

REVIEW

## Push-pull alkenes: structure and $\pi$ -electron distribution \*

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*Abstract:* Push-pull alkenes are substituted alkenes with one or two electron-donating substituents on one end of C=C double bond and with one or two electron-accepting substituents at the other end. Allowance for  $\pi$ -electron delocalization leads to the central C=C double bond becoming ever more polarized and with rising push-pull character, the  $\pi$ -bond order of this double bond is reduced and, conversely, the corresponding  $\pi$ -bond orders of the C–Don and C–Acc bonds are accordingly increased. This *push-pull effect* is of decisive influence on both the dynamic behavior and the chemical reactivity of this class of compounds and thus it is of considerable interest to both determine and to quantify the inherent *push-pull effect*. Previously, the barriers to rotation about the C=C, C–Don and/or C–Acc partial double bonds ( $\Delta G^\ddagger$ , as determined by dynamic NMR spectroscopy) or the  $^{13}\text{C}$  chemical shift difference of the polarized C=C partial double bond ( $\Delta\delta_{\text{C=C}}$ ) were employed for this purpose. However, these parameters can have serious limitations, viz. the barriers can be immeasurable on the NMR timescale (either by being too high or too low; heavily-biased conformers are present, etc.) or  $\Delta\delta_{\text{C=C}}$  behaves in a non-additive manner with respect to the combination of the four substituents. Hence, a general parameter to quantify the *push-pull effect* is not yet available. *Ab initio* MO calculations on a collection of compounds, together with NBO analysis, provided valuable information on the structure, bond energies, electron occupancies and bonding/antibonding interactions. In addition to  $\Delta G^\ddagger_{\text{C=C}}$  (either experimentally determined or theoretically calculated) and  $\Delta\delta_{\text{C=C}}$ , the bond length of the C=C partial double bond was also examined and it proved to be a reliable parameter to quantify the *push-pull effect*. Equally so, the quotient of the occupation numbers of the antibonding and bonding  $\pi$  orbitals of the central C=C partial double bond ( $\pi^*_{\text{C=C}}/\pi_{\text{C=C}}$ ) could also be employed for this purpose.

*Keywords:* push-pull alkenes, barriers to rotation,  $^{13}\text{C}$  chemical shift differences, *ab initio* MO calculations, NBO analysis, quantification of the *push-pull effect*.

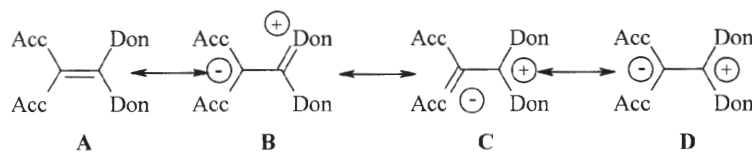
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## 1. INTRODUCTION

The  $\pi$ -bond order of ethylene is *ca.* 1, however, substituents, due either to their inductive or mesomeric effects, can increase or decrease, respectively, the double bond character. In this respect, push-pull alkenes are of special interest as they have 1 or 2 electron donating substituents on the one carbon atom together with 1 or 2 electron withdrawing substituents on the second carbon atom. Due to the contradictory character of the substituents, the olefinic C=C double bond order is reduced on the behalf of



Scheme 1.

## Estimation of the barrier to rotation

- Approximation at the coalescence temperature  $T_c$

$$k = \kappa \left( \frac{k_B T}{h} \right) e^{-\frac{\Delta G^\ddagger}{RT}} = \kappa \left( \frac{k_B T}{h} \right) e^{-\frac{\Delta H^\ddagger}{RT}} e^{-\frac{\Delta S^\ddagger}{R}}$$

