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#### The crystal and molecular structure of 6,8,15,16b,16c,17-hexahydro-16b,16cdiphenyl-7H,16H-6a,7a,15a,16a-tetraazanaphtho[5,6]azulano[2,1,8ij]naptho[f]azulene-7,16-dione — Source link

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Note

The crystal and molecular structure of 6,8,15,16b,16c,17hexahydro-16b,16c-diphenyl-7H,16H-6a,7a,15a,16atetraazanaphtho[5,6]azulano[2,1,8,-ij]naptho[f]azulene-**7,16-dione** 

## W. P. Bosman,<sup>(3)</sup>\* J. M. M. Smits,<sup>(2)</sup> R. de Gelder,<sup>(2)</sup> J. N. H. Reek,<sup>(1)</sup> and R. J. M. Nolte<sup>(1)</sup>

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The crystal and molecular structure of a clip containing molecule is described. The structure was solved by vector search methods and refined by least squares methods to  $R_1 = 0.0768$  $[I > 2\sigma(I)]$ . Crystal data: C<sub>40</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>·HCCl<sub>3</sub>, triclinic, space group P1, a = 9.302(2), b = $12.981(2), c = 15.765(2)\text{Å}, \alpha = 65.91(2)^\circ, \beta = 76.40(2)^\circ, \gamma = 80.15(1)^\circ, V = 1682.9(4)\text{Å}^3,$ Z = 2.

**KEY WORDS:** Crystal structure; receptor; clip shaped molecule.

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### Introduction

V

In the course of our studies aimed at the development of synzymes (synthetic enzymes), 1a, 1b a new series of clip shaped molecules were designed in order to get a better insight into the factors which influence the binding of dihydroxybenzene molecules into these receptors.<sup>2</sup> From earlier studies<sup>3</sup> it is known that clip molecules with 1,4 dimethoxynaphtalene (1a) or functionalized 1,4 dimethoxybenzene side walls  $(2)^4$  are not able to bind aromatic guest molecules. A possible explanation is that the methoxy groups are blocking the carbonyl groups of the diphenylglycoluril. Therefore, we synthesized a clip molecule with napthalene moieties (2,3 connected) not having the methoxy groups (1b), in order to study the role of these groups.

An X-ray diffraction experiment was undertaken to establish the three-dimensional structure of the compound synthesized. The structure appeared to be the title compound.

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### Experimental

The crystal data and a summary of the data collection, the structure solution and refinement are given in Table 1. The atomic positional and vibrational parameters are given in Table 2. Since experience showed that the diphenylglycoluril unit from similar compounds can be used as a suitable rigid fragment<sup>6</sup> for structure solution, this unit was input to a vector search program.<sup>7</sup> The phasing power of the model proved to be sufficient to solve the stucture. The hydrogen atoms of the methyl groups were obtained by rotation of an idealized methyl group to match maximum electron density in a difference Fourier synthesis. The remaining hydrogens were generated at calculated positions. All hydrogens atoms were refined riding on the parent atoms with constrained isotropic temperature factors. A difference Fourier synthesis revealed the presence of one chloroform solvent molecule which

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# is partly disordered. One of the chlorine atoms of the

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chloroform molecule was split into two parts. The corresponding occupation factors were set to add up to one during refinement.

### Discussion

The structure and atomic numbering are presented in Fig. 1.<sup>11</sup> Geometrical calculations<sup>12</sup> revealed no unusual geometrical features. Calculations with PLA-TON<sup>13</sup> revealed no higher symmetry and no further residual solvent accessible area. There is a hydrogen bond between the hydrogen atom of the chloroform molecule and the carbonyl oxygen of the diphenylglycoluril unit (O–H: 2.18(4) Å; / O–H–C: 172.(3)°). Comparing the structures of **1a** and **1b** one can conclude that the cavities of these clip shaped molecules are very similar. There are some differences like the





## Crystal structure of C40H30N4O2·HCCl3

 Table 1. Crystal data and summary of intensity data collection, structure solution, and refinement

**Table 2.** Atomic coordinates (×10<sup>4</sup>) and equivalent isotropic displacement parameters ( $\mathring{A}^2 \times 10^3$ )

