3.162	147.0	22
6	LULQAK	3.162	157.8	22
7	EXOHII	3.162	160.3	5
8	DEFSOW	3.162	172.0	17
9	CLNACA10	3.162	163.5	18
10	CLETNP	3.162	157.1	22
11	WEGPEE	3.163	166.8	17
12	FOLPUR	3.163	170.4	17
13	FACJAV	3.163	141.0	5
14	BIHXIA	3.163	145.7	17
15	ZAMWAL	3.164	153.7	5
16	OHIHUI	3.164	175.3	5
17	MOVRIY	3.164	157.7	17
18	LIDXIF	3.164	114.2	16
19	HUHRAD	3.164	150.3	18
20	HIBWIY	3.164	132.2	22
21	FITRUV	3.164	152.9	17
22	KANJOY	3.165	164.2	16
23	CEPCIJ	3.165	137.9	22
24	ACEXAI	3.165	171.3	17
25	REDJEQ	3.166	173.5	16
26	EGOXIH	3.166	172.4	17
27	DCDHNQ01	3.166	161.1	16
28	BYMCPH	3.167	162.4	17
29	EBEZIU	3.168	167.5	17
30	XULHAN	3.169	153.4	17
31	GEJFUX	3.169	173.0	17
32	DCLNAP01	3.169	166.3	17
33	CIVBAK10	3.169	143.1	17
34	QQQECG01	3.170	156.3	22
35	MSCMDS	3.170	138.7	17
36	GASDOT	3.170	157.2	22
37	BAPLUZ	3.170	160.8	17
38	SEBJAK	3.171	134.5	17
39	NUFSIQ	3.171	151.9	17
40	BOSWEL	3.171	152.7	17
41	SEBPAQ	3.172	134.5	17
42	PIQLOQ	3.172	161.1	17
43	FOKSEE	3.172	148.7	17
44	CLETNP	3.172	142.1	22
45	FAZGAO	3.173	166.2	17
46	BAQTUI	3.173	146.9	5
47	ASAVUL	3.173	154.2	5
48	XAVRIV	3.174	164.8	17
49	FOKZOV	3.174	136.4	22
50	KORZEW	3.175	166.7	22
51	ETIQED	3.175	171.5	17
52	DEFSOW	3.175	171.5	17
53	TCACAD01	3.176	148.6	18
54	SAJJAO	3.176	141.9	5
55	PCHSAN	3.176	107.5	16
56	AJAHUO	3.176	153.7	18
57	INEHAK	3.177	161.7	17
58	INEHAK	3.177	161.7	17
59	AKOYUU	3.177	169.6	22
60	YAWNIT	3.178	161.0	17
	SEGQEA	3.178	163.1	17
	LIFCAE	3.178	164.3	5
	BOSWEL	3.178	158.0	17
	SIFKEX	3.179	148.9	17
	MCBZAC01	3.179	150.7	17
	UCECAG	3.180	146.2	22
	RAVVEP	3.180	154.2	17
	IJOCIT	3.180	136.7	5
	GOLNOK	3.180	169.9	17
	GANFAC	3.181	165.5	5
	ERESEZ	3.181	173.1	5
	DCPYZO01	3.181	163.5	16
	BAFLEZ	3.181	165.9	22
	XAYYEC	3.182	168.0	22
	DCPYZO	3.182	163.5	16
	CECZUF	3.182	141.6	22
	JORFIF	3.183	165.0	22
	CBMHZP	3.183	151.3	17
	KIDCOP	3.184	162.5	22
	HUFTEH	3.184	160.8	22

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2				
3	ZUZWUM	3.185	164.1	5
4	TCMHXO	3.185	153.4	17
5	SAZMUB	3.185	158.3	5
6	HAXTOP	3.185	158.9	22
7	GAFSAH	3.185	148.6	5
8	UCAQUK	3.186	159.2	5
9	ZUZWUM	3.187	164.0	5
10	WEDJEV	3.187	163.7	17
11	JORGUS	3.187	160.7	22
12	GAPCOP	3.187	134.2	22
13	JUNHUV	3.188	158.6	17
14	JAWBIT	3.188	139.3	17
15	XEGSOS	3.189	150.9	5
16	ISADOV	3.189	171.1	17
17	EXICIX	3.189	168.3	17
18	BOQHOE	3.189	143.2	16
19	RIHJOH	3.190	164.3	17
20	IDISAQ	3.190	170.7	17
21	BEWKOD	3.190	104.1	5
22	SANTIL	3.191	139.9	5
23	LUPYIE	3.191	159.4	5
24	GAWLUM	3.191	138.0	5
25	DUGQIF	3.191	164.5	17
26	CACPEC	3.191	146.0	16
27	PUDRIP	3.192	122.4	16
28	GEXJEY	3.192	150.3	17
29	CACWIN	3.192	145.4	17
30	HEXPEF	3.193	168.8	17
31	YAKHOH	3.194	172.9	17
32	XADPAU	3.194	128.5	17
33	VOKTEU	3.194	168.2	5
34	QAFVAU	3.194	177.7	17
35	COMFRN	3.194	159.2	17
36	ZOXQAE	3.195	171.6	22
37	TRIMCA10	3.195	170.5	17
38	JEPMOG	3.195	152.6	5
39	DCTMSL	3.195	142.1	5
40	XADPEY	3.196	128.6	17
41	WANYEQ	3.196	170.7	17
42	SIWWEA	3.196	127.2	16
43	QASXEO	3.196	138.1	17
44	PUGLAE	3.196	145.9	17
45	NEGHAH	3.196	161.1	5
46	JASLAR	3.196	114.5	22
47	INELOC	3.196	174.4	17
48	TEHNUQ	3.197	171.2	16
49	AGUPUN	3.197	168.3	17
50	YEJVAK	3.198	174.4	16
51	CLETHZ	3.198	160.8	17
52	TCNONC	3.199	158.4	17
53	KEBJIL	3.199	147.6	17
54	IYIYAQ	3.199	160.1	17
55	DIKGEJ	3.199	155.9	17
56	BUMJEY	3.199	162.6	17
57	VEJWOW	3.200	173.7	5
58	PAPRAZ	3.200	162.5	5
59	LACFEB	3.200	105.6	17
60	GADGUN01	3.200	174.8	16
	BANGEC	3.200	143.9	17
	ODEHIP	3.201	170.8	17
	HILMOE	3.201	142.3	17
	GEGCOL	3.201	162.1	17
	FOBMIT	3.201	147.9	22
	BERSAS	3.201	170.4	22
	TEWJEK	3.202	141.6	22
	LINNAX	3.202	172.6	22
	GEDSUD	3.202	159.3	5
	DAJZET	3.202	168.4	17
	CHORLH01	3.202	106.5	16
	HUHQUW	3.205	177.9	22
	BAVMIU	3.205	177.9	17
	YABYOP	3.206	155.9	17
	BIHXIA	3.206	154.9	18
	MTOLNQ10	3.207	149.9	17
	POBBEN	3.208	144.2	17
	IMIDUD	3.208	151.3	17
	GUHQOP	3.208	161.0	22
	FIFXIB	3.208	152.3	22

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2				
3	CLBENQ	3.208	150.6	17
4	AMOXAP	3.208	135.4	5
5	XAYBUU	3.209	138.0	18
6	FALPEN	3.209	151.6	17
7	DYSDIN	3.209	158.7	17
8	TCXCPL	3.210	109.1	17
9	OGEZIJ	3.210	162.5	17
10	LACFEB	3.210	154.6	17
11	CNPOVN	3.210	160.9	5
12	CIVVOS10	3.210	158.3	5
13	XOCLIK	3.211	156.6	17
14	SIWWEA	3.211	178.7	16
15	MIFTEA	3.211	155.8	17
16	GARQUL	3.211	150.5	5
17	ZILSAO	3.212	160.9	22
18	WAQLEG	3.212	109.3	17
19	OHIJAQ	3.212	176.5	5
20	XAYBOO01	3.213	156.7	17
21	SIYYII	3.213	157.9	17
22	VAFBIN	3.214	166.6	22
23	RUVSOQ	3.214	111.6	17
24	HILMOE	3.214	143.2	17
25	BAZGEO	3.214	167.7	17
26	BAVNER	3.214	142.0	5
27	TEHNUQ	3.215	120.9	5
28	FABXAI	3.215	172.8	17
29	DCETSY10	3.215	145.4	5
30	AJAKUR	3.215	135.0	22
31	TEJGUK01	3.216	118.8	5
32	PABZAT	3.216	134.7	17
33	LILMAU	3.216	174.8	5
34	FOTPUZ	3.216	136.9	17
35	WECXAE	3.217	157.5	18
36	NEGJIS	3.217	162.0	17
37	BENCLN05	3.218	157.2	22
38	XORYEI	3.219	167.0	5
39	KIDCUV	3.219	163.7	22
40	CAXPOG	3.219	158.3	17
41	ZUGPOH	3.221	140.4	22
42	LUHLOP	3.221	178.9	22
43	IDIQUI	3.221	170.2	5
44	FICFIH	3.221	158.1	17
45	AEPCNQ10	3.221	163.8	17
46	VINMOU	3.222	178.0	5
47	UHAQAV	3.222	164.2	17
48	IDOMUK	3.222	155.6	5
49	ADEMIG	3.222	166.7	5
50	ZOKXAY	3.223	155.5	5
51	YAWNIT	3.223	173.4	5
52	HAXCEO	3.223	174.2	17
53	GAKXAS	3.223	169.1	17
54	CLCYBQ	3.223	160.1	17
55	CAGRAD	3.223	146.3	17
56	VAVZEX	3.224	116.1	22
57	QICTOL	3.224	159.2	17
58	LAPGOY	3.224	150.2	17
59	GEDSOX	3.224	148.0	22
60	DEXWEI	3.224	174.0	5
	COMLEV	3.224	158.0	22
	ZIYNAW	3.225	127.0	17
	WECXAE	3.225	161.7	18
	IDIDEF	3.225	154.2	18
	DOTWOY	3.225	159.0	5
	XAPWOA	3.226	173.0	22
	UDEPIC	3.226	176.8	17
	SORBIK	3.226	127.4	22
	NEGHAI	3.226	163.2	17
	CLIMIP10	3.226	154.1	5
	ATOXUC	3.226	142.7	22
	TAHPOH	3.227	133.0	5
	QAVGID	3.227	135.6	17
	FIFTET	3.227	173.0	17
	DEPMOA	3.227	160.8	17
	CLETNP	3.227	154.3	16
	CBSTHP	3.227	152.9	17
	ULAMID	3.228	157.4	17
	TUNVIH	3.228	107.3	16
	LUNRAN	3.228	155.3	17

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2				
3	COCLHP	3.228	151.8	5
4	BEJJEG	3.228	115.4	17
5				
6	TECDOV	3.229	171.3	17
7	FAQPAO	3.229	175.3	5
8	DUZTAT	3.229	159.6	17
9	YIBFEU	3.230	150.8	17
10	VUJGEM	3.230	165.9	17
11	NOQJAE	3.230	105.4	17
12	MSCMDS	3.230	160.9	17
13	DCPYZO	3.230	143.2	16
14	WEGPIH	3.231	160.4	5
15	POBBEN	3.231	136.5	17
16	LELXAB	3.231	178.5	22
17	COCLHP	3.231	172.5	5
18	NOSQER	3.232	139.2	22
19	ECUYIL	3.232	159.1	22
20	CORDAO	3.232	176.9	17
21	PUVTIJ	3.233	168.1	17
22	OBIDOS	3.233	156.4	22
23	MAYXAL	3.233	143.3	17
24	KANZOO	3.233	152.8	16
25	JORFEB	3.233	140.5	22
26	ZOHNOZ	3.234	152.9	17
27	YEKFEZ	3.234	162.2	17
28	YABYEF	3.234	146.5	5
29	RIWRUK	3.234	148.8	17
30	IWEYEO	3.234	119.6	5
31	ERERIC	3.234	142.0	17
32	DCPYZO01	3.234	142.8	16
33	NAXDEV	3.235	136.8	22
34	LAVMOK	3.235	103.8	5
35	IFAFAX	3.235	133.3	17
36	RADGAF	3.236	162.3	18
37	KOQHIH	3.236	164.9	5
38	HUHSEI	3.237	138.6	22
39	GOZGIL	3.237	169.1	17
40	DUZSIA	3.237	152.8	17
41	CLPURB	3.237	147.6	16
42	VUSHUM	3.238	172.3	22
43	UCOGEZ	3.238	147.3	17
44	PCHSAN01	3.238	149.9	17
45	KIDBUU	3.238	134.7	17
46	BOMSIF	3.238	166.1	22
47	YALWIS	3.239	129.2	17
48	NEWKOP	3.239	164.4	17
49	TEWJEK	3.240	164.0	22
50	SIKQUY	3.240	172.3	17
51	OHIBOW02	3.240	166.2	17
52	OBIDOS	3.240	164.0	22
53	CLAHMB02	3.240	163.5	17
54	CLAHMB01	3.240	163.5	17
55	CUXTOE	3.241	141.2	5
56	AHUQID	3.241	155.0	17
57	VAWDOM	3.242	159.0	17
58	SAYRUF	3.242	173.7	17
59	RIJNIH	3.242	163.3	17
60	TICMAT	3.243	150.2	22
	QAFVEY	3.243	153.2	17
	HAVLUL	3.243	155.1	17
	GAYQEC	3.243	137.0	5
	GADHAU	3.243	153.3	17
	LAVLEZ	3.244	174.9	17
	HIPNUP	3.244	153.2	5
	RIHJOH	3.245	145.8	17
	CUZZUS	3.245	157.5	22
	WEKWOY	3.246	129.9	5
	TEYCOP	3.246	154.5	22
	TCACAD02	3.246	150.4	18
	MAXLED	3.246	161.0	5
	NOQJIM	3.247	150.5	22
	GURCUR	3.247	149.4	17
	ZECQUT	3.248	165.1	17
	YESDAB	3.248	161.2	17
	VUBZOH	3.248	174.7	22
	TAHBOT	3.248	138.4	16
	OKEPUP	3.248	153.5	17
	LEJYUU	3.248	134.6	17

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2				
3	NEGHA I	3.249	149.5	17
4	IDIZOL	3.249	129.2	17
5	DAJZET	3.249	142.1	22
6	TCLOBQ	3.250	160.3	17
7	IJEPOC	3.250	173.0	17
8	GOHKAP	3.250	168.0	17
9	CAHMOO	3.250	175.1	22
10	QAFTUM	3.251	148.6	18
11	PUYQUV	3.251	144.6	17
12	KAVDUG	3.251	160.0	17
13	GARQIZ	3.251	153.7	5
14	GANDII	3.251	143.0	5
15	DCLNAP01	3.252	173.7	17
16	SANTIL	3.253	168.2	5
17	NTCPOL01	3.253	155.6	22
18	KIDCOP	3.253	101.8	17
19	GAXLEW01	3.253	116.9	17
20	XAYBOO	3.254	154.0	17
21	IWOCOM	3.254	165.1	17
22	HEVWIO	3.254	151.4	17
23	XEGSOS	3.255	135.6	17
24	XAYBUU	3.255	143.1	5
25	VORVAZ	3.255	165.3	5
26	TCPpra	3.255	151.6	17
27	PEYWIZ	3.255	136.2	5
28	IJOCIT	3.255	155.9	5
29	NUVVAB	3.256	162.6	18
30	MONTOY	3.256	147.7	17
31	FUMBAQ10	3.256	138.8	17
32	FUMBAQ	3.256	138.8	17
33	DUGMOH	3.256	153.4	17
34	CLVINA	3.256	133.9	16
35	BIDLIJ	3.256	154.7	17
36	AHINAG	3.256	121.8	5
37	YUDSUL	3.257	167.0	5
38	YABXUU	3.257	155.6	17
39	XIHMOQ	3.257	148.5	17
40	KACKAB	3.257	164.3	5
41	EZENE C	3.257	158.1	5
42	AMAVIT	3.257	150.3	17
43	XOSBAI	3.258	134.3	17
44	RAFDEH	3.259	120.6	16
45	MAXLAZ	3.259	149.5	5
46	ACMGHX	3.259	154.6	17
47	TCPXAC	3.260	138.1	17
48	JIGRAS	3.260	160.3	16
49	YAWNIT	3.261	133.1	5
50	VUHVUP	3.261	143.0	17
51	LAKJOW	3.261	156.8	17
52	CUPJIG	3.261	157.1	17
53	BUMTEI	3.262	121.2	5
54	BANGEC	3.262	125.6	5
55	XEGLEA	3.263	169.7	17
56	NEGKEP	3.263	158.9	17
57	CUVWIZ	3.263	110.7	22
58	CLMPCL01	3.263	150.2	16
59	WOTNIC	3.264	150.1	17
60	PUYSIL	3.264	156.3	5
	MECOAN10	3.264	169.1	17
	LUNRER	3.264	154.2	17
	HUZBIN	3.264	150.7	22
	GAXLEW01	3.264	155.0	17
	POBBEN	3.265	166.5	17
	IPYCNP	3.265	166.5	16
	DAGPAD	3.265	169.0	5
	RACQIW	3.266	159.6	17
	NEGHA I	3.266	111.2	17
	LAKJUC	3.266	150.1	17
	HODSUO	3.266	163.0	17
	DEPMOA	3.266	153.0	5
	CAPLAH	3.266	154.9	17
	ZAMWAL	3.267	131.4	5
	NAKMUH	3.267	165.9	5
	HEGRIU	3.267	155.9	22
	BIKBAZ	3.267	128.0	5
	ASUXUH	3.267	155.4	17
	PARGOE	3.268	164.2	17
	CMNBEN10	3.268	150.3	22

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2				
3	AYEDUD	3.268	160.2	22
4	GIGMOY	3.269	169.1	16
5	DATQUL	3.269	142.2	16
6	NAKMUH	3.270	150.1	17
7	EOQUNX	3.270	149.2	5
8	PIWRES	3.271	162.6	17
9	OBIDUY	3.271	114.2	22
10	FIFXIB	3.272	163.5	5
11	TUSPOM	3.273	150.6	18
12	SEZMEP	3.273	115.5	5
13	JIHPOF	3.273	172.4	17
14	ECAXAH	3.273	161.7	17
15	AKOYUU	3.273	142.8	22
16	ZOYJOM	3.274	169.7	17
17	ZEXSUQ	3.274	155.0	5
18	MCDGAL	3.274	107.2	5
19	DATQEV	3.274	160.1	16
20	HIBWIY	3.275	155.2	22
21	CNPNTC	3.275	151.4	22
22	ZIYMOJ	3.276	170.8	17
23	SEGQEA	3.276	137.8	18
24	LAPGIS	3.276	151.6	17
25	HUQNAI	3.276	159.1	17
26	HAXXEJ	3.276	141.8	22
27	FIRZAH	3.276	137.1	5
28	DEFSOW	3.276	143.2	5
29	CLACAL10	3.276	143.0	17
30	BOLLUJ	3.276	151.7	5
31	TCLOBQ	3.277	148.1	17
32	SANTIL	3.277	101.7	5
33	NUPKOY	3.277	149.6	17
34	LUNRER	3.277	152.5	17
35	KOCSIE	3.277	137.2	5
36	CIMHIP	3.277	150.3	17
37	ZEGCUJ	3.278	125.9	22
38	YAFFEQ	3.278	161.0	5
39	NUKTIW	3.278	150.9	17
40	CUWSAO	3.278	128.7	17
41	XAZVUQ	3.279	155.3	16
42	TRIMCA10	3.279	165.6	5
43	GARQUL	3.279	108.0	17
44	YOZKED	3.280	134.9	17
45	WIZQIF01	3.280	173.7	17
46	MEGZAA	3.280	177.8	16
47	TOCPIM	3.281	177.5	17
48	IDIQUI	3.281	153.4	17
49	HIBWEU	3.281	148.7	22
50	DAJZET	3.281	155.2	5
51	NEGHOW	3.282	160.0	17
52	HAXWUY	3.282	117.0	22
53	CEFDEW	3.282	129.2	17
54	NUHTEP	3.284	158.1	17
55	JODTEB	3.284	130.7	5
56	DUZSIA	3.284	143.7	17
57	BUTPUB	3.284	124.2	17
58	BUTPUB	3.284	124.2	17
59	PCHSAN	3.285	151.7	17
60	NAXDEV	3.285	148.2	22
	BABXUX	3.285	143.0	5
	ARAYUN	3.285	149.4	5
	INEHAK	3.286	147.3	17
	FUHGUK	3.286	131.7	22
	CEKWAQ	3.286	122.2	5
	JURMOY	3.287	145.4	17
	FIYLOO	3.287	129.0	16
	ZIZTAD	3.288	141.2	17
	KIDCOP	3.288	143.3	22
	DMXCTY	3.288	160.6	5
	WEDJEV	3.289	159.0	17
	UFECUD	3.289	168.0	17
	HIHJUD	3.289	168.7	5
	DOYGIH01	3.289	143.3	5
	DOVWUG	3.289	153.0	17
	XACVEC	3.290	116.2	17
	FIZGEA	3.290	145.6	17
	SUQFAL	3.291	155.6	17
	FIZGOK	3.291	146.2	17
	BAWZOO	3.291	140.7	18

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3	WACTEA	3.292	161.2	5
4	CIMCUW	3.292	154.8	17
5	LUHLOP	3.293	113.3	5
6	BUMJEY	3.293	161.9	17
7	BEQBUU	3.293	169.3	5
8	THTOXC	3.294	140.1	17
9	KAJDAB	3.294	133.5	17
10	FOLPUR	3.294	128.3	17
11	CLACET02	3.294	156.6	18
12	TUNVIH	3.295	146.1	17
13	GERDIQ	3.295	150.2	5
14	CLMOCT	3.295	176.7	17
15	AIMCTY	3.295	100.0	5
16	SORBIK	3.296	156.8	22
17	KIDCUV	3.296	147.6	22
18	TEVJUJ	3.297	166.4	17
19	TELQUW	3.297	131.8	17
20	SICQAW	3.297	127.5	17
21	LIZCOM	3.297	170.7	5
22	JORFEB	3.297	139.9	17
23	IDOGEN	3.297	160.9	16
24	CMDCN	3.297	161.4	17
25	TANWAH	3.298	157.1	17
26	HESNEY	3.298	155.1	5
27	GEDSOX	3.298	153.2	22
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list of Br...N contacts in ascending order  
structures with N(atom) < 50

code: CBr4 carbon tetrabromide  
XF perfluoroalkyl- or perfluorophenyl-Br  
AZOL 5-membered azo ring-Br  
TCNQ tetracyanoquinodimethane-Br  
C=C=N conjugated nitrile acceptor  
F fluorophenyl-Br  
NO2 nitrophenyl-Br  
BARB barbituric acid-Br

acceptor code:

23 =N-  
4 C=N nitrile  
19,20 NHR amino or amide

refcode	Br...N	C-Br-N	acceptor	chemical environment
FEGYEV	2.531	180.0	23	CBr4 (possible rotatnl. disorder)
JICWIB10	2.720	171.1	23	BARB
IKUHUR03	2.829	179.1	23	XF
JICWIB10	2.830	174.6	23	BARB
KAVFIX	2.841	177.8	23	XF
IKUJAZ	2.841	174.3	23	XF
IKUJON	2.881	170.9	23	XF
FEJFAB	2.884	169.9	23	CBr4
AWAKIS05	2.885	163.4	23	AZOL
AWAKIS02	2.917	163.0	23	AZOL
FUSWEV	2.932	177.9	23	AZOL
NAKXEC	2.952	174.1	4	TCNQ
AWAKIS	2.953	162.9	23	AZOL
BRTETZ	2.960	166.0	23	AZOL
BCACEN	2.978	177.2	4	C=C=N
IKUJON	2.984	162.5	23	XF
WEFLAV	2.985	174.5	4	XF
SETWOD10	2.998	158.7	4	C=C=N
SETWOD	2.998	158.7	4	C=C=N
BRADOS	3.011	178.1	23	AZOL
WEFKUO	3.012	171.6	4	XF
SILKED	3.013	175.7	4	TCNQ
BEPYRZ10	3.019	175.7	23	AZOL
IFAHIH	3.022	169.7	23	AZOL
SILKED	3.024	177.9	4	TCNQ
QIHDAM	3.025	172.3	23	XF
PEXGOO	3.037	165.7	4	TCNQ
FOMRAB	3.048	166.0	4	F
KUXKET	3.050	169.8	23	NO2
NUBCES	3.052	168.9	23	AZOL
NABVIV	3.072	176.7	23	AZOL
LERHAR	3.074	162.3	4	C=C=N
GIDJUY	3.075	177.3	4	
HOFMUK	3.077	173.7	4	AZOL
HUYUYV	3.078	173.9	23	AZOL
PAMZUZ	3.085	163.2	23	
PEXGOO	3.095	168.5	4	TCNQ
SILKED	3.099	175.5	4	
TIQDAY	3.103	173.2	4	
POJNUX	3.105	173.8	23	
WASHEE	3.109	158.5	23	
MIFXEE	3.110	173.3	4	
SOYFUH	3.120	162.2	4	
DATWAX	3.121	167.6	4	
DATWAX	3.124	151.1	4	
DATWEB	3.134	173.5	4	
DADRUW	3.134	171.5	4	
GOTQEL	3.138	162.8	23	
DBPHCN	3.146	170.8	4	
HIPPAX	3.147	164.2	23	
BIYFAO10	3.148	173.5	4	
SOMKIO	3.156	170.0	4	
ACOKEI	3.156	164.6	4	
FOKSIH	3.166	168.9	23	
NAKXEC	3.167	157.5	4	
HERBAH	3.178	159.4	23	
BIYFEU10	3.184	159.2	4	
YEDTIL	3.189	162.4	23	