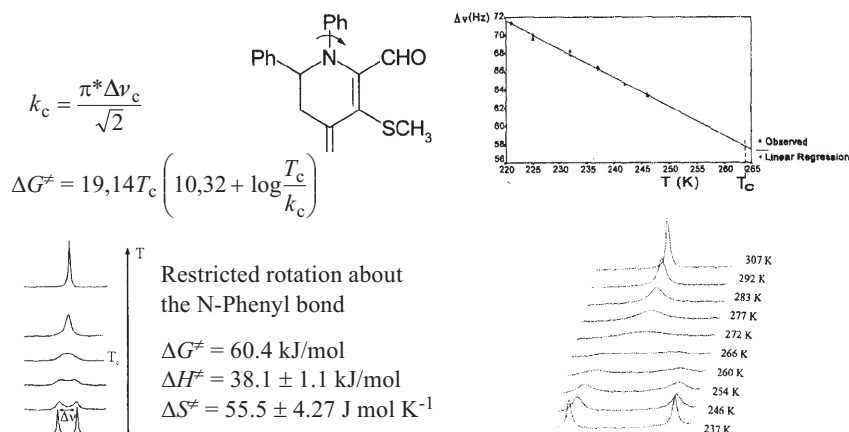


Fig. 1. Estimation of rotational barriers by (i) approximation at the coalescence temperature  $T_c/\text{K}$  and (ii) by complete line shape analysis.

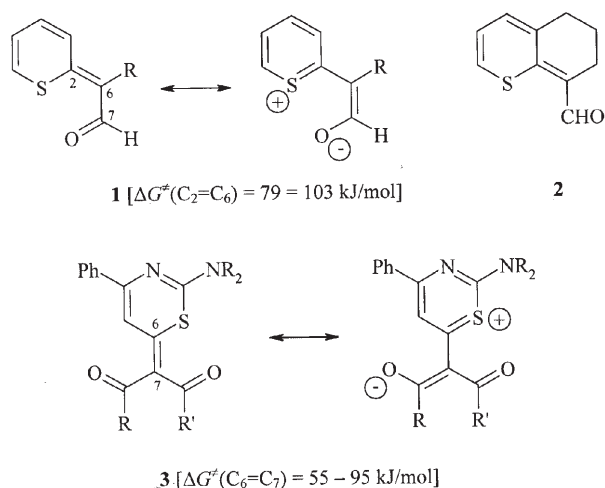
the increased bond orders of the bonds between the two olefinic carbon atoms and their respective electron donor and acceptor substituents. This effect is readily apparent by the restricted rotations about the C–Don and C–Acc partial double bonds (depictions **B** and **C** in Scheme 1) which can be studied quantitatively by dynamic NMR spectroscopy. For a feasible experimental examination of the dynamic behavior of the central olefinic C=C double bond (depiction **A**), better represented by a partial double bond (depiction **D**), the presence of two electron acceptor substituents and at least one donor substituent is necessary.<sup>1</sup> The barrier to rotation ( $\Delta G^\ddagger$ ) about this C=C double bond can be readily employed as a measure of the push-pull character of the alkene.<sup>1,2</sup> Rotational barriers can be measured at or near the coalescence temperature of the dynamic rotational process, or further afield by complete line shape analysis (Fig. 1).<sup>1–4</sup> 2D EXSY NMR experiments have also been employed for quantifying this process.<sup>5</sup>

However, the dynamic NMR window is rather small (*ca.* 30–100 kJ/mol, depending on the available NMR equipment)<sup>6</sup> and often, even for cases expected within this range, the rotational barrier cannot be determined due to heavily-biased conformers either due to electronic or steric effects, or structural peculiarities such as ring-closed systems or symmetry relationships. As a result there have been several proposals to replace the barrier to rotation as a quantitative measure of the *push-pull effect*. In this context, the classification of push-pull alkenes according to the number and character of substituents present and some representative and interesting conclusions will be reported in this micro review.