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Cry	stal data		x	y	Z	Uea	
	Compound	$C_{40}H_{30}N_4O_2 \cdot HCCl_3$					- eq	
$\begin{array}{ccccc} Crystalization & Chloroform & 0(2) & -735(2) & 4113(2) & 3096(1) & 523 \\ Crystal system & Triclinic & N(2) & 3760(3) & 4025(2) & 3043(2) & 232 \\ Crystal system & Triclinic & N(2) & 3760(3) & 4025(2) & 3043(2) & 244 \\ Temperature, K & 208(2) & N(1') & 869(3) & 506(2) & 2539(2) & 253 \\ ccl cl constants" & N(2) & 3370(4) & 7141(3) & 3671(3) & 488 \\ h & A & 13.765(2) & C(1) & 5370(4) & 7141(3) & 3671(3) & 488 \\ h & A & 13.765(2) & C(2) & 6062(4) & 6466(3) & 377 \\ c. & A & 15.765(2) & C(3) & 33893(4) & 7058(3) & 4066(3) & 477 \\ c. & A & 15.765(2) & C(4) & 5269(4) & 5733(3) & 3071(2) & 355 \\ p. & 76.40(2) & C(5) & 3089(4) & 6732(3) & 3965(2) & 3448(2) & 255 \\ Cell volume, Å' & 16829(4) & C(5) & 3089(4) & 6732(3) & 3967(2) & 3244(2) & 244 \\ \gamma^* & 80.15(1) & C(6) & 3762(3) & 5572(2) & 3448(2) & 255 \\ Cell volume, Å' & 16829(4) & C(7) & 2857(3) & 4976(2) & 3234(2) & 246 \\ \gamma^* & 80.15(1) & C(6) & 3762(3) & 5877(2) & 3448(2) & 255 \\ Cell volume, Å' & 16829(4) & C(11) & 4387(3) & 3071(2) & 3248(2) & 246 \\ Pana min^{-1} & 0.317 & C(10) & 1632(3) & 3816(2) & 4881(2) & 277 \\ Formola unitxoint cell & 2 & C(8) & 418(3) & 4544(2) & 3783(2) & 226 \\ Intensity data collection & C(12) & 1343(3) & 3071(2) & 3783(2) & 286 \\ Crystal dimensions, mm & 0.99 \times 0.13 \times 0.39 & C(16) & 1173(3) & 684(3) & 5653(2) & 236 \\ Crystal dimensions, mm & 0.99 \times 0.13 \times 0.39 & C(16) & 1173(3) & 684(3) & 5653(2) & 236 \\ Corrections & 3. every 7200 seconds & C(18) & 148(4) & -115(3) & 5244(2) & 377 \\ Cange & up to 56 & C(7) & 2379(3) & 1137(2) & 2141(2) & 277 \\ Structure solution and refinement & C(12) & 207(3) & 5598(2) & 2990(2) & 240 \\ Corrections & 1.00 - 10.2 & C(20) & 410(4) & -1274(4) & 6337(2) & 399 \\ derange ^{0} & up to 56 & C(1) & 3142(4) & 7348(3) & 1500(2) & 344 \\ Lorenz, polarization & Local programs & C(11') & 3142(4) & 7348(3) & 1500(2) & 344 \\ Lorenz, polarization & Local programs & C(11') & 316(3) & 1128(2) & 277 \\ Corrections & Local programs & C(11') & 3164(2) & 1284(2) & 278 \\ Corrections & Local programs & C(11') & 3164(2) &$	Color/shape	Colorless/regular	O(1)	4945(2)	3638(2)	1730(1)	33(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Crystallization	Chloroform	O(2)	-735(2)	4113(2)	3906(1)	32(1)	
$\begin{array}{cccc} Crystal system Triclinic N(2) 3760(3) 4025(2) 3043(2) 24 (2) 5760(3) 4025(2) 3043(2) 24 (2) 5760(3) 400($	Formula weight	718.05	N(1)	1518(2)	4633(2)	3926(2)	23(1)	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Crystal system	Triclinic	N(2)	3760(3)	4025(2)	3043(2)	24(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Space group	P1	N(1')	869(3)	5062(2)	2539(2)	25(1)	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Temperature, K	208(2)	N(2')	3354(3)	5245(2)	1623(2)	23(1)	
a, A       9,30(2)       C(1)       20,0(4)       646(3)       3180(3)       47(         c, Å       15,76(2)       C(3)       3893(4)       7058(3)       406(3)       47(         c, Å       15,76(2)       C(4)       5269(4)       5735(3)       307(12)       35( $\beta, *$ 76,40(2)       C(5)       3089(4)       6325(3)       396(2)       34( $\gamma, *$ 80.15(1)       C(6)       3762(3)       5572(2)       3448(2)       25(         Cell volume, Å'       1682.9(4)       C(7)       2857(3)       497(6)       3310(2)       234(2)       24(         D <sub>wkr</sub> g m <sup>-1</sup> 0.317       C(10)       1652(3)       381(2)       47(8)       28(2)       206(2)       25(         P <sub>war</sub> mm <sup>-1</sup> 0.317       C(10)       1632(3)       3316(2)       4881(2)       27(7)         P(000), electrons       744       C(11)       433(3)       307(2)       438(3)       5542(2)       29(         Diffaccometer/scan       Enral-Nomis CAD-4/w-scan       C(12)       1943(3)       2241(2)       433(2)       26(       1327(3)       231(2)       431(3)       5542(2)       29(       26(       1173(3)       684(3)       5	Cell constants <sup>a</sup>		C(1)	5370(4)	7141(3)	3671(3)	$\frac{23(1)}{48(1)}$	