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3	XAGNOJ	3.192	169.0	23
4	ZEBZAH01	3.196	168.4	23
5	ZEBZAH	3.196	167.9	23
6	XAGNUP	3.198	164.4	23
7	TAQVIR	3.198	176.3	23
8	DADSAD	3.198	149.0	4
9	NAWYAM	3.202	162.5	23
10	MTBCEY	3.202	165.4	4
11	MDBADN	3.202	172.2	4
12	BPZCHX10	3.209	168.7	23
13	IDIFOR	3.210	163.8	23
14	MBRMAD01	3.218	172.2	4
15	XESQOB	3.224	167.9	23
16	VAZVIC	3.226	169.3	4
17	MPODZO10	3.226	171.7	23
18	WALYIS	3.227	156.8	4
19	HERBAH	3.236	173.3	23
20	XEHLAY	3.237	166.8	23
21	KEDHUW	3.239	163.9	20
22	XAGNID	3.240	172.4	23
23	IFAHON	3.240	167.5	23
24	PBROZH	3.241	174.3	23
25	BZAZCY	3.246	177.7	4
26	YOXGOH	3.247	179.8	4
27	ABPHAK10	3.251	173.8	23
28	MDMBAD	3.257	175.5	4
29	CAZGEP10	3.261	165.1	4
30	ILISIF	3.264	177.5	23
31	HUYUYUV	3.264	166.5	23
32	BRMALN	3.264	168.2	4
33	UBEZAC	3.272	170.8	23
34	KUBRUU	3.274	177.5	23
35	GEDCEY	3.284	165.0	4
36	DBPHCN	3.288	166.9	4
37	KAMCOQ01	3.294	139.5	4
38	VATROY	3.297	154.8	23
39	NAWYAM	3.299	125.9	23
40	OGEWOM	3.306	148.0	23
41	MOTZIE	3.310	168.2	23
42	VAWMUB	3.318	170.4	4
43	XAGNUP	3.323	161.4	23
44	TAPZEP	3.323	156.3	23
45	KATCOX	3.327	150.5	4
46	BIJLEL01	3.335	160.7	23
47	MISSEM	3.337	157.2	4
48	NAQSON	3.339	178.3	23
49	KALYUR	3.349	142.0	4
50	CODBOM	3.353	168.7	4
51	CAJLOO	3.357	178.8	4
52	DINJUF10	3.362	168.2	23
53	JIGWIF	3.367	149.8	19
54	BENWAT	3.371	167.1	23
55	XEBSIH	3.373	179.8	23
56	IYEYUG	3.375	158.1	23
57	MAJTUN	3.377	152.2	23
58	LUQMIT	3.383	144.3	23
59	WANWOX	3.387	166.7	23
60	KOTMIP	3.387	151.2	23
	FUDTIH	3.388	165.7	23
	IFAHON	3.389	145.1	23
	MEBCOM	3.391	146.8	23
	BPMBPA	3.392	167.5	23
	EMEJIP	3.400	146.2	23
	BPMBPA	3.401	168.2	23
	EMEJIP	3.404	145.3	23
	CODBIG	3.404	163.3	4
	HERBAH	3.405	139.0	23
	DATWEB	3.406	155.6	4
	DMPPIXZ	3.410	163.0	23
	WANXOY	3.411	160.2	4
	RONLEL	3.412	139.0	23
	CASJIQ	3.413	135.7	23
	BAZCHP	3.417	163.4	23
	HOMQAB	3.418	112.8	23
	DATDEI	3.419	160.9	4
	XACGIS	3.422	111.5	19
	KAMCOQ	3.423	147.0	4
	XAGNUP	3.424	160.2	23

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3	RADTEW	3.424	156.8	4
4	NAWYAM	3.426	102.5	23
5	VUJLAN	3.428	167.0	23
6	VAWNAI	3.429	166.0	4
7	VAWNAI01	3.431	167.1	4
8	ABORIT	3.431	174.9	4
9	YAFXAE	3.434	139.9	4
10	LOLGAU	3.434	164.3	23
11	VAWNAI	3.436	168.3	4
12	DADRUW	3.440	114.2	23
13	BMATZO	3.440	160.6	23
14	KAMCOQ01	3.441	130.6	23
15	HPCPPU	3.443	150.7	23
16	NEGKOZ	3.450	154.0	4
17	IPEWOP	3.451	155.2	23
18	HERBAH	3.457	156.4	23
19	IDIGAE	3.463	126.6	23
20	YEHKIF	3.465	170.4	23
21	SOMKIO	3.465	139.0	4
22	XAGNUP	3.472	143.0	23
23	BRTETZ	3.472	144.9	23
24	DIFFUT	3.473	139.4	19
25	QAHZUV	3.474	168.5	23
26	XUVXUH	3.475	153.4	4
27	BDNPOL	3.476	145.8	23
28	TUFSES	3.479	106.6	23
29	TEJSIK	3.481	116.7	23
30	WALYIS	3.482	163.1	4
31	FOKSIH	3.486	154.8	23
32	BRMPYR	3.489	166.1	23
33	CACPIG	3.492	132.7	23
34	IBUNIC	3.493	106.9	23
35	BIYFEU10	3.493	135.1	4
36	YANTOX	3.494	160.3	4
37	OLASID	3.494	100.2	23
38	RADTEW	3.498	156.4	4
39	CABXEI	3.499	174.0	23
40	ZAJNUT	3.502	167.0	23
41	FAMXUN	3.504	159.3	4
42	LOLFOH	3.508	109.7	23
43	PIKVEK	3.509	160.0	23
44	-----sum of intermolecular atomic radii			
45	MOTZEA	3.511	158.7	23
46	XAQCAU	3.514	159.7	23
47	KAGGUV	3.516	147.7	23
48	SEGZEJ	3.517	164.7	23
49	OBASUF	3.518	118.8	23
50	YANTAJ	3.521	154.6	4
51	AHELEE	3.521	100.9	23
52	PANBOW	3.525	158.2	4
53	DADRUW	3.526	132.3	4
54	OLASID	3.528	137.7	19
55	DADSEH	3.528	116.6	4
56	OCATES	3.529	175.2	4
57	NIBQAQ	3.529	133.5	23
58	TUFSES	3.531	132.2	19
59	HAMXUP	3.534	106.2	23
60	CUQLIJ	3.536	161.1	23
61	MUJCUP	3.537	161.0	23
62	BPMBPA	3.539	126.1	23
63	XUSBES	3.542	120.2	23
64	RAPVAG	3.542	111.1	19
65	QALNUN	3.542	158.5	23
66	MIXPAK	3.543	149.4	4
67	RAPVAG	3.547	104.7	23
68	QEQSAG	3.549	133.7	19
69	EYONUB	3.550	129.5	4
70	DADSEH	3.551	120.1	4
71	XOHDAZ	3.554	163.3	4
72	KEDHUW	3.555	103.2	20
73	KAZCUK	3.555	152.9	23
74	HOFMUK	3.556	108.6	19
75	DATWEB	3.557	165.9	4
76	NAWYAM	3.559	100.5	23
77	LAQVAB	3.559	154.2	23
78	MUKKOS	3.562	140.4	23
79	CIKQES	3.562	136.6	23
80	BRMOIN	3.562	114.1	23

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3	UFEGUH	3.564	143.5	23
4	CAMYUL	3.564	123.2	23
5	JICWIB10	3.565	139.3	23
6	KAJDIJ	3.567	142.9	23
7	KAZCUK	3.569	114.5	19
8	ABPHAK10	3.569	176.7	23
9	YANTIR	3.574	162.4	4
10	JAWCIT	3.577	146.3	19
11	BIJLEL01	3.577	125.4	23
12	BCMSFA	3.577	145.6	4
13	CITGAN	3.579	123.1	23
14	PEFCIN	3.580	149.1	4
15	XATFUU	3.581	162.8	4
16	GOPFAS	3.582	137.7	19
17	WIJCUN	3.584	131.5	23
18	SILKED	3.587	111.8	4
19	EWIYIS	3.589	103.1	23
20	BUMDES	3.592	157.8	23
21	VITVEZ	3.593	172.3	23
22	FAMYIC	3.593	156.0	4
23	KALYUR	3.594	101.5	4
24	DADSAD	3.596	115.2	4
25	HEMVEA	3.599	136.9	19
26	BRCYTS	3.599	107.0	23
27	IDIGAE	3.600	136.0	23
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list of Br...O contacts in ascending order  
structures with N(atom) < 50

code: CBr4 carbon tetrabromide  
XF perfluoroalkyl- or perfluorophenyl-Br  
AZOL 5-membered azo ring-Br  
TCNQ tetracyanoquinodimethane-Br  
F fluorophenyl-Br  
NO2 nitrophenyl-Br  
BARB barbituric acid-Br  
URAC uracyl O=C acceptor

acceptor code:  
17 C=O carbonyl or S=O  
5 -O-  
16 OH oxygen  
22 NO2 oxygen

refcode	Br..O	C-Br-O	acceptor	chemical environment
LUTPIZ	2.846	165.5	17	dibromophenol ring
GOWDOL	2.856	166.8	17	
THTOXD	2.876	170.8	17	CBr2-SO2
KAMCUW	2.892	172.2	17	URAC
KOFHAO	2.897	175.4	17	URAC
BADNAV	2.898	165.2	17	URAC
LUTPIZ	2.903	161.8	17	dibromophenol ring
JIGHUC	2.908	175.6	17	O=C-CBr=C=O
ECABOA	2.910	179.1	17	CBr SO2
TUFSES	2.916	172.9	17	URAC
KIYDIF	2.919	170.5	16	
HIHYIG	2.928	168.4	16	
XOBRIP	2.929	169.8	22	NO2
IWUKIU	2.934	172.9	17	SO2
ABMHFO	2.939	174.4	17	
SATPOT	2.943	163.9	17	
DXPREP01	2.951	172.9	5	epoxide O
HBBBLA	2.952	170.0	17	
DAMSAM	2.954	177.1	17	
GAJWIX	2.955	168.5	17	
RAKYUY	2.956	167.9	17	
HABPAB	2.958	171.0	17	
AXEJUI	2.960	158.5	16	
FIYDUN	2.962	164.5	16	
GOLLOI	2.965	176.6	17	
WUNGUH	2.967	172.0	22	
JIPJEX10	2.967	171.1	22	
JIPJEX	2.967	171.1	22	
CAYTIG	2.967	166.4	17	
BRADOM	2.969	166.6	5	water
RASYIT	2.972	175.0	17	
CACXAG	2.973	174.2	17	
CACXAG	2.976	163.1	17	
RASYIT01	2.978	175.3	17	
BRPSYD10	2.979	178.3	17	
VEFMOJ	2.984	163.5	17	
YAYTOI	2.985	172.9	17	
NACXUK	2.989	171.3	22	
EBURCL10	2.989	164.4	17	
GATBIN	2.991	178.9	17	
FEQPAS01	2.992	173.8	17	
JAWCIT	2.994	170.3	17	
UGULIR	2.995	168.3	5	
GEDCUO	2.995	166.5	17	
BCMBTH	2.998	166.3	17	
QIJFAQ	2.999	170.3	5	
FOHHIT	2.999	167.7	17	
BIBGIC	3.000	166.8	17	
WUXLEG	3.003	171.8	22	
SEBFUA	3.003	169.5	16	
CEHXOC	3.003	173.0	17	
BREPCA	3.005	173.2	5	
FIYDUN01	3.007	164.8	16	
XIDPUV	3.009	160.6	22	
VEGKEY	3.009	162.8	17	
ENISAV	3.009	172.5	17	
WADFIR	3.010	157.2	17	

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3	EYOYOG	3.010	166.8	17
4	KEYLES	3.011	162.2	22
5	UFECOX	3.012	161.9	17
6	GAJWET	3.012	166.5	17
7	BAJVOX	3.016	172.5	16
8	OMIYUE	3.017	173.2	17
9	RAPVAG	3.019	170.3	17
10	EFAXEO	3.019	169.8	17
11	TUGXIC	3.021	171.7	17
12	SIFFIW	3.024	166.9	5
13	VUTDUJ	3.025	151.0	17
14	YUHWUT	3.028	174.4	17
15	BPMBPA	3.034	157.5	17
16	JUPSOC	3.038	169.4	22
17	FERGUF	3.038	173.4	17
18	MEDKUC	3.039	164.4	17
19	COMBEL	3.039	171.8	17
20	IFAHUT	3.040	174.2	17
21	HATSOL	3.040	171.3	5
22	EVASUP	3.040	166.6	17
23	DUKSUX	3.040	145.7	17
24	CACXAG	3.040	168.0	17
25	ULAMOJ	3.041	169.6	17
26	LERGUK	3.041	172.4	17
27	JIPJAT10	3.042	158.9	22
28	JIPJAT	3.042	158.9	22
29	GULFIC	3.043	170.3	17
30	EBEYIT	3.046	159.2	17
31	CACXAG	3.046	173.0	17
32	DEGGOM	3.047	172.2	17
33	BSBTHP	3.047	156.4	17
34	AMBCRO	3.047	172.5	5
35	KAMNIW	3.049	172.3	17
36	JEXPAD	3.049	171.7	22
37	THTOXD	3.053	159.9	17
38	LOTFUV	3.054	169.9	17
39	TAWDUR	3.055	174.6	17
40	LOLFUN	3.055	173.4	22
41	DUFJUJ	3.055	165.4	17
42	XERGOQ	3.056	165.5	17
43	QEZROC01	3.057	174.3	5
44	FETYIN	3.057	168.8	5
45	QIDQUP	3.058	176.4	17
46	BRHPCN	3.061	170.1	22
47	RAYTEQ	3.062	167.8	22
48	VITVEZ	3.063	161.4	22
49	VONHEL	3.064	170.8	17
50	CACXAG	3.068	155.1	17
51	NACXUK	3.069	166.6	22
52	HUMLEG	3.069	164.2	17
53	BPENTA	3.069	168.4	17
54	NUWQEB	3.071	167.2	22
55	DEGXIW	3.071	163.8	17
56	ZZZBDA10	3.072	162.2	17
57	TONDOP	3.072	168.6	17
58	TAVJAC	3.072	166.8	5
59	NACXUK	3.072	167.4	22
60	IBEXOD	3.074	170.3	17
	YAQZUM	3.075	169.8	22
	QIJFAQ	3.075	169.5	5
	FONHOG	3.076	162.9	17
	DIRQAW	3.076	173.6	17
	TUNTUR	3.077	174.7	17
	IDOZAD	3.077	164.3	17
	YAYTUO	3.078	172.1	17
	XIDPIJ	3.079	175.5	17
	OHIHES	3.080	176.6	5
	LEDJEK	3.081	169.9	17
	YOKTEX	3.082	173.6	17
	RAXVOC	3.082	177.6	17
	BREPCA	3.082	172.0	17
	BMLTAA	3.082	167.0	17
	ACBTHO	3.082	175.8	17
	ZZZOZY01	3.083	167.5	17
	MBODZO10	3.083	173.2	22
	IDIGAE	3.083	154.7	5
	WOXLIE	3.084	171.7	17
	HABPAB	3.084	160.3	17

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3	BPMBPA	3.084	153.2	17
4	BAKSUC	3.086	176.6	17
5	YEGHOH	3.087	147.4	17
6	DAVWOM	3.087	158.5	22
7	NUWQEB	3.089	163.5	22
8	LAQVAB	3.090	159.7	22
9	IPUQIT	3.090	157.6	17
10	QABVAQ	3.092	178.4	16
11	JAPWUS	3.092	169.6	17
12	INETOK	3.093	163.8	17
13	ATUTIS	3.093	171.2	17
14	PAFRUJ	3.094	169.6	17
15	FANPAL	3.094	173.3	5
16	CEJYOF	3.094	168.2	17
17	TALXAF	3.095	169.2	17
18	MUVKUJ	3.095	163.4	17
19	REQYAN	3.096	155.4	17
20	PEMZEM	3.098	153.6	22
21	RALKOF	3.099	154.5	17
22	ULAMEZ	3.100	168.9	17
23	KEMNEV	3.100	173.3	17
24	FEQPAS	3.100	173.4	17
25	ULAMOJ	3.102	172.7	17
26	REDFIP	3.102	162.5	17
27	LURJIR	3.103	156.1	17
28	QAJJAM	3.104	169.2	17
29	HAGCUO	3.104	165.1	17
30	DOHZOP	3.104	146.7	17
31	BRFLAY20	3.104	176.0	17
32	KOFGOB	3.105	174.8	17
33	DASCBH	3.105	165.7	17
34	HEVRAB	3.106	162.5	5
35	KEYBAR	3.108	173.0	17
36	TUFSES	3.109	157.3	17
37	FOHHIT	3.110	169.8	22
38	ARTEMT	3.110	161.2	17
39	ZIBVOV	3.111	170.3	17
40	BMRIZN	3.115	164.4	5
41	EFECAT	3.116	175.7	17
42	VEZJUF	3.118	170.0	5
43	DACHIZ	3.118	165.3	22
44	FUPWUI	3.119	161.8	17
45	EXICOD01	3.119	168.9	17
46	AHUDIQ	3.119	164.9	17
47	TOKYUN	3.121	163.8	17
48	IDEFON	3.121	164.0	5
49	FOSREK	3.121	162.8	17
50	FOBTAS	3.122	164.7	17
51	RORQIY	3.125	165.0	22
52	LEGZED	3.126	170.2	17
53	BAHGUM	3.126	166.1	17
54	JEXPAD	3.127	178.2	5
55	UKOMEM	3.129	161.7	5
56	QEBDUW	3.129	172.6	17
57	IBEXOD	3.133	167.8	17
58	FERHEQ	3.133	178.7	17
59	NPMBPY	3.134	163.2	22
60	HEVPUT	3.136	151.6	17
	COLJUI	3.137	169.1	22
	YANBIZ	3.140	166.2	17
	LELXEF	3.140	177.1	22
	IZOPAO	3.140	161.4	17
	GANVUM	3.140	178.5	22
	EPRHOD	3.140	166.1	5
	NUSCIN	3.142	161.9	17
	FAMSER	3.144	150.2	17
	GEDCAU	3.146	169.7	17
	DAVRAU	3.147	167.1	22
	VUKTEA	3.148	162.6	17
	ECAGOF	3.150	160.9	22
	IFAHUT	3.151	153.1	17
	FIFFAC	3.154	161.0	17
	TAKBAJ	3.155	164.8	5
	PYRBZX	3.155	173.6	17
	DBRNPQ10	3.155	166.4	17
	VODRUB	3.156	159.7	17
	TBPHAN01	3.156	175.4	17
	LATPEB	3.156	162.7	22

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3	BRMNPQ10	3.156	171.6	17
4	BODTAP	3.156	164.1	5
5	REBBOQ	3.157	156.1	17
6	JEKZOP	3.157	160.5	17
7	FATLUH	3.157	162.5	17
8	VONKUE	3.158	176.7	17
9	SATPOT	3.158	158.1	17
10	QEZROC	3.158	174.0	5
11	YUYLOT	3.159	166.1	22
12	VAQXUG	3.160	158.1	17
13	TEHNOJ	3.161	176.6	17
14	EQONIH	3.161	154.7	17
15	DEGVAM	3.161	165.0	17
16	LICXUQ	3.162	177.2	17
17	AMBCRO	3.162	159.9	5
18	MCMSFB	3.163	178.8	17
19	WUTPUW	3.164	163.2	17
20	VITVEZ	3.164	161.2	22
21	MOQCIE	3.164	162.5	5
22	DIWVUA	3.165	170.8	17
23	VOPXON	3.166	164.5	22
24	VEPWIV	3.167	172.5	17
25	QAZBID	3.167	164.5	5
26	MAMSOI	3.167	160.5	5
27	LINMIE	3.167	165.8	16
28	PUVVAD	3.168	159.1	16
29	EXICOD	3.169	169.3	17
30	FEQZAC	3.170	160.5	5
31	SATPOT	3.171	176.0	17
32	QOHMUV	3.171	172.6	5
33	MISXUH	3.171	174.6	22
34	BRCYTS	3.171	150.6	17
35	TUDQUE	3.172	160.8	16
36	BZAMON	3.174	163.9	17
37	YAHBAK	3.177	163.0	17
38	BFLANH10	3.177	167.9	17
39	YAHBAB	3.178	164.5	17
40	VOFGUS	3.178	173.8	17
41	WISFAF	3.179	170.6	17
42	PBMALA01	3.179	158.1	18
43	BOBCOK	3.179	162.8	17
44	ETOLUU	3.180	178.4	16
45	YOYVAJ	3.182	165.3	22
46	UCIWEI	3.182	160.6	17
47	MIXCUR	3.183	138.5	22
48	VAQXUG	3.184	152.3	17
49	HINRUR	3.184	162.3	16
50	NACXUK	3.185	127.7	22
51	BPPRTO	3.185	167.6	17
52	UCEKIX	3.186	175.8	5
53	CACXAG	3.187	144.4	17
54	LEHRUM	3.188	177.2	5
55	KUPXAU	3.188	101.5	17
56	FOSNAC	3.188	162.9	17
57	WINNAI	3.189	168.2	17
58	DOCMEN	3.191	156.0	5
59	TEHNID	3.192	167.4	17
60	ABPZOL10	3.192	171.4	17
	YIRNUI	3.194	173.2	17
	WASJAC	3.194	159.0	17
	QEYQEQ	3.194	175.8	17
	BEDTNP10	3.195	147.8	5
	WOXKUP	3.196	178.2	17
	IDIGEI	3.196	149.9	5
	ZONLIX	3.197	179.5	5
	VASXIW	3.197	149.5	5
	SONDAA	3.198	167.4	5
	MEYWES	3.198	142.6	17
	ACAWOQ	3.199	154.9	22
	WUMMOG	3.201	166.4	17
	FUMZOC	3.201	167.4	17
	WESCEC	3.203	153.8	5
	VAYWOI	3.203	166.4	16
	BROHXN	3.203	158.5	22
	BRAMNQ10	3.203	166.7	17
	OHIHIW	3.204	174.9	5
	LURJAJ	3.205	153.2	5
	DANZEY	3.205	158.6	17