## 2. QUANTIFICATION OF THE *PUSH-PULL EFFECT*

### 2.1. Barrier to rotation about the partial C=C double bond

The static and dynamic stereochemistry of push-pull alkenes published up to 1983 has been reviewed by Sandström;<sup>1</sup> subsequent literature on this topic has



Scheme 2.

since been covered in our last relevant paper.<sup>7</sup> As already mentioned, two acceptor and at least one donor substituent are required to attain a barrier to rotation measurable on the NMR timescale and in this respect, NR<sub>2</sub> alone as the donor proved most effective,<sup>1</sup> OR as a single donor was determined at the limit<sup>8</sup> [*e.g.*, MeCOO(MeOOC)C=C(Me)OMe,  $\Delta G^\ddagger = 107.6$  kJ/mol], but SR was at least 7.5 kJ/mol higher than this and the restricted C=C rotation could not be adequately measured<sup>9</sup> [MeCOO(MeOOC)C=C(Me)SMe,  $\Delta G^\ddagger > 115.2$  kJ/mol]. The introduction of a second donor reduces the barrier to C=C rotation sufficiently and a broad structural collection has been examined.<sup>1,7</sup> The smallest barriers, *ca.* 40 kJ/mol, were found when two amino substituents were present, *e.g.*, PhC(O,S)(CN)C=C(NR<sub>2</sub>)<sub>2</sub>.<sup>1,2,7</sup>

Another case for low barriers to C=C rotation – but still measurable on the NMR timescale – is when both ground states (GS) and transition states (TS) are stabilized by pseudoaromatic structures, similar to the effects observed in various fulvenes.<sup>1</sup> In this regard, we studied a number of formylmethylene thiopyranes **1** and thiazine derivatives of Meldrum's acid **3** (Scheme 2).<sup>10,11</sup> In each case, besides  $\Delta G^\ddagger_{C=C}$ , another barrier to rotation was also obtained [ $\Delta G^\ddagger(C_6-C_7)$  in **1** and  $\Delta G^\ddagger(C_2-N)$  in **3**] and in general the C=C barrier to rotation was the larger of the two.<sup>10,11</sup> The differentiation between the two barriers was straightforward in **3** as different sites allowed for following the line shape, but the distinction was difficult in the case of **1** where only the line shape variation of the aldehyde proton could be followed. Finally, we succeeded synthetically and studied the ring-closed derivative **2** and, by application of LIS reagents, assigned the isomers/conformers that were present.<sup>10</sup>

## 2.2. <sup>13</sup>C Chemical shift differences of the olefinic carbon atoms

The practical application of the barrier to C=C rotation as a measure of the *push-pull effect* is limited to the types of compounds mentioned above. The zwit-

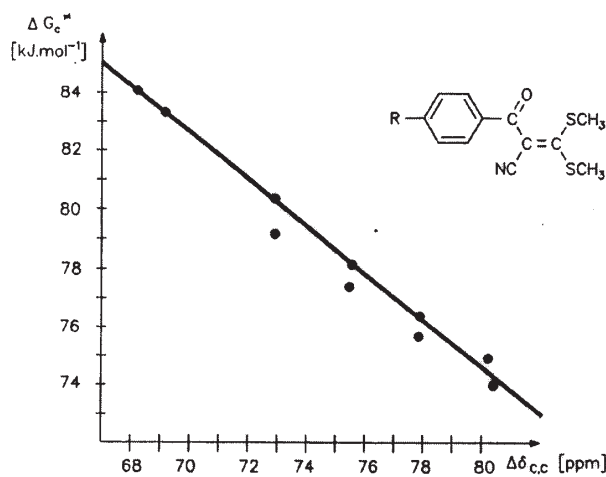


Fig. 2. Linear correlation of the barrier to restricted rotation about the central push-pull partial C=C double bond  $\Delta G^\ddagger_{C=C}$  with the <sup>13</sup>C chemical shift difference  $\Delta\delta_{C=C}$  of the two carbon atoms.