b, A         12.981(2)         C(3)         3603(4)         7050(3)         406(3)         47, $\alpha$ , $^{\circ}$ 65.92(2)         C(4)         5269(4)         5735(3)         3071(2)         35 $\beta$ , $^{\circ}$ 76.40(2)         C(5)         3089(4)         6532(3)         365(2)         344 $\gamma$ , $^{\circ}$ 80.15(1)         C(6)         3762(3)         497(62)         324(2)         24           Formula units/unit cell         2         C(8)         418(3)         4544(2)         3497(2)         24( $\rho_{ates}$ g cm <sup>-1</sup> 1.417         C(9)         4100(3)         422(2)         2106(2)         25( $P_{ates}$ min         0.317         C(10)         1632(3)         3816(2)         488(2)         27( $P_{ates}$ min         0.317         C(10)         1632(3)         326(2)         495(2)         26(           Diffractometer/scan         Emrif-Nonius CA.0-4/ $\omega$ -scan         C(12)         1943(3)         224(12)         4437(2)         26(           Crystal dimensions, mm         0.09 × 0.13 × 0.39         C(16)         1173(3)         684(3)         5653(2)         28(           Scan	a, A	9.302(2)	C(2)	6062(4)	6466(3)	3180(3)	40(1)	
c, A       15,765(2)       C(1)       269(4)       573(3)       370(12)       35(3) $\beta$ , *       76,40(2)       C(5)       3089(4)       6325(3)       3965(2)       34(3) $\gamma$ , *       80.15(1)       C(6)       3762(3)       5672(2)       344(2)       25(2)         Cell volume, ų       1682.9(4)       C(7)       2857(3)       4976(2)       3234(2)       24(2)         Formula units/unit cell       2       C(8)       418(3)       4544(2)       3497(2)       24(2)         Poster, gront       1.417       C(9)       4100(3)       422(2)       2106(2)       25(2)         Intensity data collection       C(11)       4387(3)       3071(2)       3783(2)       28(8)         Intensity ata collection       C(13)       3357(3)       2241(2)       4437(2)       26(6)         Crystal dimensions, m       0.09 × 0.13 × 0.39       C(16)       1173(3)       684(3)       5552(2)       28(2)         Scan width, *       1.5       C(17)       2479(3)       3342(2)       39(2)         Corystal dimensions, m       0.09 × 0.13 × 0.39       C(16)       1173(3)       684(4)       563(2)       278(2)         Standard reflections       3, every 7200	<i>b</i> , A	12.981(2)	C(2)	3803(4)	7058(3)	1066(3)	47(1)	
$\alpha$ , *       65,92(2)       C(7)       2203(7)       513(3)       301(12)       351(3) $\beta$ , *       76,40(2)       C(5)       3089(4)       6325(3)       365(2)       34(4) $\gamma$ , *       80,15(1)       C(6)       3762(3)       4976(2)       3243(2)       24(4)         Formula units/unit cell       2       C(8)       418(3)       4544(2)       3497(2)       24(6) $\rho_{wale}$ , mr <sup>-1</sup> 0.317       C(10)       1632(3)       3816(2)       488(2)       27(7) $F(000)$ , electrons       744       C(11)       4387(3)       2241(2)       4437(2)       26(         Intensity data collection       Enrat-Nonius CAD-4/ $\omega$ -scan       C(13)       3257(3)       2241(2)       4437(2)       26(         Crystal dimensions, mm       0.09 × 0.13 × 0.39       C(16)       1173(3)       684(3)       553(2)       38(         Scan width, *       1.00-1.02       C(20)       410(4)       -115(3)       6254(2)       37(         Scan width, k, l       -12 ≤ k ≤ 12, -17 ≤ k ≤       C(17)       2479(3)       324(2)       514(2)       27(         Scan width, k, l       -12 ≤ k ≤ 12, -17 ≤ k ≤       C(17)       2479(3)       354(2)       39( </td <td><i>c</i>, A</td> <td>15.765(2)</td> <td>C(3)</td> <td>5260(4)</td> <td>5725(2)</td> <td>4000(3)</td> <td>47(1)</td>	<i>c</i> , A	15.765(2)	C(3)	5260(4)	5725(2)	4000(3)	47(1)	
$\begin{array}{cccc} \mu, z & 76.40(2) & C13 & 3030(1) & 325(3) & 360(12) & 344(2) & 256(2) & 264(2) & 276(2) & 2324(2) & 244(2) & 266(2) & 26$	α, °	65.92(2)	C(4)	2020(4)	6225(2)	2065(2)	33(1)	
$\begin{array}{cccc} \gamma, & & & & & & & & & & & & & & & & & & $	β, °	76.40(2)	C(5)	3089(4)	6325(3)	3965(2)	34(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	γ, ,	80.15(1)	C(0)	3762(3)	5672(2)	3448(2)	25(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Cell volume, A <sup>3</sup>	1682.9(4)	C(7)	2857(3)	4976(2)	3234(2)	24(1)	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Formula units/unit cell	2	C(8)	418(3)	4544(2)	3497(2)	24(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$D_{\rm calc}, \rm g \ \rm cm^{-3}$	1.417	C(9)	4100(3)	4222(2)	2106(2)	25(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\mu_{calc}, mm^{-1}$	0.317	C(10)	1632(3)	3816(2)	4881(2)	27(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	F(000), electrons	744	C(11)	4387(3)	3071(2)	3783(2)	28(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Intensity	data collection	C(12)	1943(3)	2606(2)	4959(2)	26(1)	