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3	COMDIR	3.205	166.3	17
4	BOQRAA	3.205	151.5	17
5	SOMGEG	3.206	163.0	5
6	RAPVAG	3.207	160.0	17
7	UKEKUQ	3.208	161.1	17
8	BMALAL01	3.208	162.2	5
9	AZUZOK	3.209	151.3	17
10	IBUPIE	3.210	166.5	17
11	XAMTUB	3.211	166.7	17
12	WAS PUB	3.211	152.3	17
13	FOMRUV	3.212	175.7	17
14	FAFPOR	3.212	164.6	22
15	COMBEL	3.212	148.2	17
16	BAHQAC	3.212	155.6	17
17	DAVWIG	3.213	129.7	22
18	TBPHAN01	3.215	155.2	5
19	NACXUK	3.215	114.7	22
20	KILCUD	3.215	159.1	17
21	DOHZOP	3.215	151.8	5
22	ROHHEB	3.216	166.6	17
23	LANZIK	3.216	161.8	17
24	BOMKOD05	3.216	127.5	5
25	WISDOR	3.217	161.7	5
26	TEDDIP	3.217	172.0	5
27	GEJGOS	3.217	157.6	18
28	DBRNPQ10	3.217	168.8	17
29	COMDIR	3.217	176.7	17
30	SIPMAF	3.218	173.6	16
31	NUTNEV	3.219	150.7	22
32	JAXRUW	3.220	176.2	22
33	PBMALA01	3.222	155.8	18
34	FERHAM	3.222	175.3	17
35	BEXMOG	3.222	162.3	17
36	ULAMOJ	3.223	163.4	17
37	IFAHON	3.223	136.2	5
38	ECUPAU	3.223	161.7	5
39	DIFFUT	3.225	174.4	17
40	BRNOHA	3.225	175.1	22
41	BOMKOD	3.226	177.6	22
42	ACIQIM	3.227	150.8	17
43	FOCYEC	3.228	166.4	16
44	DUKSUX	3.231	155.9	17
45	BPCTHA	3.231	162.4	17
46	VAQXUG	3.232	168.5	17
47	RACQOC	3.232	156.6	17
48	FOHHEP	3.237	142.8	16
49	NIBNOB	3.238	172.4	5
50	KECGII	3.239	158.3	17
51	GIDRAM	3.239	173.3	17
52	PAMROL	3.240	160.6	5
53	KUPXAU	3.240	166.3	5
54	AVOCIX	3.240	173.8	5
55	FERJAO	3.241	157.0	17
56	NOZSUQ	3.242	167.4	16
57	EHESIT	3.242	145.6	22
58	RATKED	3.245	143.2	5
59	WOXLEA	3.246	162.2	17
60	YADFAK	3.247	151.4	5
	KOBFAI	3.247	145.6	17
	BRVCPC	3.247	168.3	5
	YABKUI01	3.248	165.7	17
	VAGROL	3.248	159.7	17
	GAQVAW	3.248	146.7	17
	EFAYEP	3.248	163.0	22
	WUQKUO	3.249	156.4	17
	SIHWAH	3.249	155.5	17
	SAZSES	3.249	171.1	17
	FLABPC	3.249	149.8	22
	WIVFEM	3.251	143.0	16
	NACXUK	3.252	137.0	22
	LOTHAD	3.252	166.8	17
	LAMWUS	3.254	164.0	17
	XEGNIG	3.255	168.8	17
	QANGIW	3.257	173.2	16
	HANPOB	3.257	149.8	17
	ETBCAM	3.257	156.9	17
	BRCDOP	3.257	152.0	17
	BAZCUA	3.257	154.9	17

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3	SEYGUY	3.258	156.8	17
4	JOJVUZ	3.258	164.9	17
5	NUBQQQ	3.260	156.9	17
6	KACDAT	3.262	162.1	17
7	CIKQES	3.263	160.8	5
8	BPSUCA01	3.263	163.2	17
9	BENTOE	3.264	165.7	5
10	BENBRN02	3.264	160.1	22
11	SANWAF	3.266	129.5	5
12	RUVZUD	3.266	167.4	5
13	MAHMOX	3.266	159.2	5
14	IDEKOR	3.266	155.6	17
15	IYAWIO	3.267	164.1	16
16	BUMDES	3.268	168.6	22
17	TUZWOA	3.269	153.1	17
18	WAPJED	3.270	156.3	17
19	TIKDIA	3.270	121.0	5
20	NIBQAA	3.270	168.7	17
21	KEDHUW	3.270	133.3	17
22	FEYZEP	3.270	154.1	17
23	ULAMAV	3.271	161.2	17
24	QURPOI	3.271	154.9	5
25	XONXAZ	3.272	174.0	22
26	ADAQUS	3.272	162.3	16
27	SUNLOC	3.273	165.0	17
28	NUSCIN	3.273	157.7	16
29	ZEKBOG	3.274	159.2	17
30	ETIXUA	3.274	152.2	17
31	DASNIU	3.274	150.4	5
32	OXALYB	3.275	168.9	17
33	BOCCUR	3.276	157.1	5
34	BIBGIC	3.276	151.2	17
35	XECNUP	3.277	155.3	17
36	LOLGAU	3.277	159.3	22
37	AZOKOP	3.277	151.9	17
38	PASVAH	3.278	166.0	16
39	CDBOTN	3.278	178.9	5
40	BOMVEE	3.278	103.8	5
41	BHELIN10	3.278	174.9	17
42	VORLIX	3.279	151.5	17
43	MAQHES	3.279	154.6	17
44	KORROY	3.279	168.8	5
45	CEFFOJ	3.279	160.0	17
46	PIWKAH	3.280	169.9	17
47	BOMKOD05	3.280	177.7	22
48	DIFFUT	3.281	108.3	16
49	DIQDOW	3.282	153.2	5
50	CUMTIP	3.283	150.4	17
51	NACXUK	3.284	156.6	22
52	JAWCEP	3.285	149.9	5
53	BAXOZO	3.285	160.1	17
54	ECAHAS	3.287	160.1	22
55	VOLQAO	3.288	146.4	17
56	ETOKUT	3.288	157.3	22
57	VITVEZ	3.289	156.6	22
58	FERHUG	3.289	166.4	17
59	MELJOC	3.290	161.7	16
60	DAVWEC	3.291	162.8	22
	RELTUX	3.292	148.7	17
	JARHUG	3.292	163.2	17
	DOJMAQ	3.293	157.0	17
	WAFKUJ	3.294	156.0	17
	OKATEZ	3.294	171.6	17
	BOMVEE	3.295	106.6	17
	BHNCHX	3.295	176.2	17
	QIBGEN	3.296	175.5	17
	DAVRAU	3.296	130.2	22
	PYRBZX	3.297	140.2	5
	MXBTCP	3.297	160.4	17
	GAJWET	3.297	155.4	17
	DOJWUU	3.297	158.6	5
	QEYQEQ	3.298	170.4	17
	ERIXUY	3.298	106.0	16
	BIKBIH	3.298	159.3	17
	ULALUO01	3.299	158.6	17
	ECAGUL	3.300	177.9	22
	JAGTOA	3.301	163.2	17
	BIZYOY	3.301	163.7	17

list of I...N contacts in ascending order  
structures with N(atom) < 50

code: CI CI4, I2 or tetraiodoethylene donor  
XF perfluoroalkyl- or perfluorophenyl-I  
AZOL 5-membered azo ring-I  
TCNQ tetracyanoquinodimethane-I  
C=C=N conjugated nitrile acceptor  
ACTY iodoacetylene donor  
F fluorophenyl-I  
NO2 nitrophenyl-I  
BARB barbituric acid-I

acceptor code:  
23 =N-  
4 C=N nitrile  
19,20 NHR amino or amide

refcode	Br..N	C-Br-N	acceptor	chemical environment
ISIHUN	2.748	174.1	23	XF
MEKWO	2.792	175.8	23	XF
MEKWO	2.793	175.8	23	XF
QIHCAL	2.811	179.3	23	XF
WANPOR	2.817	170.5	23	ACTY
WANPIL	2.827	169.7	23	ACTY
WANNOP	2.828	169.7	23	ACTY
QIHCEP	2.843	178.7	23	CI
QIHCOZ	2.845	169.1	23	CI
QIHBE0	2.851	177.3	23	XF
IHUMON	2.885	174.7	23	CI
IHUMUT	2.916	168.4	23	CI
ULOKUB	2.928	170.8	23	XF
ICACEN	2.932	177.3	4	C=C=N
MOFFUI	2.934	174.0	23	XF
QIHBIS	2.944	169.1	23	XF
IHUNEE	2.949	175.4	23	XF
CADRAB	2.963	174.1	23	AZOL
EBIJEF	2.967	174.6	4	XF
EBIJIJ	2.968	177.0	4	XF
IETPYA10	2.974	176.5	23	CI
EBIHIH	2.981	176.2	4	XF
HOFGEO	2.987	180.0	23	iodopyridine
HEXAIF10	2.989	176.5	23	CI
HEXAIF10	2.989	176.5	23	CI
LUKMIN	2.999	170.6	23	XF
EBIHUT	3.002	176.5	4	XF
CEKFUU	3.002	174.8	4	C=C=N
EBIHON	3.012	174.0	4	XF
EBIJOP	3.023	177.5	4	XF
TOYGIX	3.025	171.4	23	AZOL
QIHBAK	3.032	176.0	23	
HEXAIF10	3.037	175.8	23	CI
VEBQEZ	3.043	166.7	23	
EBIJAB	3.046	176.6	4	XF
VEBQEZ	3.055	176.1	23	
HUMLOQ	3.060	172.6	4	XF
CADRAB	3.062	171.0	23	AZOL
WOJQAN	3.066	173.0	23	CI
JAQMAQ	3.067	177.2	23	XF
CEKFUU	3.074	174.4	4	C=C=N
ETOZOC	3.085	177.9	23	AZOL
BERQUK	3.101	171.8	23	AZOL
ISIJEZ	3.111	169.4	23	XF
ACOKIM	3.117	167.3	4	XF
WOJQOB	3.123	163.2	23	CI
IOBNIT01	3.127	180.0	4	iodobenzonitrile
SIDFIU	3.128	164.3	4	TCNQ
PUXLOJ	3.128	164.2	23	
LALMEQ	3.146	177.9	4	
DBIBZN	3.153	171.9	4	bifurcated I...N...Br
ISIJEZ01	3.158	169.6	23	XF
FIYYES	3.200	173.0	23	
HIPPEB	3.230	163.8	23	
JAYFEV	3.231	175.0	23	
CAMSUF	3.253	148.6	23	

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LALNUH	3.259	175.9	4
NELSON	3.263	172.6	4
YAGSEE	3.287	162.0	4
FIYYES	3.290	165.1	23
RIYKOZ	3.301	155.1	23
CESLIV	3.302	170.3	23
KECGUU	3.305	176.6	4
MOPHUU	3.334	174.3	23
SAWZIA	3.344	163.3	4
OCIQUN	3.385	142.9	4
TAPNOO	3.405	176.0	4
QALPAV	3.425	162.6	23
MOPPOW	3.487	160.1	23
XIHCOG	3.532	142.8	23
LABVUF	3.536	155.7	23
FOMJUN	3.544	170.2	23
FEXXIQ	3.553	174.0	23
EBUHEO	3.555	118.1	23
QALPAV	3.577	160.4	23
MEBMAH	3.586	144.7	4
MIXREQ	3.590	164.3	4
NAYYES	3.592	153.7	23
MMXIPA10	3.600	159.5	23
EDAGIZ	3.609	121.0	23
XUHQAS	3.611	166.6	23
IFOVII	3.613	170.4	4
DIMYUT10	3.634	164.6	23
NEGLIU	3.667	138.9	4
ITNOBE01	3.667	180.0	23
-----sum of intermolecular atomic radii			
BEBMEB	3.670	108.0	23
NEGLIU	3.674	146.9	4
ZILBIF	3.678	125.7	23
YESZAX	3.678	178.2	4
TEXVAT	3.678	145.1	23
BERQUK	3.687	107.3	23
BERQUK	3.694	105.9	23
ICAQ EJ	3.698	102.1	23
ZILBIF	3.704	106.0	23
XUDXEZ	3.704	101.3	23
KOVGEH	3.713	169.9	23
ZEMKUX	3.714	166.0	23
RIYKUF	3.715	158.3	23
QETWOB	3.715	108.8	19
WAWFUW	3.718	174.5	23
HIPPEB	3.722	126.4	23
CAMSOZ	3.723	116.4	23
KOVGEH	3.730	157.7	23
IAZPYM	3.733	105.6	4
KOVGEH	3.736	161.9	23
CAMSOZ	3.738	116.9	23
GOMBOZ	3.740	105.7	23
GUWDEH	3.742	175.5	23
YESZAX	3.746	110.6	4
OMOKIK	3.758	151.0	23
RAYCID01	3.759	180.0	23
PIQP IO	3.762	154.9	23
DIMYED10	3.786	169.0	23
AYUQE Q	3.788	111.6	23
CAMSIT	3.791	172.0	23
ZONYIK	3.799	175.2	23

list of I...O contacts in ascending order  
structures with N(atom) < 50

code: XF perfluoroalkyl- or perfluorophenyl-I  
AZOL 5-membered azo ring-I  
NO2 nitrophenyl-I  
URAC uracyl O=C acceptor  
ACTY iodoacetylene

acceptor code:

17 C=O carbonyl or S=O  
5 -O- or N-oxide  
16 OH oxygen  
18 CO-R oxygen acid or ester  
22 NO2 oxygen

	refcode	Br..O	C-Br-O	acceptor	chemical environment
1					
2					
3					
4					
5	OCOMUO	2.755	170.3	5	XF
6	QOJKUV	2.858	174.1	5	tetraiodopyrrole
7	IYAYUC	2.861	170.4	17	ACTY
8	KOCVIH	2.872	172.7	17	URAC
9	QETWOB	2.895	177.1	17	URAC
10	KIYDEB	2.920	169.4	16	AZOL
11	KORXEU	2.922	174.4	17	iodothiophene
12	KEDDUS01	2.928	162.7	17	SO2-CI2-SO2
13	TOYPUS	2.934	175.4	17	ACTY
14	QOJKOP	2.941	175.1	5	tetraiodothiophene
15	PADHUY	2.945	175.9	17	XF
16	QADBIH	2.949	166.9	17	iodothiophene
17	QOJLAC	2.957	176.4	5	tetraiodopyrrole
18	IDOXUR	2.958	171.0	17	URAC
19	DAXKOC	2.964	171.0	17	
20	XIHCOG	2.988	163.0	22	NO2
21	KORXUK	2.990	177.6	17	iodothiophene OS
22	MAYJAY	2.991	173.3	17	
23	ITHYRM10	2.991	174.3	17	
24	XORYUY	2.992	171.3	22	NO2
25	KORXOE	2.996	175.2	17	iodofuran OS
26	FENROF	2.996	162.0	22	
27	OLASUP	3.003	172.7	17	URAC
28	KORXIY	3.007	169.8	17	iodofuran OS
29	DOHZUV	3.010	156.6	17	
30	MAYHUQ	3.016	171.9	17	
31	KOVGEH	3.032	179.0	22	
32	IHQUSO01	3.039	168.7	17	
33	ITYRMA10	3.041	163.4	17	
34	XIHFEZ	3.042	161.0	17	
35	DIMYUT10	3.042	168.9	22	
36	JAXHOG	3.048	169.8	17	
37	ZEMKUX	3.054	176.1	22	
38	OMOKIK	3.054	167.8	22	
39	ZILBIF	3.063	175.9	17	
40	RIWTOG	3.067	174.4	17	
41	YAHJEX	3.071	173.3	22	
42	LAGMEM	3.071	162.8	17	
43	TITHYN10	3.072	173.7	17	
44	RIWTOG	3.074	173.8	17	
45	DIMYED10	3.075	173.9	22	
46	CACHOD	3.081	170.0	17	
47	EYITAH	3.082	174.7	17	
48	EHULOI	3.084	171.0	17	
49	MTIXTP	3.096	169.8	17	
50	LEBQIS	3.099	167.4	17	
51	KOVGEH	3.101	172.7	22	
52	NAWFEX	3.102	169.6	17	
53	XUDXOJ	3.105	167.0	22	
54	YESMEO	3.108	173.5	5	
55	XERGIK	3.112	173.2	5	
56	HECMIM	3.113	169.4	17	
57	FOGRID	3.114	170.7	5	
58	JEBPAI	3.123	174.1	17	
59	AEHIBQ	3.124	168.8	17	
60	MEZHAA	3.125	172.1	22	
	KAFREO	3.126	170.5	17	
	IFITEW	3.131	170.4	16	
	XATMIP	3.132	167.6	17	
	GERNUM	3.138	177.7	17	
	SUXZAM	3.139	171.3	5	
	XUHQAS	3.151	169.4	22	
	IBSAZO	3.151	172.5	17	
	YEJLII	3.153	171.5	22	
	CAMSOZ	3.161	166.9	22	
	ZILBIF	3.163	166.5	17	
	HIFYIE	3.163	172.4	17	
	CAMSUF	3.165	176.4	22	
	DIMCXD	3.167	162.5	17	
	DIPMOB10	3.168	157.7	17	
	YONPIA	3.171	159.9	17	
	DUKZIS10	3.174	163.2	17	
	CAMSOZ	3.177	167.6	22	
	FOZKOU	3.179	164.3	17	
	YAJREH	3.181	169.4	16	
	BMLTAB	3.182	167.7	17	

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3	MMXIPA10	3.183	166.0	5
4	RIJCIW	3.185	172.8	17
5	QEBXUQ	3.188	179.5	17
6	JIKHUG	3.190	157.7	17
7	GUWDEH	3.190	160.9	22
8	EBUHEO	3.190	147.7	5
9	UMULUJ	3.194	168.4	5
10	SIKWOY	3.194	176.2	17
11	KOVGEH	3.196	168.6	22
12	IADRCH	3.204	169.9	17
13	FORGOI	3.204	172.5	17
14	BEBMEB	3.205	160.4	22
15	DITHPA10	3.206	168.2	5
16	WURTUY	3.207	163.3	22
17	BOPDOZ	3.210	177.9	17
18	DALBOH	3.218	170.8	17
19	XUDXUP	3.220	162.0	22
20	GEHSES	3.225	167.2	17
21	PAZQAJ	3.229	171.0	17
22	EWIHAT	3.232	171.5	17
23	TIBENQ	3.234	155.5	17
24	CAMSIT	3.239	167.6	22
25	KATFOB	3.241	169.8	22
26	CAGTAF	3.243	157.1	17
27	BEFRUZ	3.243	155.6	17
28	EYOFED	3.249	163.2	22
29	LODDAJ	3.252	158.9	5
30	CXMIPA	3.256	161.4	5
31	KOVGEH	3.258	164.7	22
32	GOMBOZ	3.258	154.6	17
33	AMXIPA	3.261	173.7	17
34	RACVOH	3.262	175.2	22
35	AYUQEQ	3.262	166.8	22
36	YEJLII01	3.266	154.5	22
37	ITNOBE01	3.267	161.1	22
38	ZAQTOA	3.269	177.8	17
39	IENBCL	3.269	160.5	17
40	FEXCOB	3.269	153.4	17
41	MEZGUT	3.279	155.0	17
42	QODSEH	3.281	145.9	5
43	IPTHIM10	3.286	157.1	17
44	REQYIV	3.294	155.1	17
45	KAFREO	3.294	138.0	17
46	XUWVIU	3.302	162.5	17
47	XUHQAS	3.303	149.3	22
48	QETFAW	3.303	159.6	22
49	GAPWUP	3.308	156.0	5
50	DALBOH	3.311	170.1	17
51	GIQQAY	3.318	172.0	5
52	MTIXTP	3.320	172.3	17
53	MEZGIH	3.320	156.2	22
54	XORYOS	3.323	140.8	22
55	ZONYIK	3.327	163.8	22
56	XORYIM	3.327	152.2	22
57	MMXDPA	3.327	158.5	5
58	MACMEJ	3.333	161.8	17
59	VONFEJ	3.335	158.1	5
60	MEBMAH	3.337	149.5	17
	XAVHEI	3.345	156.4	18
	HEVJEX	3.349	177.7	16
	TECLUJ	3.351	145.9	17
	SATKII	3.360	173.9	17
	WUXCOH	3.361	146.5	22
	FOMKAU	3.363	171.6	22
	XOQCAH	3.366	171.5	22
	HIFYAW	3.366	171.2	5
	KOYNUH	3.367	170.4	17
	WAWMEN	3.368	159.7	22
	WAWFUW	3.368	160.3	22
	POKFUQ01	3.370	151.5	5
	HADBOD	3.373	166.1	17
	RAYCID01	3.375	161.6	22
	EYITAH01	3.375	177.5	17
	BANMUY	3.377	169.5	17
	MEZGON	3.380	162.4	22
	CAMSUF	3.381	155.1	22
	FEXDAO	3.385	155.1	22
	FEFLAE	3.385	154.2	22

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3	IBRBPX	3.388	169.7	17
4	RATFOI	3.390	165.2	17
5	AQEXUP	3.391	154.8	5
6	WOJXOI	3.394	153.9	17
7	DOHZUV	3.395	145.2	5
8	FOZKUA	3.398	163.1	17
9	ZEMKUX	3.400	141.9	22
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11	BEBMEB	3.400	155.6	22
12	JAQNUL	3.405	157.0	22
13	KORXEU	3.408	148.4	17
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16	VADFOV	3.412	167.9	22
17	WAVXUN	3.413	145.3	22
18	KAFREO	3.414	152.1	17
19	FEXCUH	3.417	166.6	22
20	EBUHEO	3.417	132.0	22
21	DEDSIO	3.423	154.1	17
22	WOYVAH	3.425	156.3	17
23	SATGID	3.425	168.5	22
24	NIMGOF	3.428	138.5	16
25	BUHXEH	3.430	160.7	17
26	BERLIT	3.431	134.7	17
27	MEDJOV	3.432	169.5	17
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30	JAWGOE	3.443	157.7	5
31	FEXCIV	3.446	152.6	22
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35	YESZEB	3.453	161.3	22
36	NAWSIO	3.455	149.3	5
37	EZIVIS	3.457	157.2	5
38	MEZGIH	3.459	166.6	22
39	BEPPOB	3.462	169.3	5
40	ZONYIK	3.466	157.9	22
41	UMULUJ	3.471	148.9	5
42	XOBLAB	3.477	169.7	16
43	XORYIM	3.480	128.3	22
44	WAWFUW	3.481	163.5	22
45	KOVGEH	3.482	151.8	22
46	SANZUC	3.486	157.9	5
47	HOMCIV	3.486	151.2	17
48	YEJLTI01	3.494	138.7	22
49	ATEQOF	3.496	150.2	17
50	KOVGEH	3.498	129.3	22
51	PAFXUQ	3.499	171.8	17
52	KOVGEH	3.500	113.0	22
53	JAQNUL	3.507	143.5	22
54	GUWDEH	3.511	160.9	22
55	HEVJEX	3.514	114.4	16
56	XOSCAJ	3.516	158.1	22
57	CAMSIT	3.520	154.0	22
58	RATFOI	3.523	132.9	17
59	XUDXAV01	3.527	146.8	22
60	KIYFAZ	3.535	151.2	5
	AYUQEQ	3.536	153.3	22
	XUDXAV01	3.537	164.0	22
	NASPUT	3.544	161.3	17
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	XORYIM	3.552	157.9	22
	KEDDUS01	3.559	140.2	17
	GAVSEB	3.560	170.9	17
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	HACFIA	3.567	156.4	17
	PIQPIO	3.569	143.0	16
	MATPOM	3.570	166.0	17
	GUZHUE	3.571	165.5	16
	CISLOF	3.572	168.9	5
	EZIVIS	3.573	130.4	5
	XORYIM	3.574	155.6	16
	EWIGOG	3.578	142.3	5