terionic structure (depiction **D** in Scheme 1) of these compounds was confirmed experimentally quite recently by very low-temperature X-ray diffraction analysis of the push-pull alkene 3-(1,3-diisopropyl-2-imidazolidinylidene)-2,4-pentanedione.<sup>12</sup> However, the *push-pull effect* is already present if only one donor substituent and one acceptor substituent are attached to the two ends of ethylene; an indication of this comes from the restricted rotations of the donor and acceptor substituents (depictions **B** and **C** in Scheme 1).<sup>13</sup> This strong polarization of the double bond is also readily discernible by <sup>13</sup>C-NMR due to the extreme low-field position of the olefinic carbon on the donor side and the contrastingly high-field position of the carbon atom on the acceptor side of the push-pull alkene (**D**).<sup>2</sup> Therefore, in addition to the barrier to rotation ( $\Delta G^\ddagger$ ) about the partial C=C double bond, the chemical shift difference ( $\Delta\delta_{\text{C}=\text{C}}$ ) of the two sp<sup>2</sup>-hybridized carbons constituting the double bond have also been employed to quantify the *push-pull effect*. If the compounds compared are rather similar, *e.g.*, arylcyanoketene-*S,S*-acetals with varying substitution on the phenyl ring, then  $\Delta G^\ddagger$  and  $\Delta\delta_{\text{C}=\text{C}}$  can be linearly correlated<sup>2</sup> (Fig. 2) and  $\Delta\delta_{\text{C}=\text{C}}$  can even be satisfactorily employed as a substitute for  $\Delta G^\ddagger$  in cases where  $\Delta G^\ddagger$  cannot be determined, *e.g.*, either because it lies outside the bounds set by the NMR timescale<sup>2,14</sup> or because it forms part of a ring.<sup>15,16</sup> The *push-pull effect* has been satisfactorily assessed by both these parameters in various classes of compounds including push-pull alkenes,<sup>17–22</sup> push-pull butadienes,<sup>23</sup> nitroenamines,<sup>24</sup> 1-methyl-4-(2'-methylthiovinyl)pyridinium iodide<sup>25</sup> and push-pull enynes.<sup>26</sup>

Other parameters that have been used to describe the *push-pull effect* include both the bond length and the  $\pi$ -bond order of the central C=C partial double bond. However, only poor correlations for these parameters to the corresponding barrier to rotation have resulted (*e.g.*, qualitative dependence of  $\Delta G^\ddagger_{(\text{C}=\text{C})}$  vs.  $p_{(\text{C}=\text{C})}$  has been reported<sup>27</sup>). This is due to steric hindrance effects, hydrogen bonding and the abilities of the donor and/or acceptor substituents to stabilize/destabilize either the GS or the TS of the restricted rotation.<sup>1</sup> These facts, together with the generally observed non-additivity of the substituent influences on the *push-pull effect*,<sup>14</sup> was the reason that MO calculations of push-pull alkenes at various levels of theory were performed in order to quantify the *push-pull effect* from a theoretical point of view.

### 2.3. Ab initio MO calculations to quantify the push-pull effect

The study of the electronic structure of push-pull diazenes<sup>28</sup> and push-pull dyes containing malononitrile dimer as the electron-acceptor<sup>29</sup> have previously been performed using *ab initio* HF calculations and a 6–31G\* basis set. For the TSs of the push-pull alkenes studied here (Fig. 3), since they have two donor and two acceptor substituents on either side of the central C=C double bond, they are sufficiently polarized to still be tackled by single determinant HF wave functions as the diradical contribution to the electronic structure of the TS is negligible for strongly

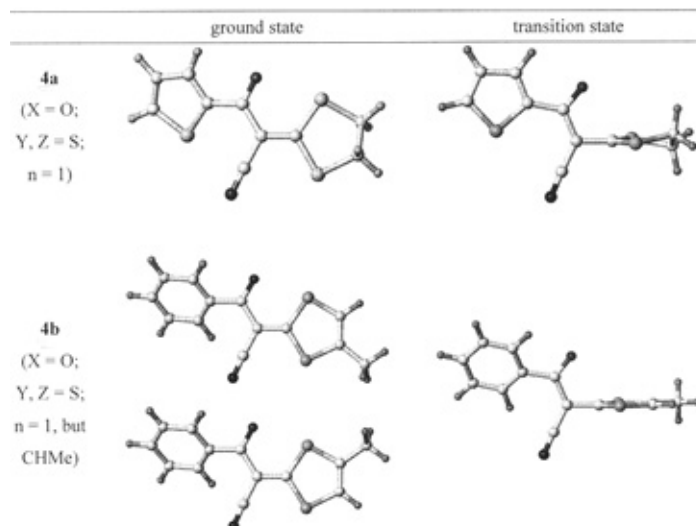
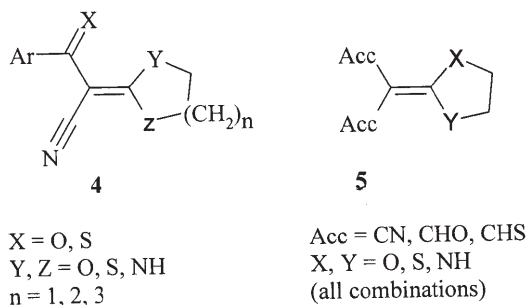