Radiation, graphite monochromatorMoKα (λ = 0.71073 Å)Cl(14)941(3)1832(3)5542(2)290 (Cl5)Cyrstal dimensions, mm0.09 × 0.13 × 0.39Cl(16)1173(3)684(3)5653(2)280Scan width, °1.5Cl(7)2479(3)324(2)5141(2)270Standard reflections3, every 7200 secondsCl(19)2718(4)-818(3)5244(2)330Decay of standards1.00–1.02C(20)410(4)-1214(3)6337(2)390Reflections measured16212C(21)1700(4)-1574(3)5834(2)39020-range °up to 56C(1')1597(5)9179(3)1626(2)460Range of h, k, l-12 ≤ h ≤ 12, -17 ≤ k ≤C(2')2974(5)8698(3)1328(2)440CorrectionsC(4')3142(4)7548(3)1500(2)340Lorenz-polarizationC(5')613(4)7568(3)2285(2)330EMPABS* correction0.993-1.011C(6')1979(3)6875(2)1992(2)260Computer programs fLocal programsC(10')-20(3)5190(3)1849(2)290Computer programsDIRDIF* (ORIENT, range bC(12')615(3)4462(2)127(2)310Structure solutionVector search methods?C(14')-226(3)3699(3)1273(2)310Computer programsDIRDIF* (ORIENT, range bC(15')314(4)3447(3)198(2)330Structure solutionKector sea	Diffractometer/scan	Enraf-Nonius CAD-4/w-scan	C(13)	3257(3)	2241(2)	4437(2)	26(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Radiation, graphite	$MoK\alpha (\lambda = 0.71073 \text{ Å})$	C(14)	941(3)	1832(3)	5542(2)	29(1)	
$\begin{array}{cccc} Crystal dimensions, mm & 0.09 \times 0.13 \times 0.39 & C(16) & 1173(3) & 684(3) & 563(2) & 288 \\ Scan width, ^{o} & 1.5 & C(17) & 2479(3) & 324(2) & 5141(2) & 27(7) \\ Standard reflections & 3, every 7200 seconds & C(18) & 148(4) & -115(3) & 6254(2) & 37(7) \\ exposure time & C(19) & 2718(4) & -818(3) & 5244(2) & 33(7) \\ Decay of standards & 1.00-1.02 & C(20) & 410(4) & -1214(3) & 6337(2) & 399 \\ C(12) & 1700(4) & -1574(3) & 5834(2) & 399 \\ 2\theta-range ^{o} & up to 56 & C(1') & 1597(5) & 9179(3) & 1626(2) & 460 \\ Range of h, k, l & -12 \leq h \leq 12, -17 \leq k \leq \\ & 17, -20 \leq l \leq 20 & C(3') & 435(4) & 8526(3) & 2090(2) & 42(7) \\ Corrections & & C(4') & 3142(4) & 7548(3) & 1500(2) & 34(7) \\ Lorenz-polarization & & C(5') & 613(4) & 7368(3) & 2285(2) & 333 \\ Lorenz-polarization & & C(5') & 613(4) & 7368(3) & 2285(2) & 333 \\ Lorenz-polarization & & & C(5') & 613(4) & 7368(3) & 2285(2) & 333 \\ Lorenz-polarization & & & & & & & \\ Lorenz-polarization & & & & & & & & & \\ Computer programs^{e} & 0.063 & & & & & & & & & \\ C(10') & -20(3) & 5190(3) & 1849(2) & 290 \\ Computer programs^{e} & Local programs & C(11') & 3013(3) & 5451(3) & 699(2) & 27(7) \\ Structure solution and refinement & C(13') & 2079(3) & 4591(3) & 726(2) & 27(7) \\ Structure solution and refinement & C(13') & 2079(3) & 4591(3) & 726(2) & 27(7) \\ Structure refinement & Full-matrix, least-squares on F^2 & C(16') & 319(4) & 3037(3) & 713(2) & 31(7) \\ ron-H atoms & Anisotropic & C(16') & 319(4) & 3037(3) & 713(2) & 31(7) \\ Gonputer programs & SHELXL'^{9} & C(16') & -256(3) & 3699(3) & 1273(2) & 316 \\ Gondness-of-fit on F^2 & 1.005 & \\ R indices (11) > 207(1) & R_1 = 0.139, wR_2 = 0.156 \\ C(10') & 5260(4) & 1138(3) & 1964(3) & 41(1) \\ Largest diff, peak and hole, & 0.648 and -0.503 & C(12') & 5560(4) & 1138(3) & 1964(3) & 41(1) \\ Cargest diff, peak and hole, & 0.648 and -0.503 & C(12') & 5260(4) & 1138(3) & 1964(3) & 41(1) \\ C(2) & 5260(4) & 1138(3) & 1964(3) & 41(1) \\ C(2) & 5260(4) & 1138(3) & 1964(3) & 41(1) \\ C(2) & 5260(4) & 1138(3) & 1964(3) & 41(1) \\ C(2) & 5260($	monochromator		C(15)	3499(3)	1137(2)	4531(2)	26(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Crystal dimensions, mm	$0.09 \times 0.13 \times 0.39$	C(16)	1173(3)	684(3)	5653(2)	28(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Scan width, °	1.5	C(17)	2479(3)	324(2)	5141(2)	27(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Standard reflections	3, every 7200 seconds	C(18)	148(4)	-115(3)	6254(2)	37(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		exposure time	C(19)	2718(4)	-818(3)	5244(2)	33(1)	
Reflections measured16212C(21)1700(4) $-1574(3)$ 5834(2)39(20-range °up to 56C(1')1597(5)9179(3)1626(2)46(Range of h, k, l $-12 \le h \le 12, -17 \le k \le$ C(2')2974(5)8698(3)1328(2)44(Corrections17, $-20 \le l \le 20$ C(3')435(4)8526(3)2090(2)42(CorrectionsC(4')3142(4)7548(3)1500(2)34(Lorenz-polarizationC(5')613(4)7368(3)2285(2)33(EMPABS's correction0.993-1.011C(6')1979(3)6875(2)1992(2)26(Independent reflens (obs., $I_o$ 8106(4210)C(7')2239(3)5598(2)2290(2)23( $2 \alpha(I_o)$ Eucal programsC(11')3013(3)5451(3)699(2)27(Computer programs*Local programsC(11')3013(3)5451(3)699(2)27(Structure solutionVector search methods7C(14')-226(3)3699(3)1273(2)31(Computer programsDIRDIF* (ORIENT, reformsC(15')2617(4)3947(3)198(2)33(Structure refinementFull-matrix, least-squares on $F^2$ C(16')319(4)3037(3)713(2)31(non-H atomsSee experimentalC(19')2314(4)2492(3)-382(2)38(Computer programsSHELXL9C(19')2314(4)2492(3)-382(2)38(Computer programsSHELXL9C(19')2314(4) <td>Decay of standards</td> <td>1.00-1.02</td> <td>C(20)</td> <td>410(4)</td> <td>-1214(3)</td> <td>6337(2)</td> <td>39(1)</td>	Decay of standards	1.00-1.02	C(20)	410(4)	-1214(3)	6337(2)	39(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Reflections measured	16212	C(21)	1700(4)	-1574(3)	5834(2)	39(1)	