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3	VONFEJ	3.581	153.7	5
4	XMTDIB	3.590	164.1	5
5	KOVGEH	3.594	138.9	22
6	EDAWUB	3.600	152.9	17
7	IPEKET	3.602	125.2	17
8	-----sum of intermolecular			interatomic radii
9	CADRAB	3.610	152.1	5
10	DIMYED10	3.618	113.2	22
11	XUDXAV	3.620	125.6	22
12	FEXCIV	3.623	171.0	22
13	CADRAB	3.624	148.2	5
14	KOVGEH	3.626	113.9	22
15	YEJLII	3.627	150.8	22
16	WOYVAH	3.632	119.5	17
17	MEZHAA	3.633	110.8	17
18	LIBZOL	3.633	163.4	5
19	YAMRAG	3.636	115.6	5
20	BAGYAK	3.638	156.1	5
21	NETYEQ	3.640	154.0	17
22	WIPBOM	3.646	158.5	17
23	LAGMEM	3.646	117.7	5
24	IBRBPX	3.646	148.2	5
25	WOYVAH	3.649	100.2	17
26	XOSCAJ	3.652	139.7	22
27	EZIVIS	3.652	139.4	5
28	RACVOH	3.655	111.5	17
29	EDAVOV	3.658	145.4	17
30	VONFEJ	3.660	149.3	17
31	WOYVAH	3.662	114.0	16
32	FEXDAO	3.668	169.5	22
33	IBILEK	3.669	162.5	5
34	IPCDEC	3.672	148.9	5
35	OMOKIK	3.675	132.0	22
36	DALBOH	3.678	134.9	17
37	FOZKIO	3.682	148.1	17
38	COCHEH	3.687	150.9	17
39	QODSEH	3.688	128.3	5
40	KAFBID	3.699	151.0	18
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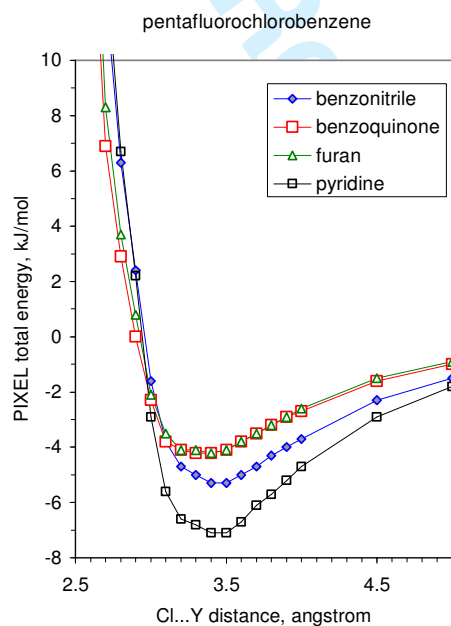
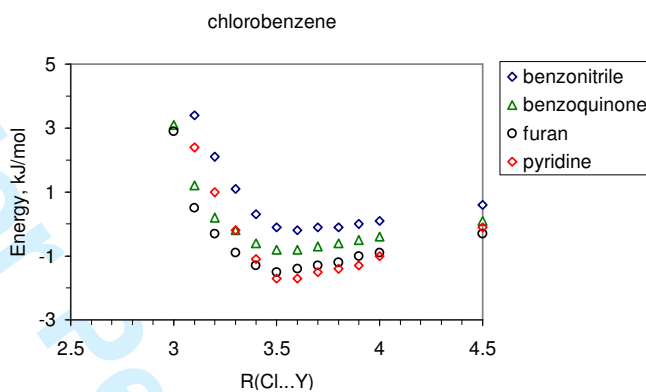
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9 **Non-conventional bonding between organic molecules. The "halogen bond" in crystalline**  
10 **systems**  
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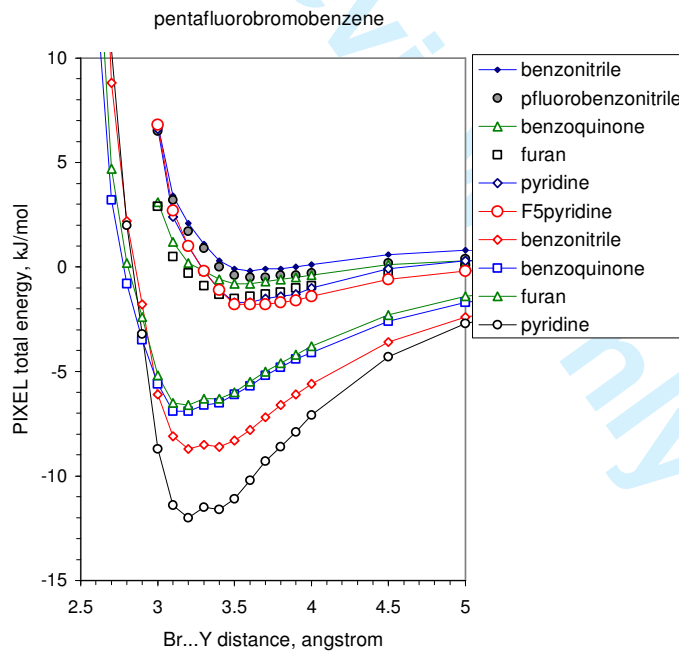
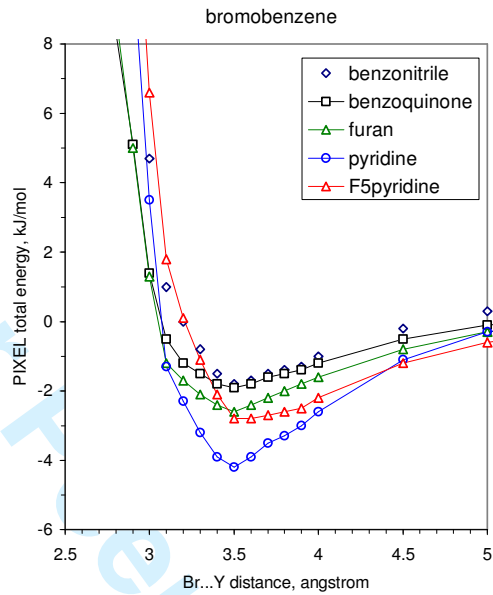
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14 A. GAVEZZOTTI

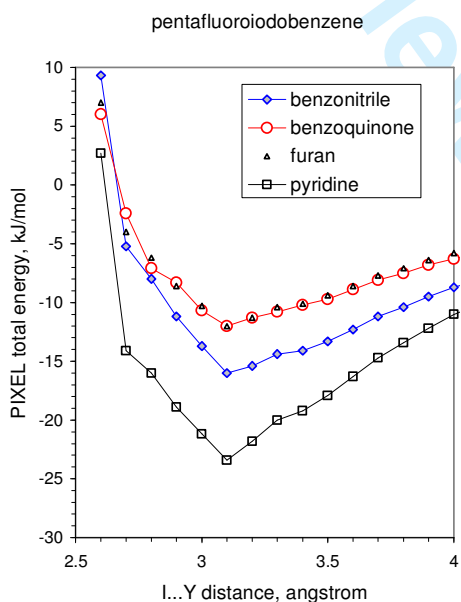
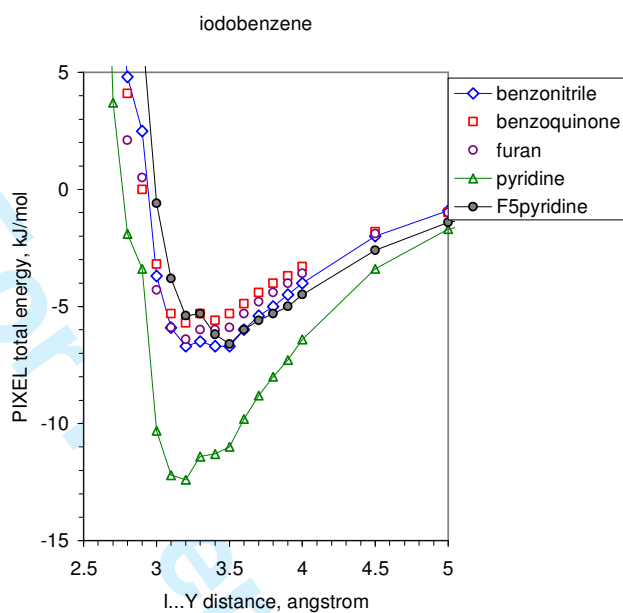
15 Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, Milano,  
16 Italy  
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27 **APPENDIX IV**  
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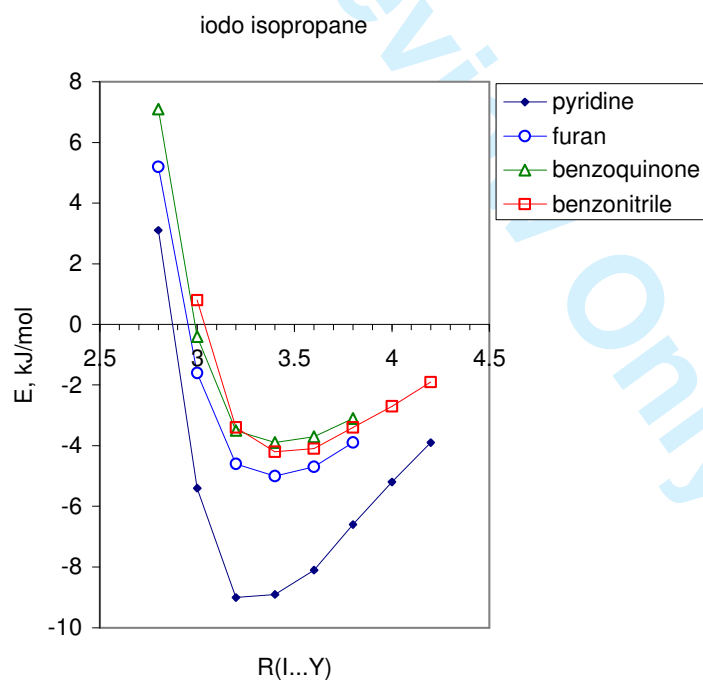
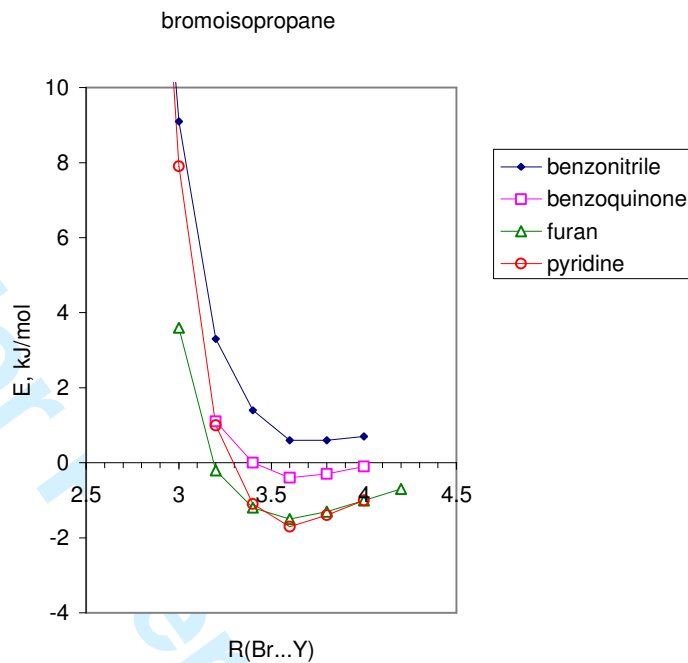
PIXEL energy curves for the interaction of halobenzenes and pentafluorohalobenzenes with several halogen bond acceptors. kJ/mol units.



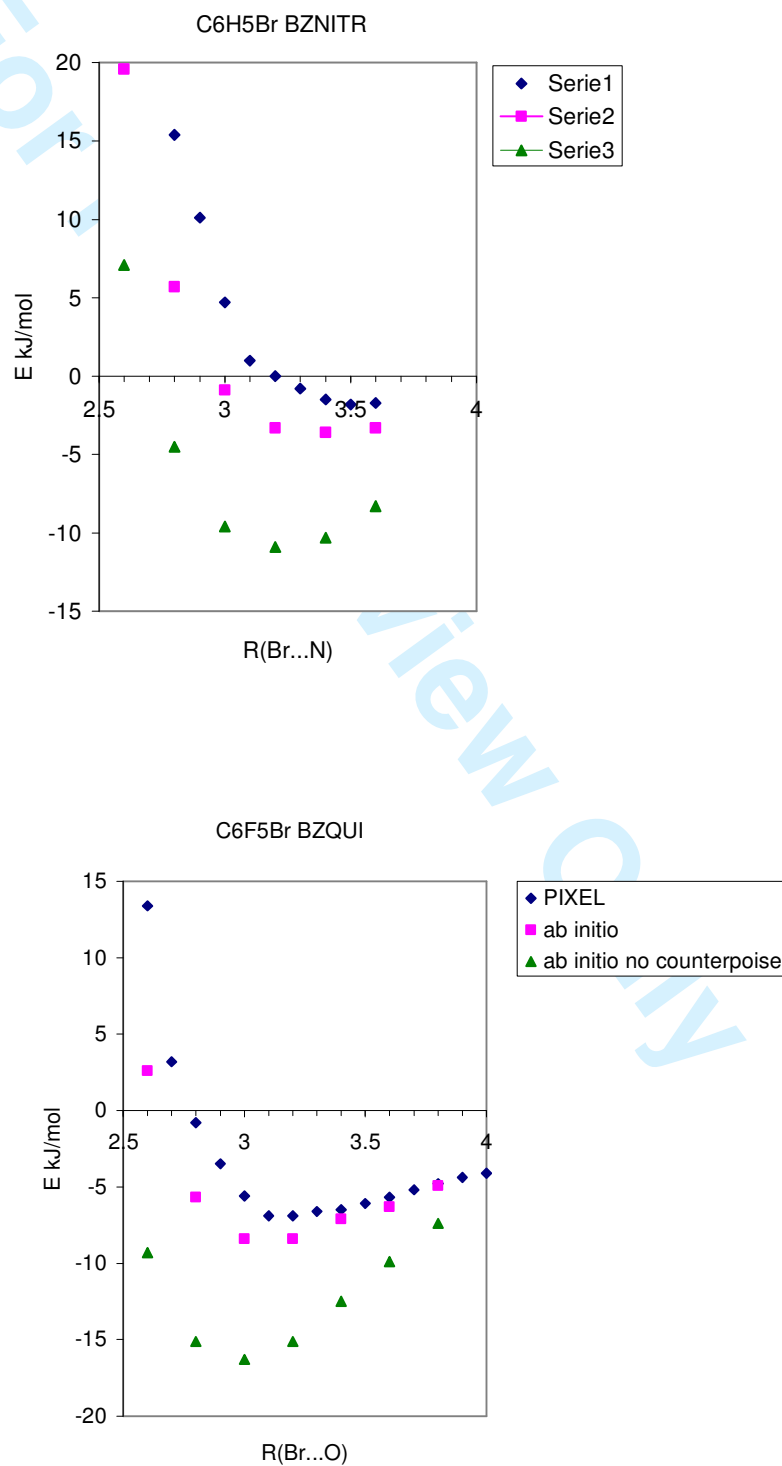




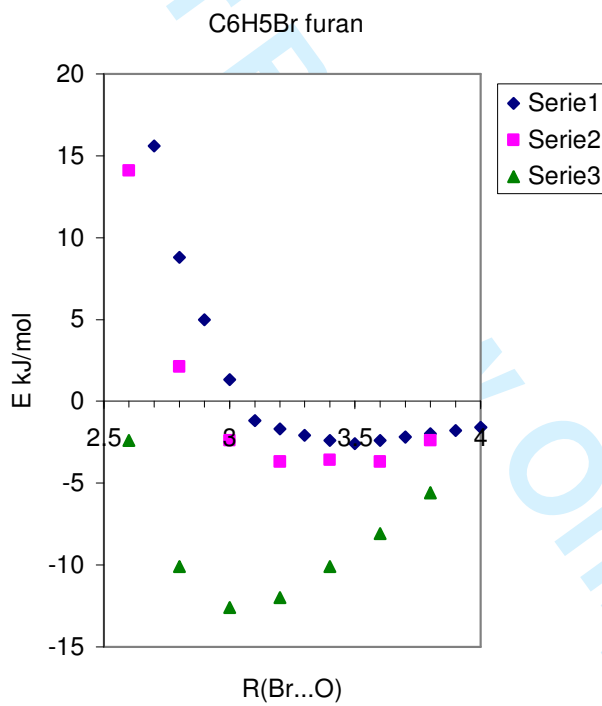
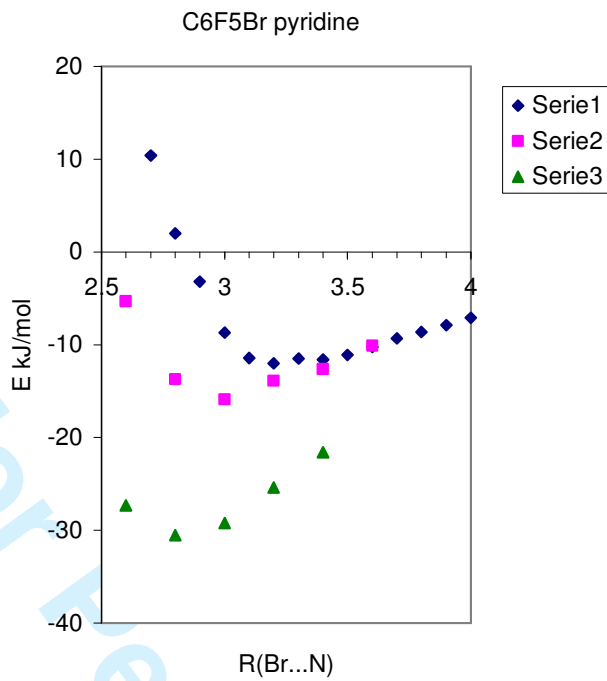
PIXEL interaction energy curves for the bromoisopropanes (kJ/mol)



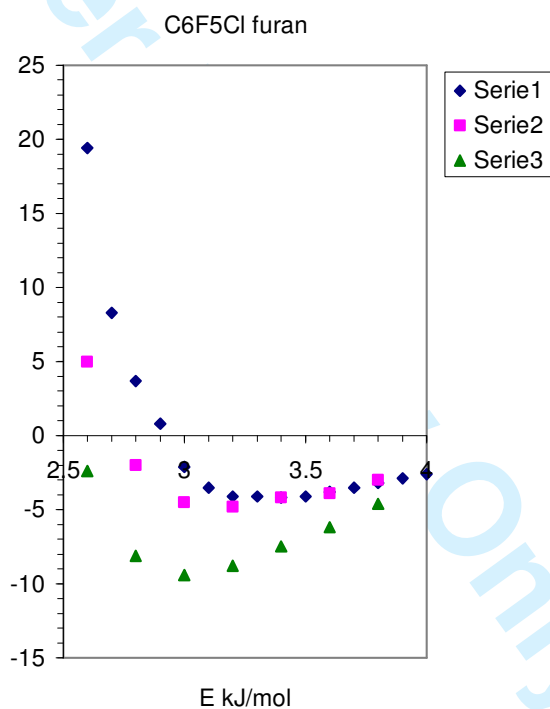
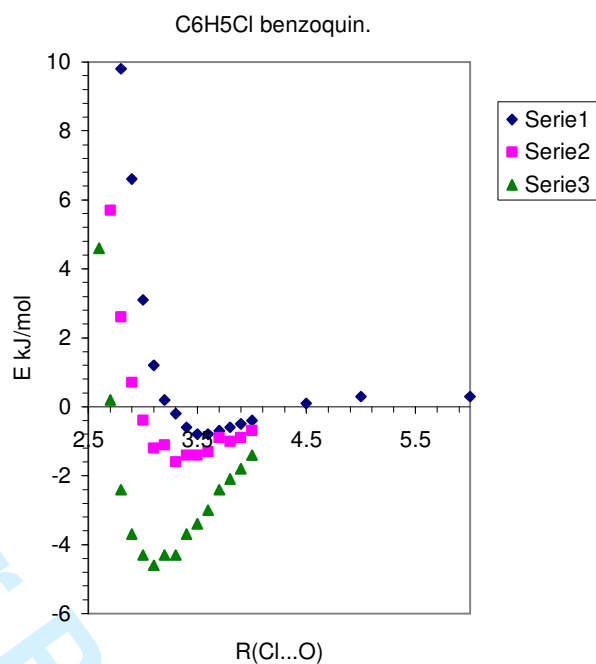
Results for the dimer interactions. Blue: PIXEL results; red: ab initio with counterpoise correction; green: ab initio no counterpoise. The horizontal axis is the C-X...Y distance (X= Cl, Br, I; Y = N, O). PIXEL: DGDZPV wavefunction; ab initio: 6-31G\*\* wavefunction for Cl, Br, DGDZPV wavefunction for I.



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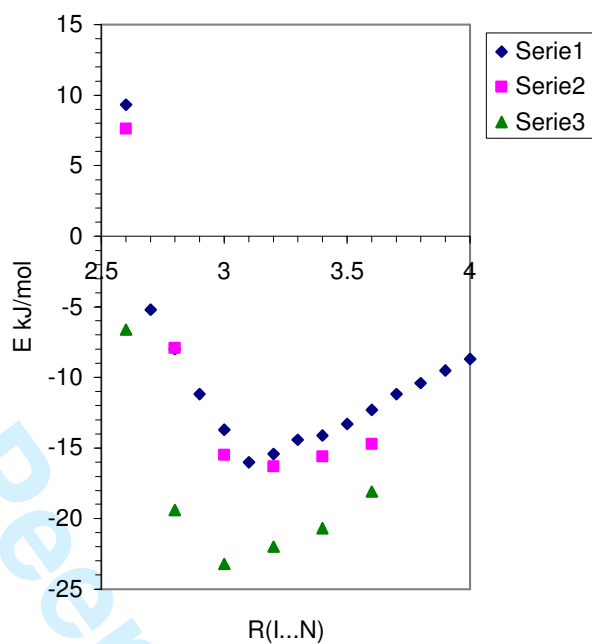


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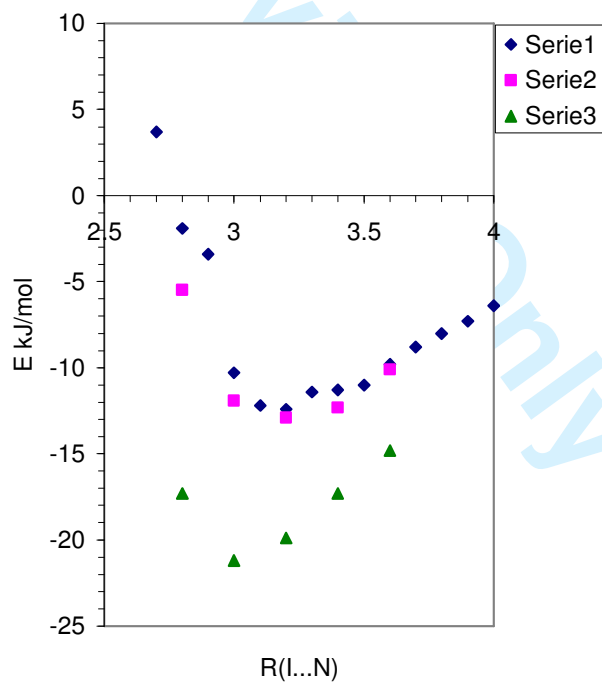


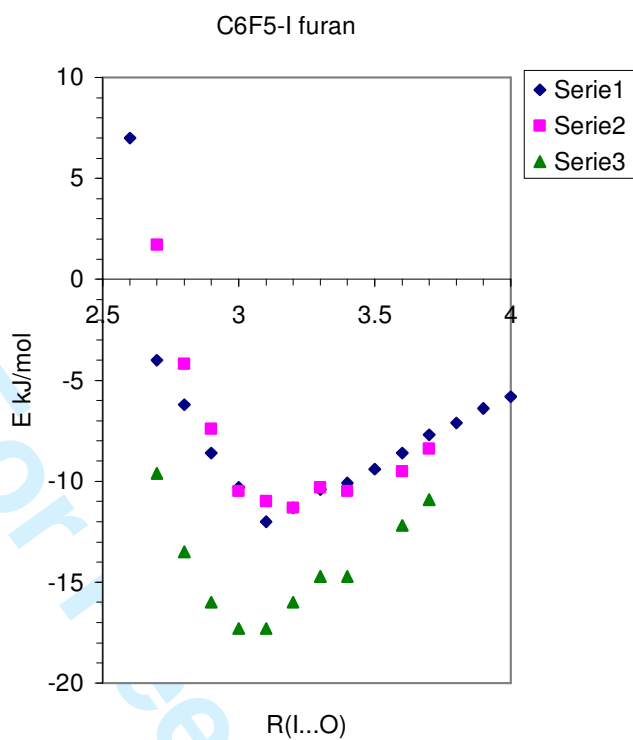


C6F5-I benzonitrile



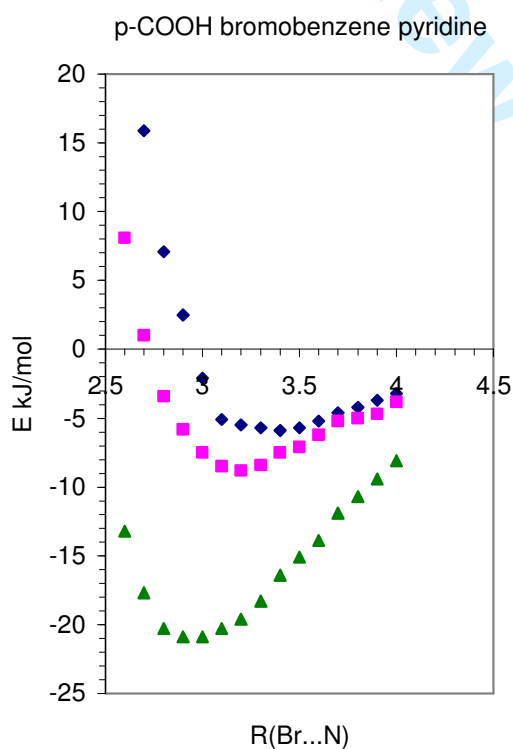
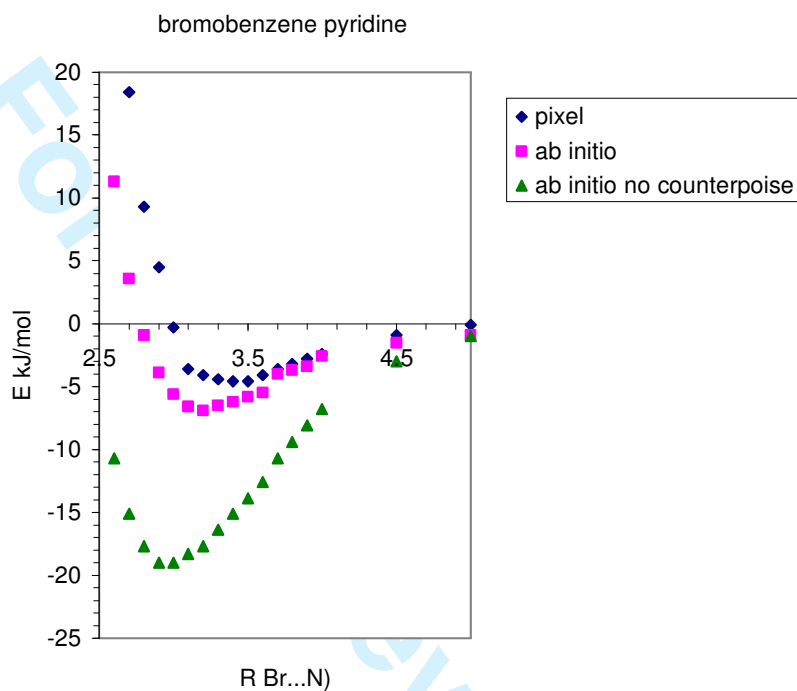
C6H5-I pyridine