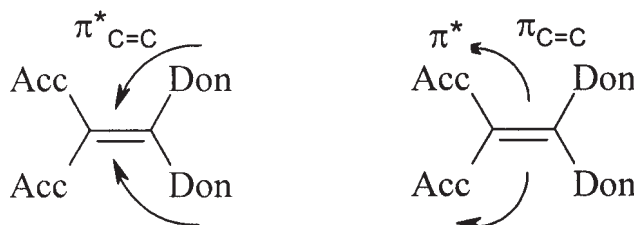
Fig. 3. Depiction of the GSs and TSs for the restricted rotation about the central C=C partial double bond in compounds **4a** and **4b**.

polarized push-pull compounds.<sup>18,19,30,31</sup> However, if the barrier to rotation is too high to be studied by DNMR, then the rotational barrier cannot, in fact, be calculated at the HF level of theory as the system then needs to take into account the diradical nature of the rotational TS and the calculations must be performed using multi-configurational methods.<sup>31a</sup> Alternatively, one can employ an extrapolation procedure which estimates the TS energy ( $\theta = 90^\circ$ ) from the HF energies calculated for conformations which are twisted to some degree ( $\theta < 60^\circ$ ).<sup>32</sup>

In this manner, the barrier to C=C rotation in a variety of push-pull alkenes **4**, as well as model push-pull alkenes **5** (Scheme 3), could be described well theoretically<sup>7</sup> and successful correlation between theoretically calculated and experimental barriers to rotation were obtained in both cases. In this vein, the correlation of the present barriers to C=C rotation with the bond length of the corresponding partial C=C double bond (which was only found to be poor previously<sup>1</sup>) was again examined. Indeed, it was found that the correlation remained poor; however, if com-



Scheme 3.



Scheme 4.

parable compounds only were correlated then fine linear dependences resulted. Due to different levels of steric hindrance and the additional possibility of GS stabilization by hydrogen bonding, different ascents for the linear dependencies were obtained for the various similar groupings.<sup>7</sup> With this encouraging result in hand, Kleinpeter *et al.*<sup>7</sup> studied the model compounds **5** further by NBO analysis.<sup>33</sup> By NBO analysis, the occupation numbers of the various molecular orbitals for both bonds and lone pairs in the compounds were assessed and the different donor/acceptor combinations compared accordingly. The conclusion drawn from these theoretical calculations is that the acceptor activity in push-pull alkenes can be characterized best by the occupancy of the  $\pi$  orbital of the C=C partial double bond and the corresponding donor activity by the occupancy of the  $\pi^*$  orbitals of this same bond. Both parameters are of decisive influence on the corresponding C=C bond length and for this reason the quotient of the two occupancies could be correlated successfully with the C=C bond length (Scheme 4). Indeed, the correlation is very clear: strong donors increase  $\pi^*$  orbital occupation, thereby increasing the bond length, and strong acceptors reduce  $\pi$  orbital occupation thereby also lengthening the C=C partial double bond. It is clearly evident therefore that the length of the central C=C partial double bond of push-pull alkenes is a simple characterizing parameter for the *push-pull effect* and the quotient of the occupancy numbers of the  $\pi$  and  $\pi^*$  orbitals of this bond is another. Actually, it is a much better one, more sensible and much broader in its description, even at the HF/6-31G\* level of theory, of the *push-pull effect* present in the push-pull alkenes studied.<sup>34</sup>