Range of h, k, l $-12 \le h \le 12, -17 \le k \le$ $17, -20 \le l \le 20$ $C(2')$ $2974(5)$ $8698(3)$ $1328(2)$ $44(1)$ Corrections $17, -20 \le l \le 20$ $C(3')$ $435(4)$ $8526(3)$ $2090(2)$ $42(1)$ Corrections $C(4')$ $3142(4)$ $7548(3)$ $1500(2)$ $34(1)$ Lorenz-polarization $C(5')$ $613(4)$ $7368(3)$ $2285(2)$ $33(1)$ EMPABS <sup>5</sup> correction $0.993-1.011$ $C(6')$ $1979(3)$ $6875(2)$ $1992(2)$ $26(1)$ Independent reflens (obs., $I_o$ $8106(4210)$ $C(7')$ $2239(3)$ $5598(2)$ $2290(2)$ $23(1)$ $2 ar(I_o)$ $C(1')$ $-203(3)$ $5190(3)$ $1849(2)$ $29(1')$ Computer programsLocal programs $C(11')$ $3013(3)$ $5451(3)$ $699(2)$ $27(1)$ Structure solutionand refinement $C(12')$ $615(3)$ $4462(2)$ $1281(2)$ $27(1)$ Structure solutionVector search methods <sup>7</sup> $C(14')$ $-226(3)$ $3699(3)$ $1273(2)$ $31(1)$ Computer programsDIRDIF <sup>8</sup> (ORIENT, $C(15')$ $2617(4)$ $3947(3)$ $198(2)$ $33(1)$ Structure refinementFull-matrix, least-squares on $F^2$ $C(16')$ $19(4)$ $3037(3)$ $713(2)$ $31(1)$ Non-H atomsAnisotorpic $C(16')$ $-555(4)$ $2267(3)$ $679(2)$ $38(1)$ Computer programsSHELXL <sup>9</sup> $C(19')$ $2314(4)$ $2492(3)$ $-382(2)$ $38(1)$ Computer programs <td>2θ-range °</td> <td>up to 56</td> <td>C(1')</td> <td>1597(5)</td> <td>9179(3)</td> <td>1626(2)</td> <td>46(1)</td>	2θ-range °	up to 56	C(1')	1597(5)	9179(3)	1626(2)	46(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Range of $h, k, l$	$-12 \leq h \leq 12, -17 \leq k \leq$	C(2')	2974(5)	8698(3)	1328(2)	44(1)	
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		$17, -20 \le l \le 20$	C(3')	435(4)	8526(3)	2090(2)	42(1)	
Lorenz-polarizationC(5')613(4)7368(3)2285(2)33(7)EMPABS* correction0.993-1.011C(5')613(4)7368(3)2285(2)33(7)Independent reflens (obs., $I_o$ 8106(4210)C(6')1979(3)6875(2)1992(2)26(7) $2 \circ r(I_o)$ 2 $2 \circ r(I_o)$ C(1')-20(3)5598(2)2290(2)23(7) $R_{merge}^{-b}$ 0.063C(10')-20(3)5190(3)1849(2)29(7)Computer programs*Local programsC(11')3013(3)5451(3)699(2)27(7)Structure solution and refinementC(13')2079(3)4591(3)726(2)27(7)Computer programsDIRDIF* (ORIENT, refinementC(13')2079(3)4591(3)726(2)27(7)Structure solutionVector search methods?C(14')-226(3)3699(3)1273(2)31(7)Computer programsDIRDIF* (ORIENT, ron-H atomsC(15')2617(4)3947(3)198(2)33(7)AnisotropicC(16')319(4)3037(3)713(2)31(7)3156(3)175(2)32(7)Shift/esdLess than 0.04C(19')2314(4)2492(3)-382(2)38(7)Shift/esdLess than 0.04C(20')-6(4)1664(3)116(3)41(7)No. of restraints/parameters0/464C(21')1434(4)1767(3)-406(3)42(7)Goodness-of-fit on $F^2$ 1.005Chloroform moleculeChloroform moleculeCloroform factors for the disordered Cl(3	Corrections		C(4')	3142(4)	7548(3)	1500(2)	34(1)	
EMPABS5 correction $0.993-1.011$ $C(6')$ $100(0)$ $1205(2)$ $250(2)$	Lorenz-polarization		C(5')	613(4)	7368(3)	2285(2)	33(1)	
Independent refloms (obs., $I_o$ 8106(4210) $C(7')$ $D(7)(3)$ $D(3)(2)$ $D(7)(2)$	EMPABS <sup>5</sup> correction	0.993-1.011	C(6')	1979(3)	6875(2)	1992(2)	26(1)	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Independent reflcns (obs., $I_o$	8106(4210)	C(7')	2239(3)	5598(2)	2290(2)	23(1)	
$R_{merge}^{b}$ 0.063 $C(10')$ $L0(3)$ $L0(3')$ $L0$	$> 2\sigma(I_o))$		C(10')	-20(3)	5190(3)	1849(2)	29(1)	
Computer programsLocal programs $C(11')$ $5015(3)$ $3451(3)$ $099(2)$ $21(1)$ Structure solution and refinement $C(12')$ $615(3)$ $4462(2)$ $1281(2)$ $27(1)$ Structure solutionVector search methods <sup>7</sup> $C(13')$ $2079(3)$ $4591(3)$ $726(2)$ $27(1)$ Computer programsDIRDIF <sup>8</sup> (ORIENT, $C(14')$ $-226(3)$ $3699(3)$ $1273(2)$ $31(1)$ Computer programsDIRDIF <sup>8</sup> (ORIENT, $C(16')$ $319(4)$ $3037(3)$ $713(2)$ $31(1)$ Structure refinementFull-matrix, least-squares on $F^2$ $C(16')$ $319(4)$ $3037(3)$ $713(2)$ $31(1)$ non-H atomsAnisotropic $C(16')$ $319(4)$ $3037(3)$ $713(2)$ $31(1)$ H-atomsSee experimental $C(19')$ $2314(4)$ $2492(3)$ $-382(2)$ $38(1)$ Computer programsSHELXL <sup>9</sup> $C(20')$ $-6(4)$ $1664(3)$ $116(3)$ $41(1)$ No. of restraints/parameters $0/464$ $C(21')$ $1434(4)$ $1767(3)$ $-406(3)$ $42(2)$ Goodness-of-fit on $F^2$ $1.005$ $C(11)$ $6549(1)$ $390(1)$ $2701(1)$ $70(1)$ R indices (II > $2\sigma(I)$ ] $R_1 = 0.139, wR_2 = 0.122$ $C(19')$ $5260(4)$ $1138(3)$ $1964(3)$ $41(1)$ Largest diff. peak and hole, $0.648$ and $-0.503$ $C(11)$ $6549(1)$ $390(1)$ $2701(1)$ $70(1)$ $C(12)$ $5260(1)$ $1102(1)$ $90(1)$ $2701(1)$ $70(1)$ </td <td>R<sub>merge</sub><sup>b</sup></td> <td>0.063</td> <td>C(11')</td> <td>3013(3)</td> <td>5451(3)</td> <td>600(2)</td> <td>27(1)</td>	R <sub>merge</sub> <sup>b</sup>	0.063	C(11')	3013(3)	5451(3)	600(2)	27(1)	