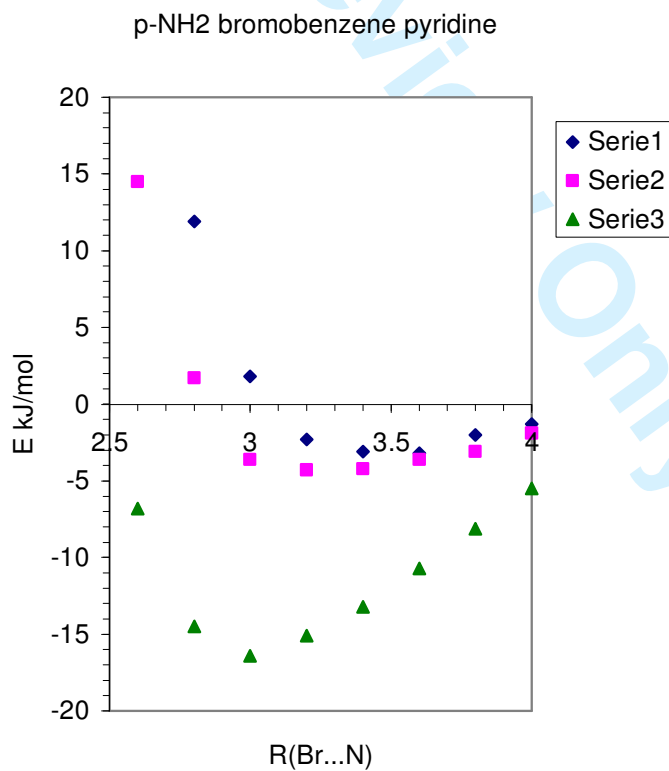
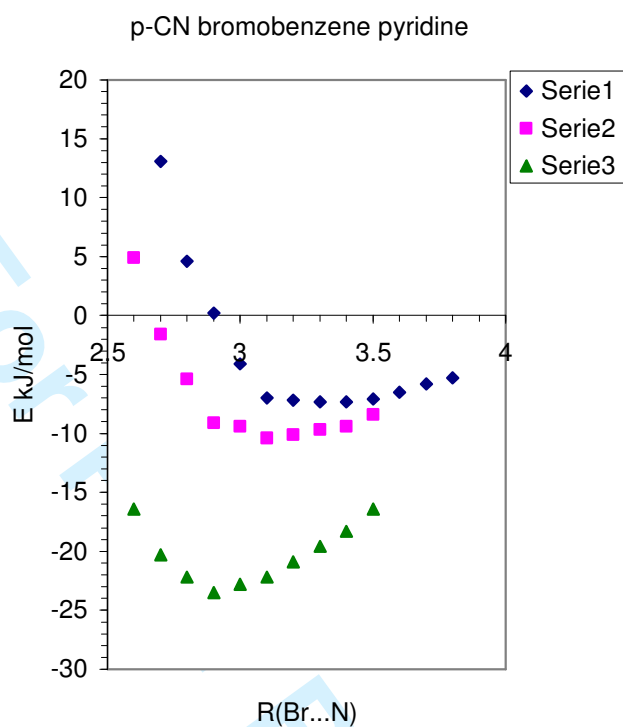




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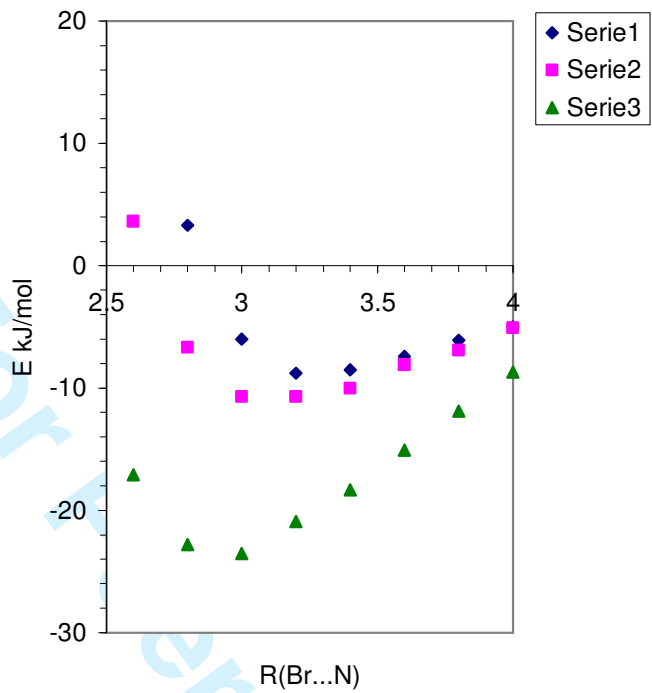
Interaction energy curves for 4-substituted bromobenzenes with pyridine. Blue: PIXEL results; red: ab initio with counterpoise correction; green: ab initio without counterpoise correction.



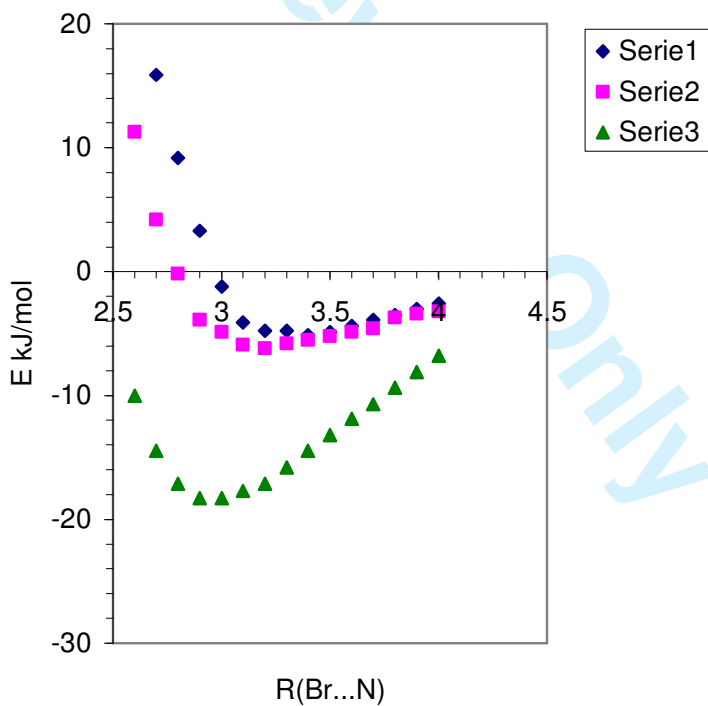


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p-NO<sub>2</sub> bromobenzene



p-OH bromobenzene



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9 **Non-conventional bonding between organic molecules. The "halogen bond" in crystalline**  
10 **systems**  
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27 **Supplementary material:**  
28 **Figures**  
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Figure 1Sa. DDF for Cl...Y contacts.

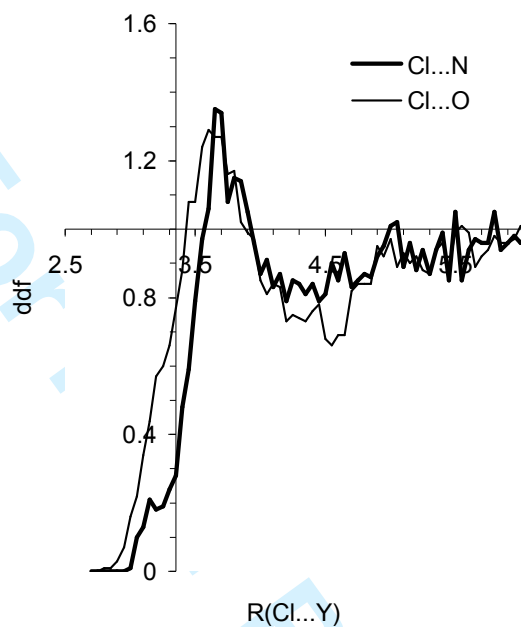


Figure 1Sb. DDF for I...Y contacts

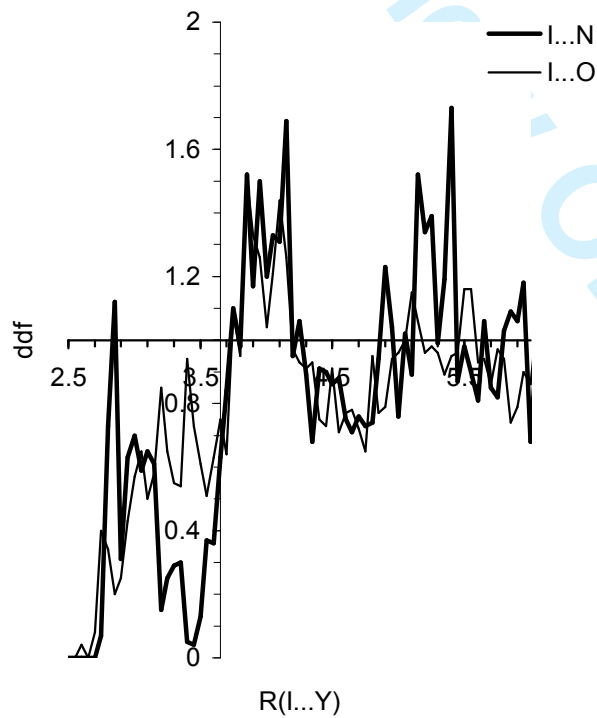
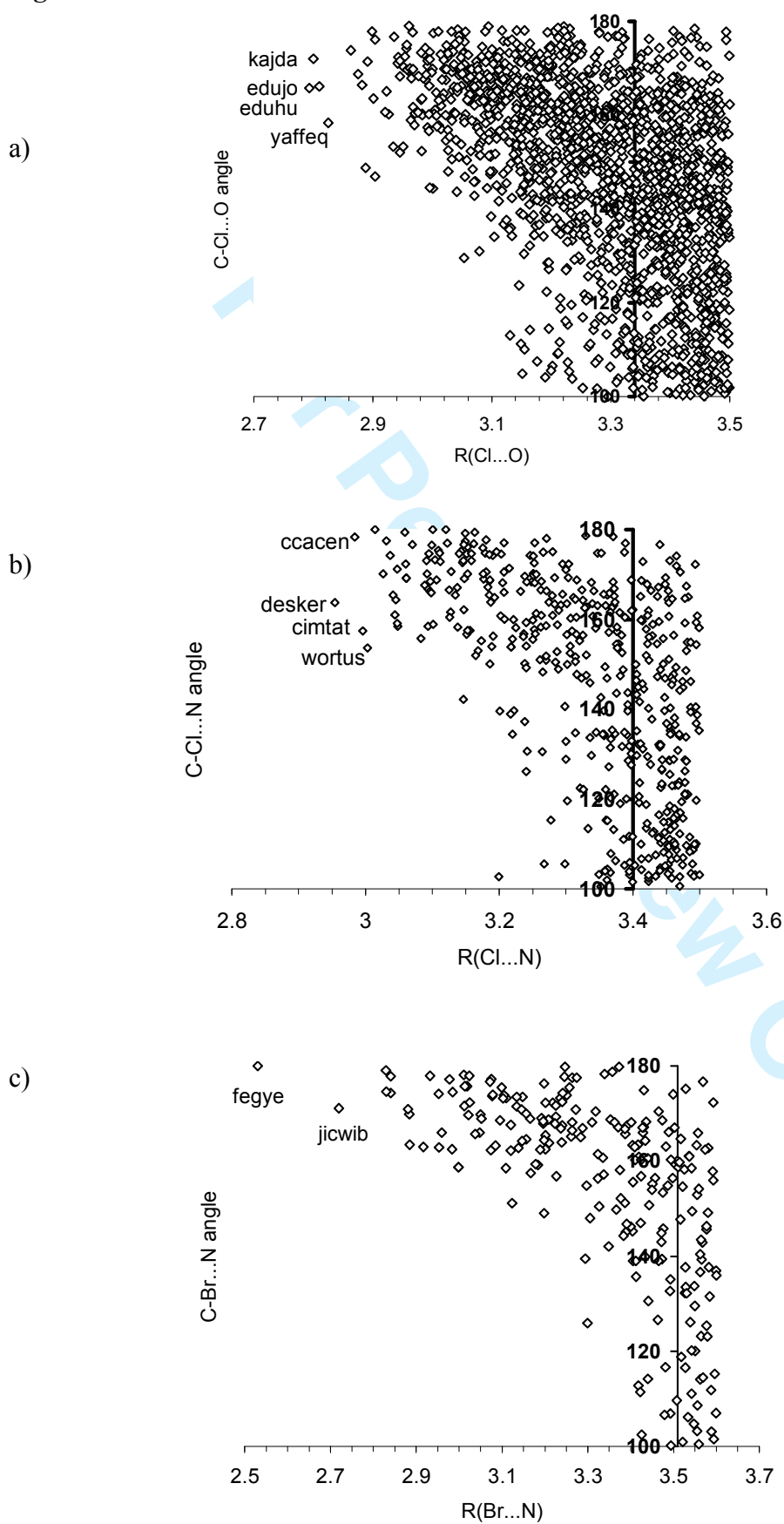


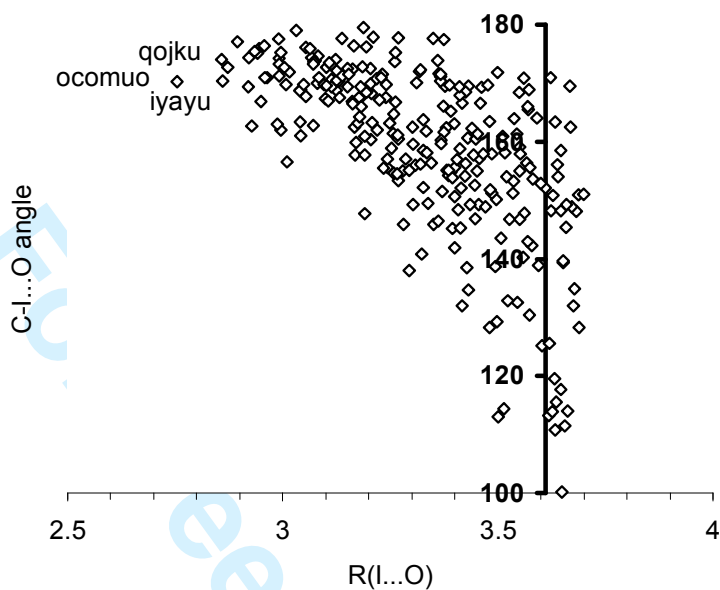
Figure 3S





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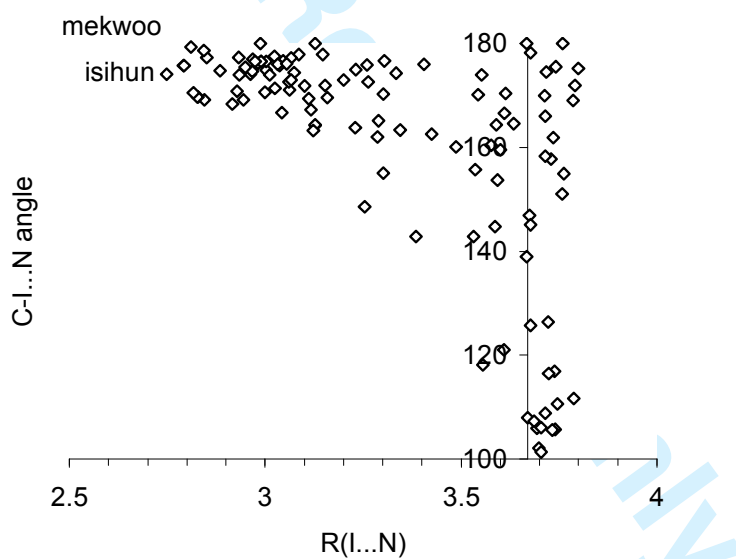
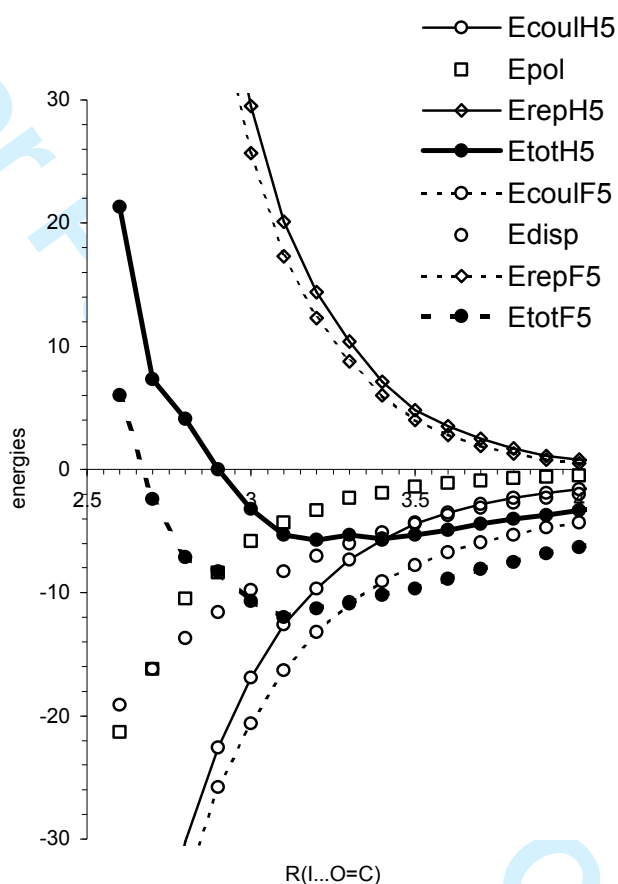


Figure 3S. Angle-distance plots for Cl...O, Cl...N, Br...N, I...O, I...N contacts from the CSD.

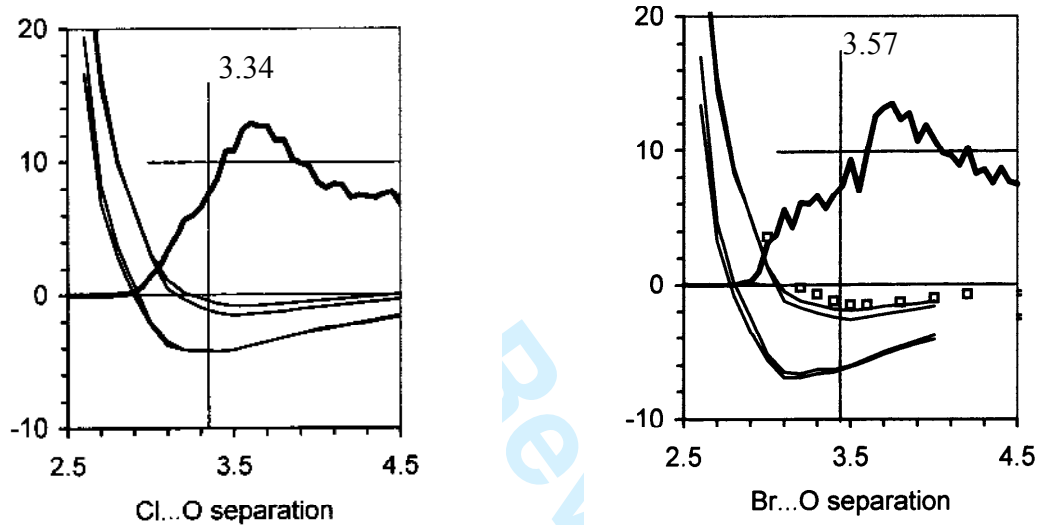
**Figure 5Sb.**

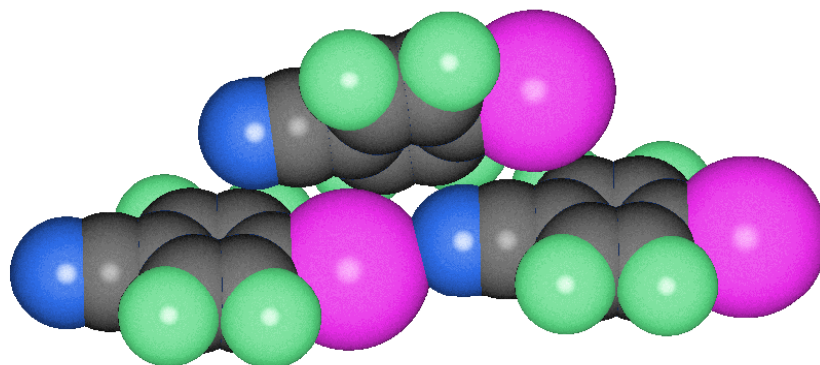
PIXEL energies for the interaction between iodobenzene (H5) or pentafluoriodobenzene (F5) and benzoquinone. Coulombic, polarization, dispersion and repulsion components. Total energy: heavy lines.



**Figure S8.**

DDF curves (heavy lines) with superimposed the PIXEL energy curves for interaction of Cl and Br compounds with N and O acceptors. The vertical bar marks the sum of the standard intermolecular atomic radii.