TABLE I. Occupation numbers of the bonding and antibonding  $\pi$  orbitals of the push-pull double bond<sup>a</sup> together with the bond length of the corresponding bond and the <sup>13</sup>C chemical shift difference of the ethylene carbon atoms

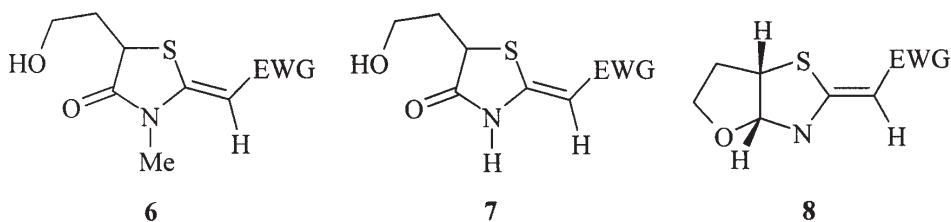
Compounds	EWG	$\Delta\delta_{\text{C=C}}/\text{ppm}$	$\pi_{\text{C=C}}$	$\pi^*_{\text{C=C}}$	$\pi^*/\pi$	bond length $p/\text{\AA}$
<b>6a</b>	COPh	66.0	1.89135	0.2285	0.12081318	1.341
<b>6b</b>	CO <sub>2</sub> Et	69.1	1.90554	0.21892	0.11488607	1.337
<b>6c</b>	CONH(CH <sub>2</sub> )Ph	72.9	1.91414	0.21858	0.11419227	1.336
<b>6d</b>	CN	93.3	1.92029	0.23301	0.12134105	1.337
<b>7a</b>	COPh	66.7	1.88854	0.22905	0.12128417	1.34
<b>7b</b>	CO <sub>2</sub> Et	69.3	1.90487	0.21757	0.11421777	1.335

TABLE I. Continued

Compounds	EWG	$\Delta\delta_{C=C}/\text{ppm}$	$\pi_{C=C}$	$\pi^*_{C=C}$	$\pi^*/\pi$	bond length $p/\text{\AA}$
<b>7c</b>	CONH(CH <sub>2</sub> )Ph	57.8	1.91140	0.21423	0.11208015	1.334
<b>7d</b>	CN	93.6	1.92101	0.22703	0.11818262	1.334
<b>7e</b>	CONHPh	60.5	1.90560	0.22173	0.11635705	1.337
<b>8a</b>	COPh	78.0	1.87071	0.27132	0.14503584	1.352
<b>8b</b>	CO <sub>2</sub> Et	83.3	1.89226	0.25734	0.13599611	1.347
<b>8c</b>	CONH(CH <sub>2</sub> )Ph	83.8	1.90386	0.25097	0.13182167	1.345
<b>8d</b>	CN	105.0	1.91628	0.25898	0.13514726	1.344

<sup>a</sup> Quantum chemical calculations were performed on SGI Octane R12000 and SGI Origin workstations using the *Gaussian 98* software package.<sup>47</sup> The molecules were optimized at different levels of theory using the keyword *opt*, optimization of TSs of the rotation about central double bond using *opt = ts* and *calcfc*. Chemical shieldings were calculated at different levels of theory using the GIAO method and referenced to TMS shielding values (calculated at the same level of theory) to obtain chemical shifts. The *NBO 5.0* population analysis<sup>48</sup> was implemented by linking to the *Gaussian 98* program package<sup>47</sup> with the keywords *nlmo* for NLMO analysis and *print* for graphical evaluation. NRT analysis was performed within the *NBO 5.0* population analysis with *nrt* and *nrtthr = 10*. Results were portrayed using the program *SYBYL*.<sup>49</sup>