tructure solution and refinement $C(12)$ $015(3)$ $4402(2)$ $1281(2)$ $27($ $C(12)$ $015(3)$ $4402(2)$ $1281(2)$ $27($ $C(13')$ $207(3)$ $4591(3)$ $726(2)$ $27($ $C(13')$ $207(3)$ $4591(3)$ $726(2)$ $27($ $C(13')$ $207(3)$ $4591(3)$ $726(2)$ $27($ $C(14')$ $-226(3)$ $3699(3)$ $1273(2)$ $31($ $C(14')$ $-226(3)$ $3699(3)$ $1273(2)$ $31($ $C(15')$ $2617(4)$ $3947(3)$ $198(2)$ $33($ $C(15')$ $2617(4)$ $3947(3)$ $198(2)$ $33($ $C(15')$ $2617(4)$ $3947(3)$ $71(2)$ $C(15')$ $2617(4)$ $3947(3)$ $71(2)$ $C(15')$ $2617(4)$ $3947(3)$ $71(2)$ $C(15')$ $2617(3)$ $679(2)$ $38($ $C(19')$ $2314(4)$ $2492(3)$	Computer programs <sup>c</sup>	Local programs	C(12')	615(3)	1462(2)	1281(2)	27(1)	
Structure solutionVector search methods7 $2079(3)$ $4397(3)$ $720(2)$ $270(2)$ Structure solutionDIRDIF*(ORIENT, TRACOR) $C(14')$ $-226(3)$ $3699(3)$ $1273(2)$ $310(2)$ Structure refinement non-H atomsFull-matrix, least-squares on $F^2$ $C(16')$ $319(4)$ $3037(3)$ $713(2)$ $310(2)$ Structure refinement non-H atomsFull-matrix, least-squares on $F^2$ $C(16')$ $319(4)$ $3037(3)$ $713(2)$ $310(2)$ Structure refinement non-H atomsSee experimental Computer programsSee experimental SHELXL9 $C(19')$ $2314(4)$ $2492(3)$ $-382(2)$ $380(2)$ Shift/esdLess than 0.04C(20') $-6(4)$ $1664(3)$ $116(3)$ $410(2(2)')$ $200(2)$ No. of restraints/parameters Goodness-of-fit on $F^2$ $1.005$ Chloroform moleculeChloroform moleculeR indices (all data) $R_1 = 0.139$ , $wR_2 = 0.122$ $e \cdot Å^{-3}$ Chloroform molecule $C(11)$ $5260(4)$ $1138(3)$ $1964(3)$ $410(22) : 0.50(5)(2)$ ColorChloroform molecule $C(11)$ $5260(4)$ $1138(3)$ $1964(3)$ $410(22) : 0.50(5)(2)$ ColorC(11) $6549(1)$ $390(1)$ $2701(1)$ $700(1)$ ColorC(20) $5860(4)$ $1138(3)$ $1964(3)$ $410(2)$ ColorC(20) $5860(4)$ $1138(3)$ $1964(3)$ $410(2)$ ColorC(20) $5860(4)$ $1138(3)$ $1964(3)$ $410(2)$ ColorC(20) <td colspan="2">Structure solution and refinement</td> <td>C(12')</td> <td>2070(3)</td> <td>4402(2)</td> <td>726(2)</td> <td>27(1) 27(1)</td>	Structure solution and refinement		C(12')	2070(3)	4402(2)	726(2)	27(1) 27(1)	
Computer programsDIRDIF*(ORIENT, TRACOR) $C(14^{\circ})$ $-226(3)$ $3699(3)$ $1273(2)$ $31(2)$ Structure refinement non-H atomsFull-matrix, least-squares on $F^2$ $C(16^{\circ})$ $319(4)$ $3037(3)$ $713(2)$ $31(2)$ Maisotropic H-atomsAnisotropic 	Structure solution	Vector search methods <sup>7</sup>	C(13)	2019(3)	4591(5)	1272(2)	27(1) 21(1)	
Structure refinement non-H atomsFull-matrix, least-squares on $F^2$ C(15)2617(4)3947(3)198(2)33( 198(2)Structure refinement non-H atomsFull-matrix, least-squares on $F^2$ C(16')319(4)3037(3)713(2)31(H-atoms 	Computer programs	DIRDIF <sup>8</sup> (ORIENT.	C(14)	-220(3)	2047(2)	1275(2)	31(1)	
Structure refinement non-H atoms H-atomsFull-matrix, least-squares on $F^2$ $C(16')$ $319(4)$ $3037(3)$ $713(2)$ $31(2)$ $31(2)$ H-atoms Computer programsAnisotropic See experimentalAnisotropic See experimental $C(17')$ $1770(3)$ $3156(3)$ $175(2)$ $32(1)$ Shift/esd No. of restraints/parameters Goodness-of-fit on $F^2$ Less than 0.04 $0/464$ $C(19')$ $2314(4)$ $2492(3)$ $-382(2)$ $38(1)$ R indices $[I > 2\sigma(I)]$ R indices (all data) $R_1 = 0.059$ , $wR_2 = 0.122$ $R_1 = 0.139$ , $wR_2 = 0.156$ $C(10')$ $-6(4)$ $1664(3)$ $116(3)$ $41(1)$ Cocupation factors for the disordered Cl(31) and Cl(32) : $0.50(5)$ $C(91)$ $5260(4)$ $1138(3)$ $1964(3)$ $41(1)$ Cl(1) $6549(1)$ $390(1)$ $2701(1)$ $70(1)$ $70(1)$ $70(1)$ $e \cdot Å^{-3}$ $A^{-3}$ $A^{-3}$ $A^{-3}$ $A^{-3}$ $A^{-3}$ $A^{-3}$ $A^{-3}$	Sompator problams	TRACOR)	C(15)	2617(4)	3947(3)	198(2)	33(1)	
Since of the formation	Structure refinement	Full-matrix, least-squares on $F^2$	C(16')	319(4)	3037(3)	/13(2)	31(1)	