SCHAKAL

Figure S10. The fundamental motif in the crystal packing of 4-cyano-tetrafluoroiodo- and -bromobenzene (ACOKIM and ACOKEI). Black: C, green: F, blue: N, violet: I or Br. Drawing by Schakal.[34]

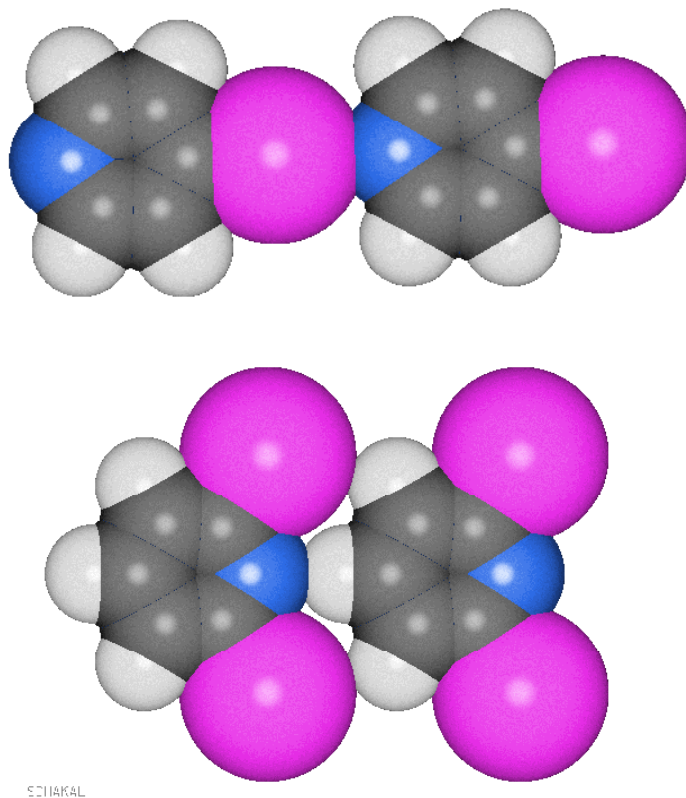


Figure S11. The line-up motif in HOFGEO and XUGLEQ. Black: C, blue: N, violet: I. Drawing by Schakal.[34]

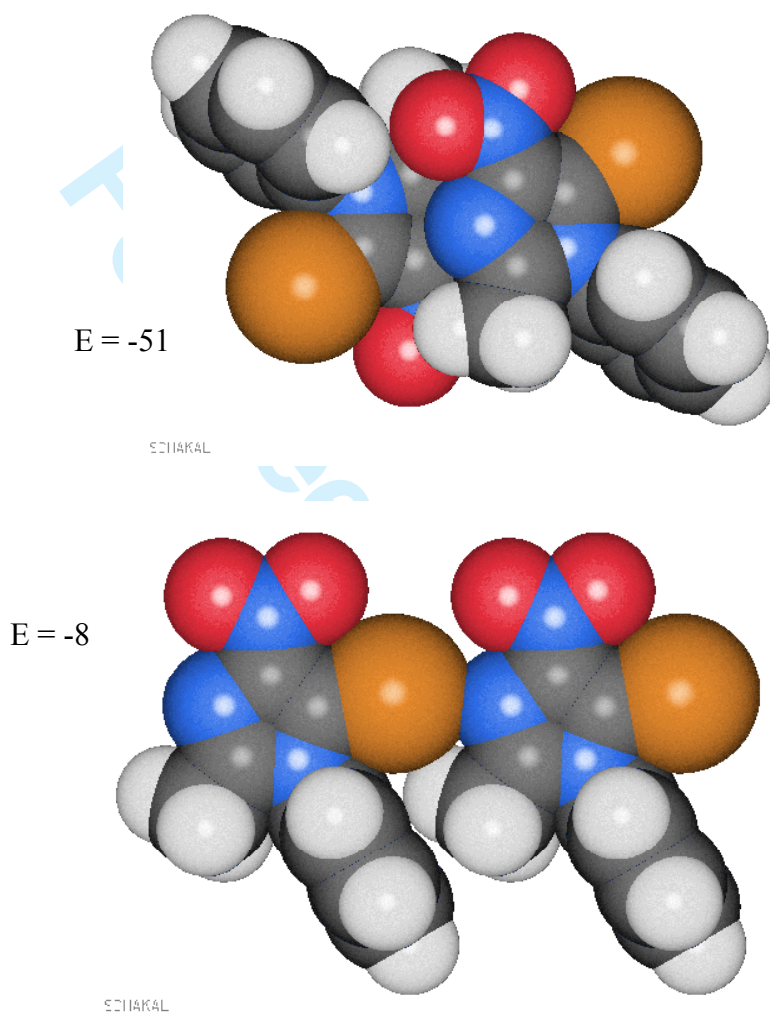


Figure S12. Two packing motifs in the crystal structure of AWAKIS05: top, the stacking of opposite dipoles; bottom, the Br...N halogen bonding. Dimer cohesion energies ( $\text{kJ mol}^{-1}$ ) are shown, see Table 5. Black: C, blue: N, red: O, ochre: Br. Drawing by Schakal.[34]

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4 **Non-conventional bonding between organic molecules. The "halogen bond" in**  
5 **crystalline systems**  
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16 For Anthony Stone  
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21 The intermolecular interaction in organic crystals, when a close contact between  
22 a halogen atom and an oxygen or nitrogen atom is present, is investigated by  
23 surveys of existing crystal structure determinations in the Cambridge Structural  
24 Database and by theoretical methods. Short halogen-oxygen and –nitrogen  
25 contacts are restricted to systems with peculiar electronic and steric properties.  
26 Energy well depths for sample systems range from almost nil to about 20 kJ  
27 mol<sup>-1</sup>, considerably less than for hydrogen bonding, with which halogen  
28 bonding can hardly compete. The width of the energy wells suggests that some  
29 short contacts may correspond to just permissive (i.e. energetically neutral)  
30 approach, or even to compressed bonding. The strongest bond is attainable only  
31 by aromatic iodine, highly activated by electron-attracting substituents, in  
32 molecular complexes with strong and sterically unhindered Lewis bases; only in  
33 such special cases is the halogen bond the most relevant cohesive factor in the  
34 crystal structure. In the PIXEL energy dissection scheme, the largest  
35 contribution to halogen bonding comes from Coulombic plus first-order  
36 polarization terms. Dispersive interactions between parallel aromatic systems  
37 are often more stabilizing and should not be neglected in assessing the tendency  
38 of halogen compounds to form linear aggregates in polar crystal structures.  
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## 1. Introduction

In a cast of mind that suits particularly well the computer modeller in organic chemistry, chemical bonding results as atomic nuclei reach a minimum-energy configuration within their accompanying electron cloud. Structure prediction is the search for that optimum configuration by several degrees of approximation, from dot-and-dash sketches to sophisticated quantum chemical calculations. Practical chemistry, the breaking and the making of chemical bonding, is an aspect of structure prediction with a certain amount of control: the ability to convince nuclei and electrons to shift from one minimum-energy configuration to another. The above definitions neither require nor involve the recognition of atom-atom bonds; they apply equally well to a single benzene molecule or to a benzene-hexafluorobenzene molecular complex. Actually, since this paper is concerned exclusively with the computer simulation of intermolecular constructions, there are a number of advantages in abandoning the restrictive view of chemical bonding as something related to any particular pair of atomic nuclei.

A first-principles definition of an atom-atom bond is provided by bond path analysis in the Atoms in Molecules theory [1], but a number of rather subtle points must be considered [2] to reconcile that approach with more traditional chemical thinking. We follow a different line of thought. In older models of intermolecular interaction, indeed a crude approach, atomic nuclei are taken as interaction centres, and everything that is stabilizing/attractive is wrapped up into a negative empirical term in the inverse sixth power of distance, and everything that is repulsive into a positive inverse-power or exponential term: the atom-atom potential method of Kitaigorodski [3] and Williams [4]. Such methods only yield bulk total interaction energies. The gap to physical realism was filled by Stone in a number of milestone developments: the Distributed Multipole Analysis (DMA) method [5] and the Intermolecular Potential Theory [6].

Nowadays, high quality molecular wavefunctions - and hence charge density distributions for the interacting molecules - can be easily obtained by standard molecular orbital calculations. The ultimate delocalization is achieved when each charge element in the molecular charge distribution, a three-dimensional 'pixel' of charge, is considered as the elementary interaction unit [7]. When two charge density boxes approach, electron clouds are considered unperturbed by the field of the approaching partner, a restrictive approximation whose adverse effects are reduced by the inclusion of an explicit



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5 polarization term, and by appropriate parameterization and screening. Numerical  
6 integration allows a fast and accurate evaluation of Coulombic-polarization energies, and a  
7 reliable estimate of London-type dispersion terms and of repulsion proportional to the total  
8 overlap integral. While the Coulombic term and the overlap integral are exact, polarization  
9 and dispersion terms crucially depend on the procedure for distribution of the  
10 polarizabilities (a field to which Stone has given substantial contribution [8]) and on a few  
11 numerical parameters; repulsion depends on the validity of the proportionality assumption  
12 [9]. Detail is given in Appendix I (Supplementary material). Although none of these terms  
13 is unequivocally defined by first principles, their combination with careful and  
14 parsimonious parameterization gives a physically realistic description of bonding, and  
15 what is even more important, such a description speaks a language that sounds familiar to  
16 the wider chemical community.  
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26 Patently, and purposefully, the PIXEL approach does away with the concept of atom-  
27 atom intermolecular bonds. Continuous use of this method in the field of organic crystal  
28 chemistry has demonstrated that in spite of its many assumptions, its results compare  
29 favourably with those of *ab initio* calculations [10] for a small fraction of the computing  
30 time, and are reliable and useful in the description of intermolecular bonding, [11-13]  
31 especially because the total energy is partitioned into Coulombic-polarization and  
32 dispersion terms, clarifying the different types of interaction.  
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38 In this paper we probe the PIXEL method in the description of the nature and supposed  
39 structure-driving properties of the "halogen bond", defined as a X...Y intermolecular  
40 interaction with X = Cl, Br or I, and Y = N or O. The recognition of short intermolecular  
41 X...O contacts is about 30 years old.[14] A theory of the halogen bond was first built on  
42 the spectroscopy of small gas-phase molecules;[15] the seed of this idea has migrated into  
43 the field of large molecules and crystals, with classification based on close proximity of X  
44 and Y atoms in organic crystals.[16] **The topic had already attracted Anthony Stone's  
45 attention,[17] but we report here our analysis of the distribution of such contacts in  
46 the larger samples of organic crystals now available,** and a systematic quantitative  
47 evaluation of the relative stability of several kinds of intermolecular pairing in molecules  
48 that can produce close X...Y contacts. Simultaneous consideration of energies and contact  
49 frequencies allows a more balanced assessment of the phenomenon, showing that some  
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4 conclusions based only on geometrical evidence need be reconsidered more carefully on  
5 energy terms.  
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8 In analogy with the hydrogen bond, the C-X group is called the 'donor', and the Y-  
9 carrying molecule is called the 'acceptor', although in terms of electron availability the  
10 terms should be reversed, C-X being a Lewis acid and Y being a Lewis base.  
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## 13 14 15 16 17 **2. Methods**

18 The Cambridge Structural Database (CSD) [18] yields crystal structures of molecules that  
19 contain the X...Y (X = Cl, Br, I, Y = N, O) atomic pairs, with the following quest: a) X  
20 and Y elements present in the same crystal structure, heaviest element = X; b) 3D  
21 coordinates determined without errors, disorder, refinement problems, or more than two  
22 molecules in the asymmetric unit; **c) conventional crystallographic R-factor < 0.075 (in**  
23 **the CSD, each crystal structure is identified by an 6- or 8-letter alphabetic string**  
24 **called a "refcode")**. We get 6427, 5468, 3619, 2281, 914 and 729 crude hits, respectively.  
25 After screening and renormalization of H-atom positions,[19] only structures with less than  
26 50 atoms are included not to "dilute" too much the interaction between the two atoms of  
27 interest. After all filtering we get 3699, 2954, 2007, 1318, 547 and 417 final hits,  
28 respectively. Distance density functions (DDF) [20] are calculated for atomic pairs over  
29 each sample of crystal structures. A DDF is formally analogous to a radial density function  
30 (RDF), in that DDF = 1 is equivalent to a random distribution; but a DDF refers to a  
31 collection of static information on distances between atom pairs in different environments,  
32 hence it shares none of the thermodynamic implications of a real RDF coming from  
33 dynamic information on the distribution of such pairs in a homogeneous system (e.g. a  
34 liquid). DDF's are just convenient graphic tools for the display of the distribution of  
35 interatomic distances in collections of crystal structures.  
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50 For the calculation of intermolecular energies, the PIXEL method is here applied in its  
51 standard formulation (see Appendix I) to all pairs formed between a choice of possible  
52 donors, represented by the halobenzenes and 2-haloisopropanes (CH<sub>3</sub>-CHX-CH<sub>3</sub>), and  
53 acceptors, represented by furan and benzoquinone for oxygen, and by pyridine and  
54 benzonitrile for nitrogen. The computational efficiency of the PIXEL method allows the  
55 use of the benzene ring as a model donor carrier and of  $\pi$ -electron delocalized systems for  
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4 the model acceptor carrier, thus conferring more chemical realism to the simulation than do  
5 the much smaller fragments (e.g.  $\text{CH}_3\text{X}$ ,  $\text{X}_2$ ,  $\text{NH}_3$ ,  $\text{HC}\equiv\text{CX}$ , of limited interest in real  
6 organic chemistry) usually affordable in high-level *ab initio* calculations. The presence of  
7 the phenyl ring allows a test of the method in reproducing the electron-withdrawing or -  
8 releasing effects of substituents (the 'Hammett' effect). The internal geometries of these  
9 model molecules were standardized (see Appendix II, Supplementary material).  
10 GAUSSIAN [21] was used to obtain the valence charge densities for PIXEL calculations  
11 (these include 3d electrons for Br and I), and for a separate calculation of counterpoise-  
12 corrected dimerization energies for comparison with the PIXEL results. The MP2/6-  
13 31G\*\* level (basis set available up to  $Z=54$ ) or the MP2/DGDZVP level (basis set  
14 including iodine) were used. Extensive tests in this case as well as in former experience  
15 show that the change of basis set has little effect on the PIXEL calculations as long as a  
16 reasonably large basis set is used.

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18 For aromatic dimers the PIXEL calculation was carried out with donor and acceptor  
19 coplanar; in all cases, with C-X bonds pointing at Y acceptors with C-X...Y angle of  $180^\circ$ ,  
20 for a X...Y separation ( $R_{\text{XY}}$ ) from 2.6 to 4.0 Å in steps of 0.1 Å. In some cases an identical  
21 calculation was carried out by *ab initio* MP2 (with steps of 0.2 Å) for comparison.  
22 Appendix II has some sample atomic coordinates for dimers. The resulting energy curves  
23 were visually examined to estimate the optimum interaction energy ( $E^\circ$ ) and separation  
24 ( $R^{\text{eq}}$ ). The flexibility of the interaction was estimated by determining the shortening and  
25 the lengthening from  $R^{\text{eq}}$  ( $R_{\text{int}}$  and  $R_{\text{ext}}$ , respectively) that correspond to an energy increase  
26 of  $RT$  ( $2.5 \text{ kJ mol}^{-1}$ ) from  $E^\circ$ .

### 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 **3. Results**

#### 46 47 48 49 **3.1 C-X...Y contacts in crystals, X=Cl, Br, I, Y=O, N.**

50 Table 1 shows the actual count of short X...Y distances, which are listed in detail in  
51 Appendix III (Supplementary material). When considering these data one must be aware of  
52 intrinsic biases in the distributions, which are far from the extension and randomness  
53 which are prerequisites for real statistical treatments. For example, in general organic  
54 chemistry chlorine is a more common atom than bromine or iodine - hence the differences  
55 in the first column of Table 1. Social biases also emerge: for instance, the population of  
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4 very short ( $< 3.0 \text{ \AA}$ ) Br...N and I...N distances is a scant one and is mostly provided by the  
5 dedicated work of one school[16,22,23] on a well defined chemical environment, the X<sub>2</sub>-  
6 or tetrafluoro-X<sub>2</sub>-benzenes interacting with bipyridyl, azostyryl or  
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8 hexamethylenetetraamine acceptors; many of these compounds have been explicitly  
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10 prepared with *ad hoc* systems to demonstrate the effects of halogen-bonding activation. In  
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12 spite of these warnings, the results in Table 1 on overall frequencies suggest that short  
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14 X...Y contact is rather sporadic (i.e. of low frequency); that oxygen is a more frequent  
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16 halogen-bond acceptor than nitrogen, while the frequency of halogen-bond donor  
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18 performance is I>Br>Cl. The latter conclusions are in agreement with previous  
19  
20 results.[23,24]  
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22 Distance density functions for Br...N and Br...O are shown in Figure 1. The curves are  
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24 rather noisy due to the limited number of data (see Table 1), but they nevertheless show a  
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26 shoulder between 2.7 and 2.9  $\text{\AA}$ . Similar shoulders appear for Cl...N and Cl...O (but  
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28 smaller; see Figure 1Sa, Supplementary material) and for I...N and I...O (more developed;  
29  
30 see Figure. 1Sb). These shoulders, with an intensity  $< 1$ , reveal and count a very minor  
31  
32 population of short X...Y confrontations. For comparison, Figure 2 shows the DDF for the  
33  
34 conventional N-H...O=C hydrogen bond over the same Br/N population of crystal  
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36 structures, with a well developed peak at the hydrogen bonding distance of about 2  $\text{\AA}$ .  
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38 There is a marked difference between the statistical incidence of a hydrogen bond and of a  
39  
40 halogen "bond".

41 Figure 3, typical for all other C-X...Y contacts (see Figure 3Sa-e, Supplementary  
42  
43 material) shows that, corresponding with the absence of a separate peak in the DDF below  
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45 the sum of intermolecular atomic radii, there is a continuous distribution of contact  
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47 distances and there is no clear break or divide at or around the sum of ordinary  
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49 intermolecular radii (see also the lists in Appendix III). **Short X...Y contacts occur with a**  
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51 **C-X...Y angle  $> 140^\circ$ . The distribution might result from a balance between a mildly**  
52  
53 **attractive X...Y power and the steric interference of side groups.** The matter will be  
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55 taken up again with a calculation of interaction energies as a function of the C-X...Y angle.

56 What are the chemical factors that favour a close X...Y approach? A study of single  
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58 crystal structures may be problematic because the choice of special cases is a dialectic  
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60 pathway to the collection of subjective evidence, and also because outliers are by definition  
not representative of the general phenomenon and very unusual structures are often just

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5 subtly wrong structures. Looking for trends in groups is much more time-consuming but  
6 much safer. Iodine and bromine are generally more active in aromatic than aliphatic  
7 environments, **as expected (see for example the compounds identified by the CSD**  
8 **refcodes SAWZIA, QALPAV, OCIQUN, YAGSEE,** with  $-(\text{CH})_n\text{I}\dots\text{N}\equiv\text{C}$  distances from  
9 3.29 Å up). In a group of halogen-bonding crystal structures (the 29 with a Br...N distance  
10  $R < 3.10$  Å and the 49 with a I...N distance  $< 3.2$  Å; see Appendix III for a detailed list) 25  
11 have a X-C<sub>6</sub>F<sub>4</sub>-X or X-(CF<sub>2</sub>)<sub>n</sub>-X moiety (activated donor); 14 have an X atom attached to a  
12 five-membered azole or oxazole ring (activated donor and acceptor); 12 involve a CX<sub>4</sub>, X<sub>2</sub>  
13 or X<sub>2</sub>C=CX<sub>2</sub> moiety; 12 include a conjugated (activated) acceptor of the type C=N-C≡N,  
14 C≡C-C≡N or C=C(C≡N)<sub>2</sub>; and 6 have the (activated) X atom on an aromatic ring with  
15 strongly electron-withdrawing substituents (fluorine atoms, CN or NO<sub>2</sub> groups). Thus,  
16 X...Y contacts become very short only when the acceptor or the donor are activated by  
17 electron-releasing or -withdrawing bonding effects, respectively. Even these are more like  
18 rules of thumb than solid correlations, however. For example, the Br...N distance in 4-  
19 cyano-bromobenzene (BRBNIT01) is 3.25 Å, and in some activated derivatives (ACOKEI,  
20 FOMRAB, MIFXEE, TIQDAY) it is shorter (3.05 to 3.16 Å) but without correlation with  
21 electron-withdrawing power of the substitution. Otherwise, in some iodo-amino-  
22 nitrobenzenes the 6 different I...O(nitro) distances range from 3.15 to 3.49 Å also within  
23 two polymorphs of the same compound (CAMSIT, CAMSUF, YEJLII and YEJLII01); and  
24 there are plenty other, similar cases.

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40 On the other hand, there are entire classes of bonding candidates, compounds with donor  
41 Br and acceptor N, which crystallize without any special Br...N confrontation. Reasons for  
42 that are multiform. Ortho-substitution on the pyridine ring, represented by ZIFSIQ (refer to  
43 Figure 4 for this discussion), presumably makes the Br...N approach sterically  
44 unfavourable. Typically, in a similar *ortho*-Br-N geometry (represented by HIFTAR) a  
45 weak R-OH...N hydrogen bond successfully competes with bromine for the nitrogen  
46 bonding terminus, and even a modest C-H...N chelation prevents bromine from  
47 approaching the N donor (represented by FONKAV). In structures represented by  
48 TAJBOV, the Br...N attraction has a steric barrier which is overcome only when the donor  
49 is strongly activated (see e.g. WOJQOB, LUKMIN). Such analyses suggest that the  
50 formation of a halogen 'bond' is very sensitive to a balance between attraction and steric  
51 hindrance.  
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4 The considerations made above for Br...Y or I...Y separations hardly apply to the  
5 equivalent Cl...Y case. One sees there a more multiform chemistry and a much more  
6 malleable cohesion, with shorter or longer separations found in many different  
7 environments and even without special activating chemical factors; that is, even less of the  
8 character of a classic chemical bond. Besides, the steric factor is understandably less  
9 important for Cl than it is for Br or I.

10 A frequency of short distances does not necessarily imply strength/stabilization, because  
11 geometry is but a poor substitute for physics; but in spite of all caveats and contradictions,  
12 eventually the overall consideration of geometric results points rather strongly to the  
13 conclusion that the X...Y bond strength is in the order Cl<Br<I. We now proceed to a  
14 quantitative evaluation of the energies involved in the interaction.  
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### 28 **3.2 Interaction energies: groundwork and validation**

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31 The results of the systematic calculation of interaction energies between halobenzenes and  
32 several acceptors lend themselves to the following considerations.

33 a) There are good correlations between the PIXEL and *ab initio* sets of results, see Tables  
34 2-4 (Appendix IV, Supplementary material, has the detail of PIXEL interaction energy  
35 curves, and the comparison between PIXEL and *ab initio* curves). The agreement goes  
36 from almost perfect coincidence for I-derivatives, to small discrepancies for Cl-  
37 derivatives, to a systematic discrepancy for Br-compounds whereby PIXEL equilibrium  
38 distances are larger by 0.1-0.2 Å and PIXEL equilibrium energies are smaller by a few kJ  
39 mol<sup>-1</sup>. This seems a small price to pay for a 100-fold reduction in computing times.  
40 Moreover, in the *ab initio* results the counterpoise correction may be less effective for a  
41 limited basis set on very electron-rich atoms. If this were indeed the case, the best estimate  
42 could lie in between the PIXEL and the *ab initio* results. At the other extreme, even *ab*  
43 *initio* dimerization energies could be underestimated due to incomplete basis sets and/or  
44 treatment of correlation.  
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56 b) The strength of the halogen bond increases in the order Cl<Br<I, and with perfluoro  
57 substitution at the donor. Cl donors form barely stable dimers only with perfluoro  
58 substitution, with Cl...O or Cl...N separation almost equal to the sum of normal  
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4 intermolecular radii (3.34 and 3.40 Å, respectively). Br donors form barely stable dimers  
5 when unsubstituted, and reasonably stable dimers with fluoro-substitution; in the latter  
6 case, equilibrium Br...O or Br...N distances are 0.2-0.4 Å shorter than the sum of  
7 intermolecular radii, 3.45 and 3.51 Å, respectively. Iodine donors form stable dimers when  
8 unsubstituted and very stable dimers with substitution, with approach distances which are  
9 considerably shorter than the sum of intermolecular atomic radii, 3.61 and 3.67 Å for I...O  
10 and I...N respectively.

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12 c) PIXEL results are strictly parallel to *ab initio* ones as concerns the electronic effects of  
13 *para*-substitution at the phenyl ring of the donor (the 'Hammett' effect, Table 4 and  
14 Appendix IV) and both sets of result show a perfect linear correlation between interaction  
15 energies and Hammett  $\sigma$ -values. The PIXEL method appears to be able to reproduce fine  
16 electronic effects even for classes of compounds for which it was not directly  
17 parameterized, thus reinforcing the validation of its adherence to physical factors.

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19 d) On the nature of the halogen-bonding effect: Figure 5 shows the energy partitioning for  
20 the interaction between pyridine and bromobenzene or 4-nitrobromobenzene in a linear C-  
21 Br...N geometry. For the unsubstituted bromobenzene, the stabilizing effect comes in  
22 almost equal parts from dispersion and from Coulomb-polarization contributions. For the  
23 'nitro-activated' nitrobromobenzene, dispersion and polarization do not change, while the  
24 Coulombic component increases so that the total interaction energy is almost doubled and  
25 the equilibrium distance is shortened. Figure 5Sb (Supplementary material) shows the  
26 analogous activation effect on the interaction between iodobenzene and benzoquinone;  
27 here repulsion plays a bigger role, and the stabilizing effect of the fluorosubstitution acts  
28 also through a reduction of the Pauli overlap between iodine and oxygen.

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30 e) For nearly all the X...Y interactions, the total stabilization is in the range 1-15 kJ mol<sup>-1</sup>,  
31 lower than that of the weak alcohol O...HO hydrogen bond ( 25 kJ mol<sup>-1</sup>) and less than one  
32 half of the hydrogen bond in carboxylic acids (40 kJ mol<sup>-1</sup>).[25,26] Only the interaction  
33 between perfluoroiodobenzene and aromatic nitrogen attains the strength of a weak  
34 hydrogen bond. This fact greatly reduces the actual synthetic scope of the halogen bond,  
35 because single molecules carrying all the necessary appendages are somewhat rare and  
36 awkward; accordingly, most reported cases of strong halogen bonding involve molecular  
37 complexes between separate donor and acceptor molecules.

### 3.3 Angular dependence of C-X...Y bonding

Figure 6 shows the results of a calculation of the angular dependence of halogen-bonding energies. A sharp destabilization on leaving the linear C-X...Y arrangement is clearly seen, in agreement with previous analyses.[17] In our picture the overall energy rise is due to a loss of Coulombic stabilization and a rise in repulsion; the Coulombic loss may result both from a loss in stabilizing interaction between X and Y electronic basins - although it is not easy to see a reason for this - or from destabilization by the unavoidable approach of C-H groups that carry the same charge (see inset, Figure 7). The increase in repulsion energy can only result from increased overlap between the charge densities of the flanking groups. Thus, the linearity of the C-X...Y bonding interaction is due, in our interpretation, in good part to the steric influence of flanking groups. In any case, the full energy map (Figure 7), easily computed thanks to the computational efficiency of the PIXEL method, has the stabilizing zone almost exactly overlapping the observed R/θ distribution.