Initial defineInitial define $C(18')$ $-555(4)$ $2267(3)$ $679(2)$ $38(2)$ H-atomsSee experimental $C(19')$ $2314(4)$ $2492(3)$ $-382(2)$ $38(2)$ Computer programsSHELXL <sup>9</sup> Less than 0.04 $C(19')$ $2314(4)$ $2492(3)$ $-382(2)$ $38(2)$ Shiff/esdLess than 0.04 $C(20')$ $-6(4)$ $1664(3)$ $116(3)$ $41(2)$ No. of restraints/parameters $0/464$ $C(21')$ $1434(4)$ $1767(3)$ $-406(3)$ $42(2)$ Goodness-of-fit on $F^2$ $1.005$ $R_1 = 0.059, wR_2 = 0.122$ $Chloroform molecule$ R indices (all data) $R_1 = 0.139, wR_2 = 0.156$ $C(91)$ $5260(4)$ $1138(3)$ $1964(3)$ $41(1)$ Largest diff. peak and hole, $0.648$ and $-0.503$ $C(11)$ $6549(1)$ $390(1)$ $2701(1)$ $70(1)$ $C(12)$ $5860(1)$ $1102(1)$ $845(1)$ $756(1)$	non-H atoms	Anisotropic	C(17')	1770(3)	3156(3)	175(2)	32(1)	
Computer programsSHELXL9 $C(19')$ $2314(4)$ $2492(3)$ $-382(2)$ $38(2)$ Shift/esdLess than 0.04Less than 0.04 $C(20')$ $-6(4)$ $1664(3)$ $116(3)$ $41(2)$ No. of restraints/parameters $0/464$ $0/464$ $C(21')$ $1434(4)$ $1767(3)$ $-406(3)$ $42(2)$ Goodness-of-fit on $F^2$ $1.005$ $C(21')$ $1434(4)$ $1767(3)$ $-406(3)$ $42(2)$ R indices $[I > 2\sigma(I)]$ $R_1 = 0.059, wR_2 = 0.122$ $C(21')$ $C(21')$ $1434(4)$ $1767(3)$ $-406(3)$ $42(2)$ R indices (all data) $R_1 = 0.139, wR_2 = 0.126$ $C(21')$ $C(21')$ $1138(3)$ $1964(3)$ $41(2)$ Largest diff. peak and hole, $0.648$ and $-0.503$ $C(1)$ $6549(1)$ $390(1)$ $2701(1)$ $70(2)$ $C(12)$ $5860(1)$ $1102(1)$ $245(1)$ $75(2)$	H-atoms	See experimental	C(18')	-555(4)	2267(3)	679(2)	38(1)	
Shift/esdLess than 0.04 $C(20')$ $-6(4)$ $1664(3)$ $116(3)$ $41(2)$ No. of restraints/parameters $0/464$ $0/464$ $C(21')$ $1434(4)$ $1767(3)$ $-406(3)$ $42(2)$ Goodness-of-fit on $F^2$ $1.005$ $R_1 = 0.059, wR_2 = 0.122$ $C(21')$ $1434(4)$ $1767(3)$ $-406(3)$ $42(2)$ R indices (all data) $R_1 = 0.139, wR_2 = 0.126$ $C(21')$ $1434(4)$ $1767(3)$ $-406(3)$ $42(2)$ Largest diff. peak and hole, $0.648$ and $-0.503$ $C(21')$ $1434(4)$ $1767(3)$ $-406(3)$ $42(2)$ C(1) $5260(4)$ $1138(3)$ $1964(3)$ $41(2)$ $C(21')$ $1138(3)$ $1964(3)$ $41(2)$ Largest diff. peak and hole, $0.648$ and $-0.503$ $C(1)$ $6549(1)$ $390(1)$ $2701(1)$ $70(2)$ C(2) $5860(1)$ $1102(1)$ $845(1)$ $75(2)$	Computer programs	SHELXL <sup>9</sup>	C(19')	2314(4)	2492(3)	-382(2)	38(1)	
No. of restraints/parameters Goodness-of-fit on $F^2$ $0/464$ $C(21')$ $1434(4)$ $1767(3)$ $-406(3)$ $42(4)$ R indices $[I > 2\sigma(I)]$ $R_1 = 0.059, wR_2 = 0.122$ Chloroform moleculeR indices (all data) $R_1 = 0.139, wR_2 = 0.156$ Coccupation factors for the disordered Cl(31) and Cl(32) : 0.50(5)Largest diff. peak and hole, $e \cdot Å^{-3}$ $0.648$ and $-0.503$ $C(21')$ $1434(4)$ $1767(3)$ $-406(3)$ $42(1)$ C(21') $R_1 = 0.059, wR_2 = 0.122$ $C(21')$ $C(21')$ $C(21')$ $C(21')$ C(91) $5260(4)$ $1138(3)$ $1964(3)$ $41(1)$ C(1) $6549(1)$ $390(1)$ $2701(1)$ $70(1)$ C(21) $5860(1)$ $1102(1)$ $845(1)$ $75(1)$	Shift/esd	Less than 0.04	C(20')	-6(4)	1664(3)	116(3)	41(1)	
Goodness-of-fit on $F^2$ 1.005Chloroform moleculeR indices $[I > 2\sigma(I)]$ $R_1 = 0.059, wR_2 = 0.122$ (Occupation factors for the disordered Cl(31) and Cl(32) : 0.50(5)R indices (all data) $R_1 = 0.139, wR_2 = 0.156$ (Occupation factors for the disordered Cl(31) and Cl(32) : 0.50(5)Largest diff. peak and hole, $e \cdot Å^{-3}$ 0.648 and -0.503Cl(1)5260(4)1138(3)1964(3)41(1)Cl(2) $5260(1)$	No. of restraints/parameters	0/464	C(21')	1434(4)	1767(3)	-406(3)	42(1)	
R indices $[I > 2\sigma(I)]$ $R_1 = 0.059, wR_2 = 0.122$ $R indices (all data)$ (Occupation factors for the disordered Cl(31) and Cl(32) : 0.50(5) $R_1 = 0.139, wR_2 = 0.156$ R indices (all data) $R_1 = 0.139, wR_2 = 0.156$ $0.648 and -0.503$ (Occupation factors for the disordered Cl(31) and Cl(32) : 0.50(5) $C(91)$ C(91)5260(4)1138(3)1964(3)Cl(1)6549(1)390(1)2701(1)Cl(2)5860(1)1102(1)845(1)	Goodness-of-fit on $F^2$	1.005		Chloroform molecule				
R indices (all data) $R_1 = 0.139, wR_2 = 0.156$ $C(91)$ $5260(4)$ $1138(3)$ $1964(3)$ $41(2)$ Largest diff. peak and hole, $0.648$ and $-0.503$ $C(91)$ $5260(4)$ $1138(3)$ $1964(3)$ $41(2)$ $C(91)$ $6549(1)$ $390(1)$ $2701(1)$ $70(2)$ $e \cdot Å^{-3}$ $C(2)$ $5860(1)$ $1102(1)$ $845(1)$	R indices $[I > 2\sigma(I)]$	$R_1 = 0.059, wR_2 = 0.122$	(Occupati	(Occupation factors for the disordered $Cl(31)$ and $Cl(32) \cdot 0.50(5)$ )				
Largest diff. peak and hole, $0.648 \text{ and } -0.503$ $e \cdot \text{Å}^{-3}$ C(91) $5200(4)$ $1138(5)$ $1904(5)$ $41(6549(1)$ $390(1)$ $2701(1)$ $70($	R indices (all data)	$R_1 = 0.139, wR_2 = 0.156$	C(01)	5260(4)	1138(3)	1064(3)	(11(1)	
$e \cdot Å^{-3}$ (1) (1) (1) (1) (1) (1) (1) (1) (1) (1)	Largest diff. peak and hole.	0.648 and $-0.503$	C(91)	6540(1)	200(1)	2701(1)	70(1)	
	e·Å <sup>-3</sup>		C(1)	5860(1)	1102(1)	2701(1)	70(1)	
CI(2) = 5009(1) = 1102(1) = 843(1) = 75(100) = 101(100)			Cl(21)	2502(11)	726(15)	2422(10)	101(2)	