### 3.4 Crystal packing and the shape of the dimerization energy curves

The results on dimer energies have an obvious bearing on the possible use of the X...Y interaction in the prediction of crystal aggregation ('crystal engineering'). In the complex compromise that allows an organic molecule to coexist in a stable way with its crystalline neighbours, equilibrium distances and depths of the energy wells should be considered along with (and are often less important than) the curvatures of the binding profiles. The data in Table 2 show that most of the X...Y approaches are only barely stabilizing, and can be compressed by 0.4-0.5 Å below the equilibrium separation with an energy expense of less than RT. In qualitative studies based only on geometries, these short separations are interpreted as the mark of strong stabilizing and attractive interaction, but they may as well result from just indifferent equilibrium at nearly zero stabilization, without repulsion. We propose to designate these close contacts as "permissive" contacts. Recognizing that some molecular arrangements are just permissive, rather than constrictive, is an important step in a correct understanding of molecular packing. The resulting continuum distribution of X...Y distances from R° up in organic crystals is also difficult to reconcile with the classical definition of a chemical bond.



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4 Figure 8 (see Figure 8S, Supplementary material, for Cl...O and Br...O equivalents)  
5 shows the distance distributions in crystals (DDF curves) superimposed on the energy  
6 curves for the formation of some typical dimers. The broad peaks in all the DDFs at 3.7-4  
7 Å, distances slightly larger than the sum of intermolecular radii, correspond to shallow  
8 minima in the energy curves at 3.5-3.7 Å, with due account of the anharmonicity of  
9 thermal vibrations (molecules spend more time on the right side of the minimum than on  
10 the left side). These topologies go as a regular 'van der Waals' approaches, with energies  
11 between 1 and 5 kJ mol<sup>-1</sup>; these include all the aliphatic donors, except perhaps for the  
12 I...N case, and nearly all chlorine donors, for which the shoulders at short separations in the  
13 DDF are barely noticeable. The Br...O and Br...N DDF's show a shoulder at short  
14 separation, corresponding to the minima in the energy curves for the highly activated  
15 perfluorophenyl donors (the dotted lines in Figure 8b show the worst discrepancies  
16 between PIXEL and *ab initio* results). For iodine donors, the well developed shoulders in  
17 the DDF at short separations overlap with the sharper minima in the energy curves, but  
18 these distributions reside mostly on the *left* side of the minimum. If one is to take these  
19 results to their final implication, many of the very short Br...N, I...N and I...O contacts  
20 observed in crystals correspond to compressed bonds, *i.e.* stabilizing but repulsive  
21 interactions. These compressed contacts must arise in compliance with some other packing  
22 requirement. After all, stretching of these interactions towards longer distances is very  
23 common and comes as no surprise, so the possibility of stretching to distances shorter than  
24 the equilibrium distance, for the same energetic expense, cannot be ruled out.

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26 The drawings in Figure 8 provide a convincing and quantitative connection between the  
27 physical nature and the geometry of the considered interactions. In our opinion no serious  
28 discussion of crystal packing or 'crystal engineering' can proceed without such information.  
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### 31 3.5 PIXEL crystal structure analysis

32 For a better understanding of the role of halogen bonding, a number of sample calculations  
33 have been carried out on molecular pairs in crystals. The energies shown in Table 5 refer to  
34 virtual dimers extracted from the crystal and brought intact into isolation (full detail  
35 including symmetry operations relating the molecules in the dimers is available in  
36 Appendix V, Supplementary information).  
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4 For the two tetrafluoro-cyano-halobenzenes ACOKIM and ACOKEI,[27] the X...N  
5 interaction ranks first in the iodo compound, but for the bromo derivative it is of the order  
6 of magnitude, or less, of ring stacking; in this case, former fashion in intermolecular  
7 denominations would have classified the leading interaction as a pairing of opposite  
8 dipoles (Figure 10S, Supplementary material). For IKUHUR03,[23] a very short Br...N  
9 separation is observed, but, even allowing for a possible underestimation of the  
10 Br...N(pyridine) interaction, the interaction between aromatic systems is largely  
11 dominating over the Br...N interaction. In the corresponding iodine compound,  
12 QIHCAL,[22] the two interactions are on an almost equal footing. In these systems one  
13 cannot rule out the hypothesis that aromatic stacking is the dominant packing factor, so  
14 that the short and linear halogen bond is in fact a secondary effect (Figure 9). In 4-  
15 iodopyridine HOFGEO [28] the I...N interaction unequivocally leads the proceedings with  
16 its huge Coulombic-polarization term. Nevertheless, no I...N interaction forms in the  
17 diiodo analogue XUGLEQ,[29] where a strong C-H...N plus C-H...I interlock more than  
18 compensates for it (Figure 11S); nor does the I...N interaction appear when a competing O-  
19 H...N hydrogen bond worth about 60 kJ mol<sup>-1</sup> can form (XIHFEZ, JAQNOF,  
20 JAQNUL,[30] complexes between iodopyridine and nitrobenzoic acids). Note that all these  
21 facts agree with the relative size of the calculated interaction energies for sample  
22 compounds and hence could have been predicted by a proper consideration of the energetic  
23 data in Tables 2-3, while qualitative structural predictions would have failed. A final,  
24 extreme case is the nitro-bromoimidazole AWAKIS,[31] where the Br...N separation is  
25 very small but the interaction ranks very low in importance; again, in times of different  
26 fashions, this compound would have made an excellent case for the dominating role of  
27 "inverted dipole" interactions (Figure 12S).

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Once again, the cases reported in Table 5 are representative of many similar cases, and  
should not be considered as special examples singled out to demonstrate a preconceived  
thesis.

#### 4. Discussion and concluding remarks

Is halogen bonding a robust concept in the crystal chemistry of organic compounds? The  
answer to this question is uncertain, as it is the answer to many other, similar questions

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4 concerning the robustness of intermolecular bonding entities. Short halogen-oxygen and  
5 halogen-nitrogen contacts form or do not form according to a large number of boundary  
6 conditions, having to do with a) electronic effects - mainly the activation of donors by  
7 electron-withdrawing groups; b) steric repulsion effects - the availability of interaction  
8 termini *vis-à-vis* encumbering side groups; c) the presence of competing hydrogen-bond  
9 donors - which nearly always prevail for the acquisition of target acceptors; and this might  
10 be a non-exhaustive list. On the other hand, even when short distances appear, they may  
11 not always be the outcome of binding stabilization, but may be the result of secondary  
12 effects under the tolerance of flat energy surfaces or even at the expense of slight repulsion  
13 up the left wall of potential energy curves. To be sure, a halogen-nitrogen contact forms  
14 even in crystals of such a large molecular unit as a porphyrin, when both iodine and N  
15 atoms stick out unhindered at the exposed corners of the molecule;[32] but there is also  
16 much evidence of Br...N contacts not forming, without an obvious explanation, even in  
17 apparently favourable conditions. Accordingly, in the DDF curves only small shoulders  
18 appear for the X...Y contact at short separation, quite unlike what happens for the classic  
19 H...Y hydrogen bond; in forcing the formation of a halogen bond, one must be careful and  
20 deliberate, just as careful and deliberate one must be to *avoid* the formation of a regular  
21 hydrogen bond.

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Theoretical calculations pose a few quantitative milestones in this intricate road map: the  
X...Y (X = Cl, Br, I; Y = O, N) "bond" among neutral organic molecules spans a  
continuum from a negligible stabilization - typical of, say, a pair of Ar atoms - up to the  
lower limit of the weak hydrogen bond in organic chemistry, or some 25 kJ mol<sup>-1</sup>; and a  
limit that can be reached only using rather exotic species as tetraiodoethylene and  
tetrafluoro-diiodobenzene. To reach bonding energies of the order of regular hydrogen  
bonds, > 40 kJ mol<sup>-1</sup>, one has to recur to such exotic pairings as the FBr...OH<sup>-</sup> dimer [33]  
or to I<sub>2</sub> as donor.[22] Thus, halogen bonding can compete with hydrogen bonding only in  
peculiar cases, perhaps with the alcohol OH group which is notoriously a kinetically poor  
crystallizer. In any event, the halogen bond is typically twice as strong as the evanescent  
C-H...O "hydrogen bond".

How reliable are our theoretical results? They come from the coincident response of  
PIXEL and *ab initio* theory, and agree as an order of magnitude with the results of much  
more sophisticated calculations on the interaction of R-X fragments with ammonia: for

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5 example, the estimates [34] of the energies for the 4-nitrophenyl-X complexes with  
6 ammonia are 6, 12 and 18 kJ mol<sup>-1</sup> for X = Cl, Br, I, to compare with the PIXEL values for  
7 activated phenyl-X with pyridine of 7, 12 and 22 kJ mol<sup>-1</sup>, respectively. As for geometry, a  
8 DFT or MP2 study [35] shows that the energy surface for the I...O interaction in the  
9 iodobenzene-dimethylsulfoxide dimer is quite flat; a typical interaction energy (without  
10 BSSE correction) is about 13 kJ/mol with an O...I distance 2.9 Å. These results are to be  
11 compared with the predicted flexibility and our values of 6 kJ mol<sup>-1</sup> and 3.3 Å for the  
12 iodobenzene-benzoquinone complex (our results show that the BSSE correction halves the  
13 interaction energy and lengthens the equilibrium distance by a few tenths of an Å, see  
14 Appendix IV). DFT results [22] for the bipyridyl-diiodobenzene and for bipyridyl-  
15 tetrafluorodiiodobenzene place the interaction energies at 14 and 24 kJ mol<sup>-1</sup> respectively,  
16 quite comparable to our results in Tables 2-3 for the pyridine analogues. PIXEL results  
17 also agree quantitatively with the IMPT results for the chlorocyanoacetylene dimer,[17]  
18 perhaps not surprisingly since some IMPT energies and geometries were used in the early  
19 stages of the parameterization of the PIXEL method.  
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31 Even more important than absolute well depths is the information on well widths, also  
32 provided by theoretical calculations. Calculations conclusively show that the postulated  
33 X...Y halogen bond can be stretched over 0.5 to 1.0 Å within an energy expense of RT,  
34 with a clear, as well as physicochemically predictable, dependence between depth and  
35 width. Such an observation poses a sharp obstacle to the utilization of halogen bonding in  
36 crystal structure prediction and control. Accordingly, the PIXEL estimates of molecule-  
37 molecule energies in organic solids show that more often than not the halogen bond plays  
38 second fiddle in the ranks of cohesive energies. The case of the halogen bond is further  
39 illustration of the delocalization principle in organic crystal chemistry: intermolecular  
40 interaction is better described in terms of bonding in which the entire electron density of  
41 the interacting molecules is involved, and by proper consideration of joint effects in  
42 clusters of first neighbours.  
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### 56 **Supplementary material available**

57 Appendix I: PIXEL theory; Appendix II: Cartesian coordinates for all the molecules in the  
58 calculation of dimers (refer to Tables 2-3); Appendix III: list of all X...Y short contacts  
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4 with CSD refcodes; appendix IV: detailed results of PIXEL calculations on dimers,  
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6 detailed results of the *ab initio* dimer energy calculations; Appendix V: details of the  
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8 molecule-molecule energy calculations in crystals; Figures 1S, 3Sa-e, 5Sb, 8S, 10S, 11S,  
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10 12S.

11 For full reproducibility of the calculations here described, the PIXEL software can be  
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13 downloaded free of charge for academic institutions from <http://users.unimi.it/gavezzot>.  
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15 Input and output files are available upon request to the author at his e-mail address.  
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Table 1. Results from a Cambridge Database survey of X...Y short separations.

contact	n. of structures in sample <sup>a</sup>	intermolecular radius /Å	contacts R < (R°-0.2) Å contact/structure	shortest observed distance /Å <sup>b</sup>
Cl...N	2954	3.34	96      0.03	2.95
Br...N	1318	3.51	102      0.08	2.72 (2.53?)
I...N	417	3.67	70      0.17	2.75
Cl...O	3699	3.40	318      0.09	2.79
Br...O	2007	3.45	364      0.18	2.85
I...O	547	3.61	166      0.30	2.76

a) Molecules with up to 50 atoms in asymmetric unit. b) See Appendix III.

Table 2. Results for the formation of a dimer between halobenzene donors and several acceptors with linear C-X...Y geometry. PIXEL charge densities: MP2/DGDZVP basis set.<sup>a</sup>

donor	C <sub>6</sub> H <sub>5</sub> -Cl			C <sub>6</sub> H <sub>5</sub> -Br				C <sub>6</sub> H <sub>5</sub> -I			
	R <sup>eq</sup>	E <sup>o</sup>	R <sub>int</sub>	R <sup>eq</sup>	E <sup>o</sup>	R <sub>int</sub>	R <sub>ext</sub>	R <sup>eq</sup>	E <sup>o</sup>	R <sub>int</sub>	R <sub>ext</sub>
benzonitrile	flat	-0.2	3.20	3.60	-1.6	3.10	-	3.34	-7.0	3.00	3.90
				3.40	-3.6	3.02	>4				
pyridine	flat	-1.6	3.25	3.50	-4.2	3.12	4.30	3.20	-12.2	2.97	3.60
								3.20	-13.0	2.94	3.55
pentafluoropyridine	-	-	-	3.62	-2.8	3.25	-	3.46	-6.8	3.15	4.13
benzoquinone	flat	-0.8	3.10	3.50	-1.8	3.02	-	3.30	-5.8	3.00	4.00
	flat	-1.5	2.90								
furan	flat	-1.5	3.10	3.45	-2.6	3.05	-	3.28	-6.4	2.98	4.20
				3.40	-4.0	2.95	3.95				
nitrobenzene (NO <sub>2</sub> )	no minimum			-				-			

a) When two lines appear, the second is for the *ab initio* result, MP2/6-31G\*\* for Cl and Br, DGDZVP for I. R<sup>eq</sup> and E<sup>o</sup> are the equilibrium X...Y separation in Å and the interaction energy in kJ mol<sup>-1</sup>, R<sub>int</sub> and R<sub>ext</sub> are the X...Y separations that correspond to an increase in energy of RT from E<sup>o</sup> (R<sub>ext</sub> not given when RT > -E<sup>o</sup>)

Table 3. As in Table 1, for perfluorohalobenzenes.

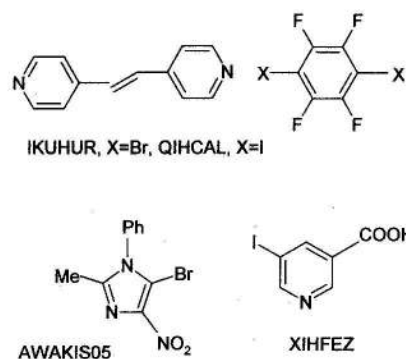
	$C_6F_5-Cl$				$C_6F_5-Br$				$C_6F_5-I$			
	$R^{eq}$	$E^\circ$	$R_{int}$	$R_{ext}$	$R^{eq}$	$E^\circ$	$R_{int}$	$R_{ext}$	$R^{eq}$	$E$	$R_{int}$	$R_{ext}$
benzonitrile	3.42	-5.4	3.05	4.30	3.25	-8.8	3.03	3.90	3.14	-15.5	2.92	3.52
									3.18	-17.0	2.95	3.60
pyridine	3.38	-7.2	3.10	4.00	3.22	-12.0	3.00	3.70	3.07	-22.5	2.90	3.37
					3.02	-16.0	2.77	3.27				
benzoquinone	3.30	-4.2	2.95	4.50	3.16	-7.0	2.95	3.87	3.12	-11.8	2.90	3.55
					3.10	-8.7	2.82	3.60				
furan	3.30	-4.2	3.00	4.50	3.17	-6.5	2.95	3.95	3.12	-11.8	2.90	3.55
	3.15	-4.9	2.82	4.0					3.15	-11.5	2.95	3.55
nitrobenzene					-				3.22	-12.2	2.97	3.67



Table 4. Results for the formation of a dimer between 1,4-*R*-C<sub>6</sub>H<sub>4</sub>-Br and pyridine with linear C-Br...N geometry. All charge densities and *ab initio* calculations at the MP2/6-31G\*\* level. See also captions to Table 2. .

substituent	Hammett $\sigma$ , Mulliken charge on Br		R <sup>eq</sup>	E <sup>o</sup>
R=NH <sub>2</sub>	-0.57	-0.12	3.37 3.24	-3.2 <sup>a</sup> -4.1
R=OH	-0.38	-0.11	3.32 3.20	-5.2 -5.9
R=H	0	-0.10	3.34 3.14	-4.7 -6.1
R=COOH	+0.44	-0.09	3.31 3.15	-6.0 -8.5
R=CN	+0.70	-0.08	3.29 3.16	-7.2 -10.0
R=NO <sub>2</sub>	+0.81	-0.07	3.26 3.06	-8.6 -10.5

a) First line: PIXEL, second line: *ab initio*.

Table 5. Interaction energies ( $\text{kJ mol}^{-1}$ ) in some molecular pairs in organic crystals.

CSD refcode	E <sub>coul</sub> +pol	E <sub>disp</sub>	E <sub>tot</sub>	contact type and X...Y distance (Å)
ACOKEI [27] Br-C <sub>6</sub> F <sub>4</sub> -C≡N	-11 -14	-19 -6	-15 -8 <sup>a</sup>	stack with N≡C on top of C-Br Br...N 3.155
ACOKIM [27] I-C <sub>6</sub> F <sub>4</sub> -C≡N	-32 -11	-10 -9	-14 -8	I...N 3.117 unspecific
IKUHUR [23]	-15 -11	-33 -29	-29 -20	parallel pyridyl rings
	-8	-25	-18	parallel pyridyl-benzene
	-7	-17	-15	parallel fluorobromobenzenes
	-47	-15	-10 <sup>a</sup>	Br...N 2.814
QIHCAL [22]			-21.1	<b>I...N 2.811</b>
			-19.6	parallel pyridyl rings
HOFGEO [28] 4-iodopyridine	-62 -10	-19 -18	-18 -11	I...N 2.988 parallel rings
XUGLEQ [29] 2,6-diiodopyridine	-37	-26	-24	C-H...N contact; no I...N contacts
AWAKIS05 [31]	-34 -37	-31 -32	-50 -51	stacked rings, antiparallel NO <sub>2</sub> groups
	-33 -37	-35 -39	-31 -36	stacked rings, antiparallel C-Br bonds
	-34	-31	-8 <sup>a</sup>	Br...N 2.952

<sup>a</sup> *ab initio* value could be lower by 5-8  $\text{kJ mol}^{-1}$ .

## References

- [1] R. F. W. Bader, *Atoms in Molecules*, Oxford University Press, Oxford, 1990.
- [2] A. M. Pendas, E. Francisco, M. A. Blanco and C. Gatti, *Chem.Eur.J.* **13**, 9362 (2007).
- [3] A. I. Kitaigorodski, in *Advances in Structure Research by Diffraction Methods*, Brill, R. and Mason, R. (ed.). Pergamon Press, Oxford 1970, vol. 3, pp.173-247.
- [4] D. E. Williams, *J. Chem. Phys.* **47**, 4680 (1967).
- [5] A. J. Stone, *Chem. Phys. Letters*, **83**, 233 (1981).
- [6] I. C. Hayes and A.J. Stone, *Mol. Phys.* **53**, 83 (1984).
- [7] A.Gavezzotti, *J. Phys. Chem.* **B106**, 4145 (2002).
- [8] G. J. Williams and A.J. Stone, *J. Chem. Phys.* **119**, 4620 (2003).
- [9] P. Soderhjelm, G. Karlstrom and U. Ryde, *J.Chem.Phys.* **124**, 244101 (2006).
- [10] W. B. Schweizer and J. D. Dunitz, *J.Chem.Theor.Comput.* **2**, 288 (2006).
- [11] A.Gavezzotti, *CrystEngComm*, **5**, 429 (2003).
- [12] P.A.Wood, R. S. Forgan, D. Henderson, S. Parsons, E. Pidcock, P. A. Tasker and J. E. Warren, *Acta Cryst.* **B62**, 1099 (2006).
- [13] J. D. Dunitz and W. B. Schweizer, *Chem.Eur.J.* **12**, 6804 (2006).
- [14] J. Z. Gougoutas and D.G. Naae, *J. Solid St. Chem.* **16**, 271 (1976).
- [15] A. C. Legon, *Angew. Chem. Int. Ed.* **38**, 2686 (1999).
- [16] P. Metrongolo, H. Neukirch, T. Pilati and G. Resnati, *Acc. Chem. Res.* **38**, 386 (2005).
- [17] J.P.M.Lommerse, A.J.Stone, R.Taylor and F.H.Allen, *J. Am. Chem. Soc.* **118**, 3108 (1996).
- [18] F.H.Allen, *Acta Cryst.* **B58**, 380 (2002).
- [19] A.Gavezzotti, *CrystEngComm*, in the press. DOI: 10.1039/B714349D.
- [20] A.Gavezzotti, *Molecular Aggregation*, Oxford University Press, Oxford, **2007**, pp. 298ff.
- [21] *Gaussian 03, Revision B.04*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota,

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4 R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M.  
5 Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R.  
6 Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W.  
7 Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg,  
8 V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A.  
9 D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S.  
10 Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi,  
11 R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M.  
12 Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A.  
13 Pople, Gaussian, Inc., Pittsburgh PA, 2003.  
14  
15 [22] R.B.Walsh, C.W.Padgett, P.Metrangolo, G.Resnati, T.W.Hanks and W.T.Pennington  
16 Cryst. Growth Des. **1**, 165 (2001).  
17  
18 [23] A.Forni, P.Metrangolo, T.Pilati and G. Resnati, Cryst. Growth Des. **4**, 291 (2004).  
19  
20 [24] G. R. Desiraju and R. L. Harlow, J. Am. Chem. Soc. **111**, 6757 (1989).  
21  
22 [25] A.Gavezzotti, J. Chem. Theor. Comp. **1**, 834 (2005).  
23  
24 [26] Ref.18, Chapter 12.  
25  
26 [27] A.D.Bond, J.Griffiths, J.M.Rawson and J.Hulliger, Chem.Commun. 2488 (2001).  
27  
28 [28] B.Ahrens and P.G.Jones Acta Cryst. **C55**, 1308 (1999).  
29  
30 [29] B.T.Holmes, C.W.Padgett and W.T.Pennington, Acta Cryst. **C58**, o602 (2002).  
31  
32 [30] B.K.Saha, A.Nangia and M.Jaskolski CrystEngComm **7**, 355 (2005).  
33  
34 [31] M.Kubicki, Acta Cryst. **B60**, 333 (2004).  
35  
36 [32] S.Muniappan, S.Lipstman and I.Goldberg, Chem. Commun. in the press, DOI:  
37 10.1039/b719625c.  
38  
39 [33] Y.-X. Lu, J.-W. Zou, Y.-H. Wang and Q.-S. Yu, J. Mol. Struct. **776**, 83 (2006)  
40  
41 [34] J.-W. Zou, Y.-J. Jiang, M. Guo, G.-X. Hu, B. Zhang, H.-C. Li and Q.-S Yu, Chem.  
42 Eur. J. **11**, 740, 2005.  
43  
44 [35] R.Glaser, N.Chen, H.Wu, N.Knotts and M.Kaupp, J. Am. Chem. Soc. **126**, 4412  
45 (2004).  
46  
47 [36] E. Keller, *SCHAKAL, A Program for the Graphic Representation of Molecular and*  
48 *Crystallographic Models*, University of Freiburg, 1993.  
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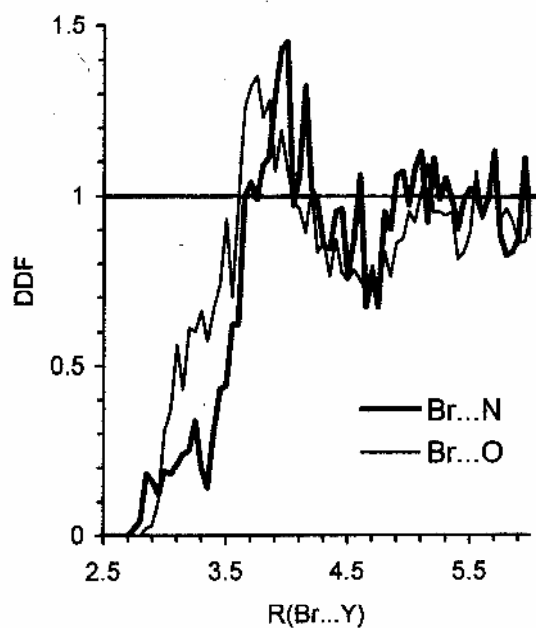


Figure 1. Normalized distance density functions for the Br...N and Br...O contacts in organic crystals. DDF= 1.0 is equivalent to a random distribution. The vertical axis marks the sum of standard intermolecular radii.

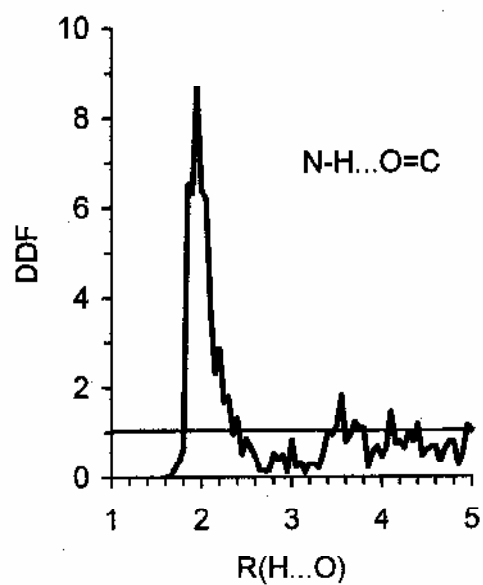


Figure 2. Normalized distance density function for the hydrogen-bonding H...O separation in N-H...O=C groups from the same crystal sample as in Figure 1.

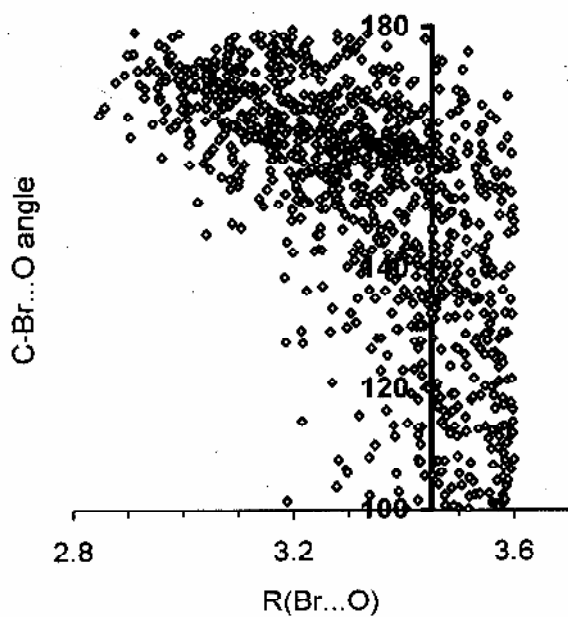


Figure 3. Angle-distance plot for the C-Br...O contact from the same crystal sample as in Figure 1. The vertical axis marks the sum of standard intermolecular radii.

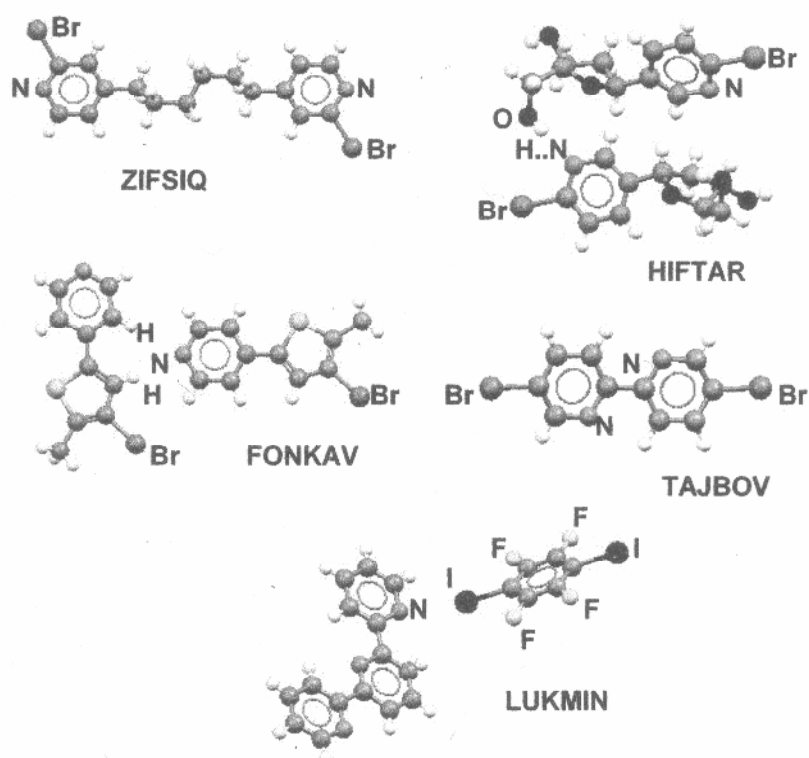


Figure 4. Molecular schemes for illustration of the text in Section 3.1. Additional examples of crystal structures of compounds not forming Br...N bonding: NAPRUS, SAWTUG, XEYLES, FARHOW, FOBSAR, GEDCOI, GEDCUO, GEDDEZ, OLOGUR, MIFCOT VEFWAF, WUVYIV, DAYLEV. WOJQOB is like LUKMIN but the donor is tetraiodoethylene.



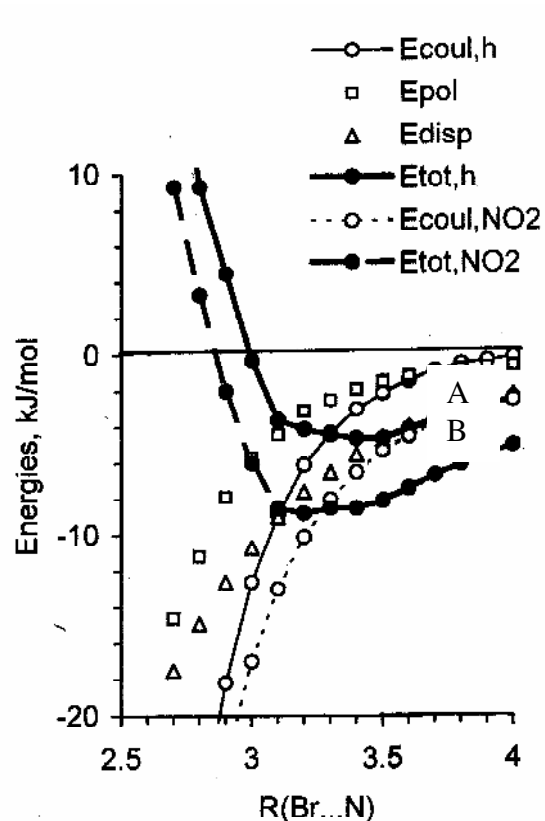


Figure 5. The nature of the Br...N interaction: polarization energy (squares), dispersion energy (triangles) and repulsion energy (not shown) are the same in unsubstituted (curve A, total energy) and 4-nitrosubstituted (curve B, total energy) bromobenzene. The difference in total energy comes from the Coulombic term.

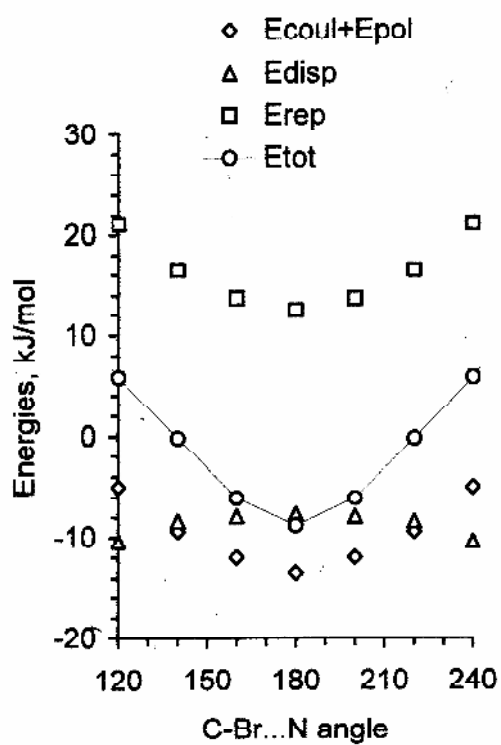


Figure 6. Angular dependence of the energy components over the Br...N interaction: bromobenzene-pyridine complex.

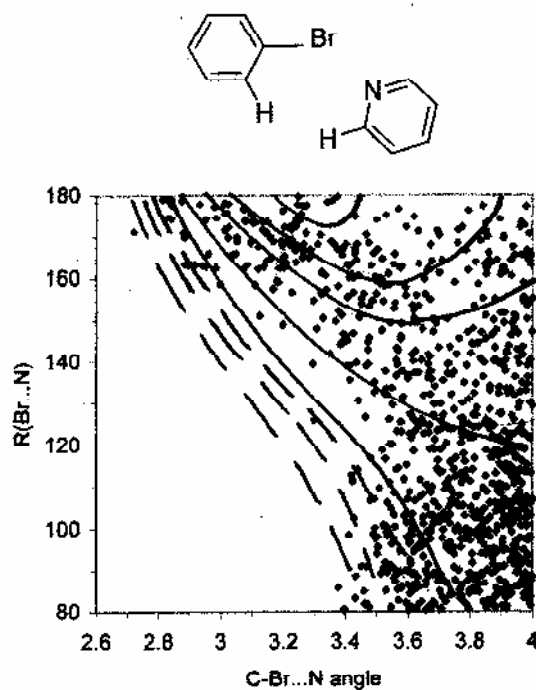


Figure 7. The angle-distance plot for the C-Br...N contact (as in Figure 3), with superimposed the PIXEL energy map (curves in steps of 2 kJ mol<sup>-1</sup>) for the bromobenzene-pyridine approach. The dotted lines are for destabilizing energies.

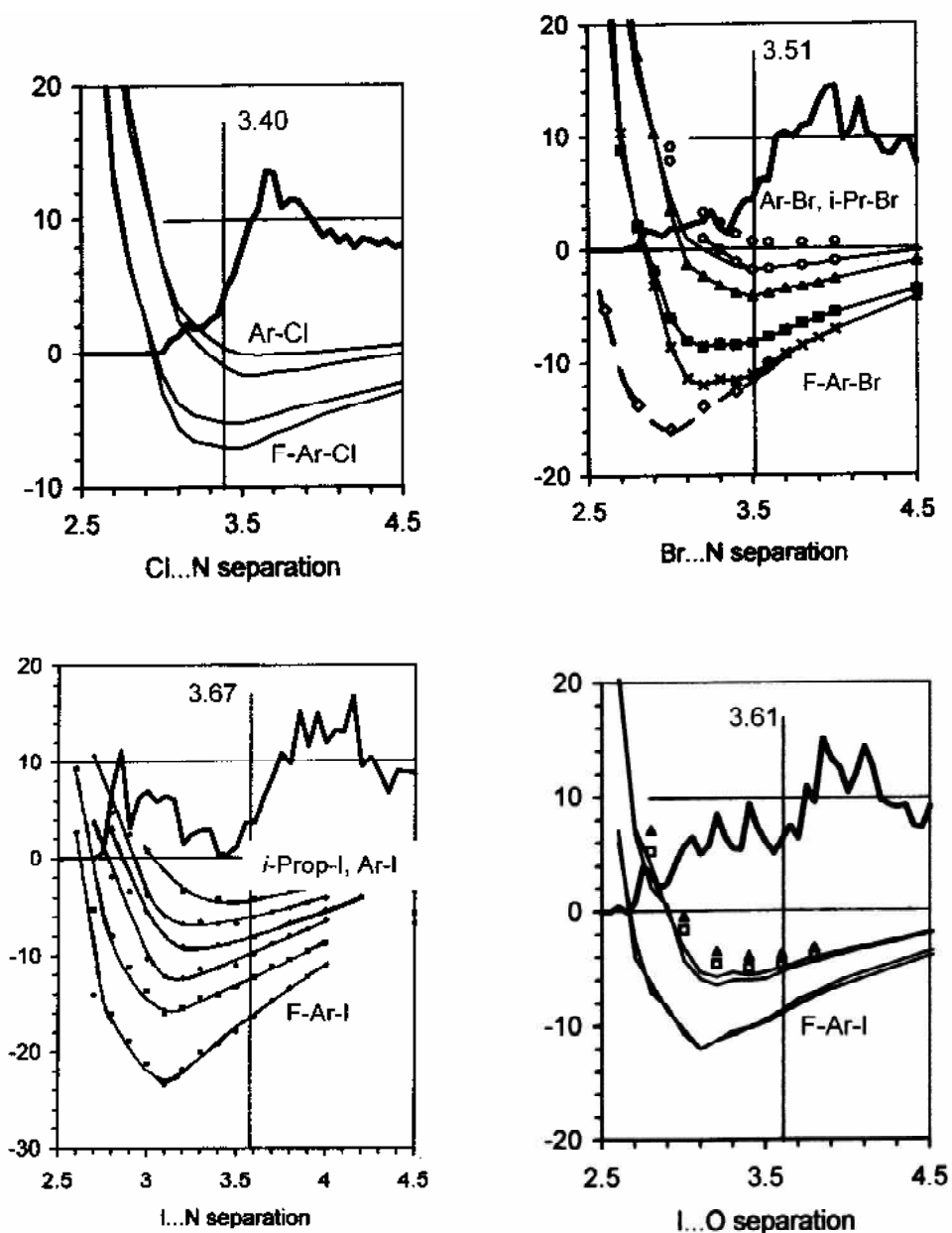
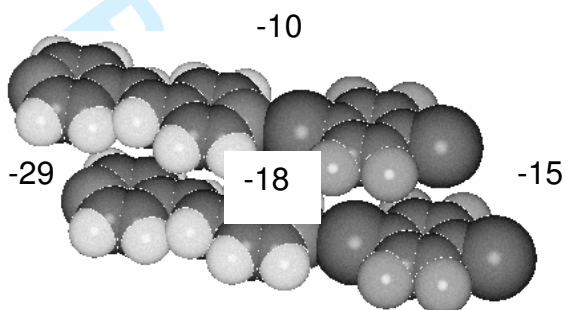


Figure 8. Distance density functions ( $\times 10$ ; heavy lines) with superimposed the PIXEL energy curves ( $\text{kJ mol}^{-1}$ ) for halo-benzenes ( $\text{Ar-X}$ ), 2-halo-isopropyls ( $i\text{-Pr-X}$ ) and perfluoro-halobenzenes ( $\text{F-Ar-X}$ ) interacting with several types of oxygen and nitrogen atoms. The vertical bars mark the sum of standard intermolecular atomic radii.

Figure 9. The closest neighbors in the crystal structure of IKUHUR03. Stacking energies and halogen bond energies are marked: -29, -18 and -15 kJ mol<sup>-1</sup> are the three stacking energies, -10 kJ mol<sup>-1</sup> is the halogen-bond energy (see Table 5). Drawing by Schakal.[36]



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9 **Non-conventional bonding between organic molecules. The "halogen bond" in crystalline**  
10 **systems**  
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14 A. GAVEZZOTTI

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27 **APPENDIX V**  
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Detail of molecule-molecule energies in crystals

for each structure:

first set: numbering of symmetry operations (as for structure deposited in the CSD files)

second set: number of interacting molecules, coulombic, polarization, dispersion, repulsion, total PIXEL energy, UNI atom-atom force field energy

ACOKEI												
1	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0000	0.0000	0.0000
2	-1.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	1.0	0.0000	0.0000	0.5000
3	-1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.5000	0.5000	0.5000
9	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0000	-1.0000	-1.0000
10	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0000	-1.0000	0.0000
14	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0000	0.0000	-1.0000
19	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0000	1.0000	0.0000
32	-1.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	1.0	0.0000	1.0000	-0.5000
64	-1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.5000	-0.5000	0.5000

energies												
1	2	6.404	-5.9	-1.2	-10.7	5.3	-12.5	-11.2	0.0			
1	3	6.322	-8.4	-2.8	-18.8	15.0	-15.0	-17.0	0.0			
1	9	10.307	-10.8	-2.9	-5.7	11.7	-7.6	-4.9	0.0			
1	10	8.280	-0.5	-0.4	-5.3	2.7	-3.6	-6.0	0.0			
1	14	6.137	-3.8	-1.2	-16.4	9.7	-11.8	-14.1	0.0			
1	19	8.280	-0.5	-0.4	-5.3	2.7	-3.6	-6.0	0.0			
1	32	6.256	-1.0	-1.3	-15.0	8.0	-9.3	-13.6	0.0			
1	64	6.322	0.4	-0.3	-5.3	0.3	-4.8	-8.1	0.0			

ACOKIM												
3	-1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.5000	0.5000	0.5000
6	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0000	-1.0000	0.0000
7	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0000	-1.0000	1.0000
8	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0000	0.0000	-1.0000
12	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0000	1.0000	1.0000
13	-1.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	1.0	0.0000	2.0000	-0.5000
17	-1.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	1.0	0.0000	3.0000	0.5000
21	-1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.5000	-0.5000	0.5000

energies												
1	3	6.508	0.0	-0.3	-4.3	0.8	-3.8	-7.3	0.0			
1	6	8.516	-2.3	-0.9	-5.8	6.4	-2.6	-6.9	0.0			
1	7	10.523	-24.0	-7.9	-9.9	27.3	-14.4	-9.2	0.0			
1	8	6.182	-12.8	-2.9	-18.9	30.8	-3.9	-15.5	0.0			
1	12	10.523	0.2	0.0	-0.2	0.0	0.0	-0.4	0.0			
1	13	6.563	-9.0	-1.7	-9.3	12.2	-7.8	-10.7	0.0			
1	17	6.413	-10.3	-4.8	-20.5	29.1	-6.6	-15.1	0.0			
1	21	6.508	-15.8	-5.2	-19.5	33.8	-6.7	-18.2	0.0			

AWAKIS05												
12	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	-1.0000	-1.0000	0.0000
14	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	-1.0000	0.0000	-1.0000
15	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	-1.0000	0.0000	0.0000
63	-1.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	-1.0	1.0000	1.0000	0.0000
64	-1.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	-1.0	1.0000	1.0000	1.0000
65	-1.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	-1.0	1.0000	2.0000	-1.0000
66	-1.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	-1.0	1.0000	2.0000	0.0000
76	-1.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	-1.0	2.0000	1.0000	0.0000
77	-1.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	-1.0	2.0000	1.0000	1.0000
79	-1.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	-1.0	2.0000	2.0000	0.0000
80	-1.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	-1.0	2.0000	2.0000	1.0000

energies												
1	12	9.725	3.9	-0.1	-0.6	0.0	3.2	-1.3	0.0			
1	14	11.546	-10.5	-2.4	-6.5	5.1	-14.3	-7.5	0.0			
1	15	6.965	-22.4	-12.5	-31.1	58.3	-7.8	-15.1	0.0			
1	63	6.629	-26.5	-6.7	-30.9	13.9	-50.1	-45.9	0.0			
1	65	16.246	4.3	-0.1	-0.1	0.0	4.1	-0.3	0.0			
1	66	7.157	-29.0	-8.1	-31.5	17.2	-51.4	-43.6	0.0			
1	76	6.423	-28.5	-8.0	-39.4	40.0	-35.9	-35.8	0.0			
1	77	7.109	3.5	-2.2	-20.1	9.5	-9.4	-15.3	0.0			
1	79	6.933	-26.1	-7.4	-35.0	37.7	-30.7	-37.0	0.0			
1	80	7.077	3.3	-1.8	-14.2	5.3	-7.3	-12.0	0.0			

HOFGEO												
1	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0000	0.0000	0.0000
2	1.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	1.0	0.2500	0.2500	0.2500
5	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.5000	0.0000	0.5000
9	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	0.0000	0.0000	-1.0000
17	1.0	0.0	0.0	0.0	-1.0	0.0	0.0	0.0	1.0	0.2500	-0.2500	0.7500
18	1.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	1.0	-0.5000	0.0000	-0.5000

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1
2
3      21  1.0  0.0  0.0  0.0 -1.0  0.0  0.0  0.0  1.0 -0.2500  0.2500  0.7500
4 energies
5  1  2  4.856  -6.9  -2.7 -17.5  16.6 -10.5  -16.3  0.0
6  1  5  6.521  -5.9  -2.6 -12.1  10.8  -9.8   -7.0  0.0
7  1  9  7.884 -45.8 -15.7 -18.4  61.7 -18.1  -8.1  0.0
8  1 17  7.393  -4.3  -2.3  -8.3  11.1  -3.8   -5.1  0.0
9  1 18  6.521  -5.9  -2.6 -12.1  10.8  -9.8   -7.0  0.0
10 1 21  7.393  -4.3  -2.3  -8.3  11.0  -3.9   -5.1  0.0
11
12      IKUHUR03 'P -1' A molecules
13  1  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0  0.0000  0.0000  0.0000
14  2  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0 -1.0000  1.0000  0.0000
15  3  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0  1.0000  0.0000  0.0000
16  4  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0  1.0000 -1.0000  0.0000
17  5  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0  1.0000 -1.0000 -1.0000
18      IKUHUR03 'P -1' B molecules
19  1  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0  0.0000  0.0000  0.0000
20  2  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0 -1.0000  1.0000  0.0000
21  3  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0  1.0000  0.0000  0.0000
22  4  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0  1.0000 -1.0000  0.0000
23  5  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0  1.0000 -1.0000 -1.0000
24 a...a energies
25  1  2  7.287  -8.0  -3.0 -28.8  19.6 -20.2  -25.0  0.0
26  1  3  6.052 -10.4  -4.2 -33.3  19.3 -28.6  -23.1  0.0
27  1  4  7.287  -8.0  -3.0 -28.8  19.6 -20.2  -25.0  0.0
28  1  5 13.624  -1.2  0.0  -0.4  0.0  -1.6  -0.6  0.0
29 a...b energies
30  1  1 10.821 -34.7 -11.4 -14.6  50.6 -10.1  2.0  0.0
31  1  2 17.394  -0.2  0.0  0.0  0.0  -0.2  -0.1  0.0
32  1  3  8.856  1.3  -0.5  -6.9  1.8  -4.3  -7.4  0.0
33  1  4  6.151  -5.1  -2.8 -24.8  14.4 -18.3  -22.7  0.0
34  1  5  6.479  -6.3  -2.4 -14.4  9.9 -13.2  -5.9  0.0
35 b...a energies
36  1  2  6.151  -5.1  -2.8 -24.8  14.4 -18.3  -22.7  0.0
37  1  3 15.133  -0.1  0.0  -0.1  0.0  -0.2  -0.2  0.0
38  1  4 17.394  -0.2  0.0  0.0  0.0  -0.2  -0.1  0.0
39  1  5 23.736  0.0  0.0  0.0  0.0  0.0  0.0  0.0
40 b...b energies
41  1  2  7.287  -2.4  -1.0 -11.8  7.3  -8.0  -9.5  0.0
42  1  3  6.052  -5.4  -1.2 -16.5  8.6 -14.5  -13.9  0.0
43  1  4  7.287  -2.4  -1.0 -11.8  7.3  -8.0  -9.5  0.0
44  1  5 13.624  -0.1  0.0  -0.1  0.0  -0.1  -0.1  0.0
45
46      QIHCAL      A molecules
47  31  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0 -1.0000  0.0000  0.0000
48  32  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0 -1.0000  0.0000  1.0000
49  33  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0 -1.0000  0.0000  2.0000
50  34  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0 -1.0000  1.0000 -2.0000
51  35  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0 -1.0000  1.0000 -1.0000
52  36  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0 -1.0000  1.0000  0.0000
53      QIHCAL      B molecules
54  1  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0  0.0000  0.0000  0.0000
55 16  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0 -1.0000  0.0000  0.0000
56 28  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0  0.0000 -1.0000  1.0000
57 31  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0  0.0000  0.0000  1.0000
58 36  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0  0.0000  2.0000  0.0000
59 41  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0  1.0000 -2.0000  1.0000
60 44  1.0  0.0  0.0  0.0  1.0  0.0  0.0  0.0  1.0  1.0000 -1.0000  0.0000
61 a...a energies
62  1 31  6.267 -13.7  -2.9 -19.7  27.0  -9.5  -16.3  0.0
63  1 36  9.448  -5.8  -2.0  -9.0  13.9  -2.9  -4.4  0.0
64 a...b energies
65  1  1 10.997 -77.2 -28.7 -24.4 109.1 -21.2  2.2  0.0
66  1 28  6.441  -9.9  -2.8 -15.7  14.1 -14.3  -7.2  0.0
67  1 41  9.159  -1.3  -1.5 -10.5  8.8  -4.5  -8.7  0.0
68  1 44  4.613 -20.2  -8.1 -40.0  53.7 -14.6 -37.0  0.0
69 b...b energies
70  1 16  6.267  -7.0  -3.0 -19.2  9.6 -19.6  -17.0  0.0
71  1 28 11.792  -2.6  -1.3  -5.1  4.0  -4.9  -1.8  0.0
72  1 44  9.448  -3.5  -2.1 -10.5  11.1  -5.0  -13.6  0.0

```