Cl(32)

 $U_{ij}$  tensor.

3579(12)

367

<sup>*a*</sup> Least-squares refinement for 25 reflections,  $9.5^{\circ} < \theta < 13^{\circ}$ . <sup>*b*</sup>  $R_{\text{merge}} = \Sigma ||F_o| - \langle |F_o| \rangle / \Sigma |F_o|$ .

# <sup>c</sup> Using neutral scattering factors and anomalous dispersion corrections.<sup>10</sup>



539(16)

2488(10)

111(4)

tapering of the cavities and the twist in the molecules. These differences are, however, a result of crystal packing effects and are consistent with the flexibility of the molecules. From binding studies we concluded that clip **1b** is indeed able to bind 1,3 dihydroxy benzene, however, with a low association constant ( $60 \text{ M}^{-1}$ ). These data suggest that the methoxy groups of **1a** are indeed playing an important role in blocking the cavity for the binding of aromatic substrates, although, other effects are likely to be involved as well. Further studies to confirm this hypothesis will be reported elsewhere.

### Bosman, Smits, de Gelder, Reek, and Nolte

- Reek, J.N.H.; Elemans, J.A.A.W.; Rowan, A.W.; Nolte, R.J.M. Submitted to JOC.
- 3. Sijbesma, R.P.; Kentgens, A.P.M.; Lutz, E.T.G.; van der Maas, J.H.; Nolte, R.J.M. J. Am. Chem. Soc. 1993, 115, 8999.
- 4. Gosling, P.A.; Recl. Trav. Chim. Pays-bas. 1993, 112, 404.
- North, A.C.T.; Philips, D.C; Matthews, F.S. Acta Crystallogr. 1968, A24, 351.
- 6. Sijbesma, R.P.; Bosman, W.P.; Nolte, R.J.M. J. Chem. Soc. Commun. 1991, 885.
- Beurskens, P.T.; Beurskens, G.; Strumpel, M.; Nordman, C.E. Patterson and Pattersons; Clarendon Press: Oxford, 1987; pp. 356–367.
- Beurskens, P.T.; Admiraal, G.; Beurskens, G.; Bosman, W.P.; Garciá-Granda, S.; Gould, R.O.; Smits, J.M.M.; Smykalla, C. The DIRDIF program system: Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1992.

### References

- 1a. Coolen, H.K.A.C.; van Leeuwen, P.W.N.M.; Nolte, R.J.M. Angewante. Chem. 1992, 31, 905.
- 1b. Coolen, H.K.A.C.; van Leeuwen, P.W.N.M.; Nolte, R.J.M. JACS 1995, 117, 11906.
- 9. Sheldrick, C:M. SHELXL-93: Program for the refinement of crystal structures; University of Göttingen: Germany, 1993.
- 10. International Tables for X-ray Crystallography Vol. IV, Kynoch Press: Birmingham, UK, 1974; pp. 99, 149.
- 11. Spek, A.L. ORTEP, part of PLATON.13
- 12. Motherwell, W.D.S. GEOM: A program for Geometrical Calculation; University of Cambridge: England, 1976,
- 13. Spek, A.L. Acta Crystallogr. 1990. A46, C34.