As a further example, compounds **6–8** (Scheme 5) were calculated<sup>35</sup> and in Table I both the theoretically calculated C=C bond lengths ( $p_{C=C}$ ) and the  $\pi^*_{C=C}/\pi_{C=C}$



Scheme 5.

quotients are given together with the experimental <sup>13</sup>C chemical shift differences ( $\Delta\delta_{C=C}$ ). The barriers to rotation for **6–8** could not be experimentally measured and, in any case, at this level of theory are also too imprecise.<sup>7</sup> The results remarkably corroborate both the  $\pi^*_{C=C}/\pi_{C=C}$  quotient and the bond length to be very amenable to describing the *push-pull effect* present in compounds **6–8** and the linear correlation obtained is presented in Fig. 4. The <sup>13</sup>C chemical shift differences ( $\Delta\delta_{C=C}$ ) correlated neither with the bond lengths nor the  $\pi^*_{C=C}/\pi_{C=C}$  quotients and thus this parameter is useful only in very rare circumstances.<sup>2</sup> But nonetheless, both the bond length and the  $\pi^*_{C=C}/\pi_{C=C}$  quotient are sensitive, particularly useful parameters to characterize the push-pull character of alkenes.

### 3. THE PUSH-PULL EFFECT

The electron density distribution  $\rho(r)$  of a push-pull alkene with two donor and two acceptor substituents was recently determined by low-temperature (21 K), high-re-



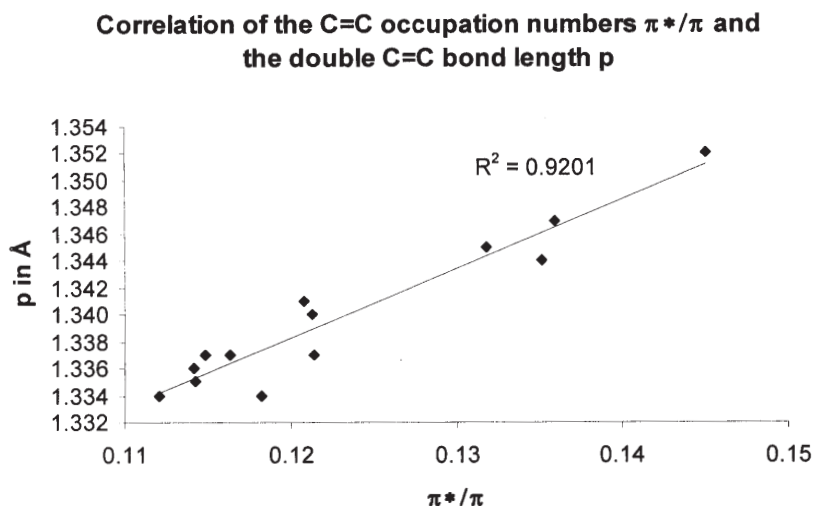


Fig. 4. Linear dependency of the bond length of the push-pull partial double bond and the quotient  $\pi^*_{C=C}/\pi_{C=C}$  in compounds 6–8.

solution X-ray diffraction analysis<sup>12</sup> and, as a result, the tetrasubstituted ethylene can appropriately be described as a zwitterion (depiction **D** in Scheme 1) with a large degree of charge transfer from the donor to the acceptor substituents. Additionally, large molecular dipole and quadrupole moments were also obtained.<sup>12</sup> The topological analysis of  $\rho(r)$  revealed that the olefinic double bond is characterized by unusual properties in comparison with standard alkenes: the partial double bond bore close resemblance to a typical single bond interspacing two conjugated double bonds, although the structure implies a low degree of conjugation between the donor and acceptor substituents.<sup>12</sup> This remarkable polarization of push-pull alkenes leads to special reactivity with nucleophilic or electrophilic reagents,<sup>23b</sup> *e.g.*, the substitution of a donor group by a nucleophile is possible only if the latter is able to better stabilize the partial positive charge, induced by the acceptor substituents present, than the former donor substituent. This reactivity behavior and further peculiarities are very characteristic for the *push-pull effect* present in the tetrasubstituted ethylene studied.<sup>36</sup>

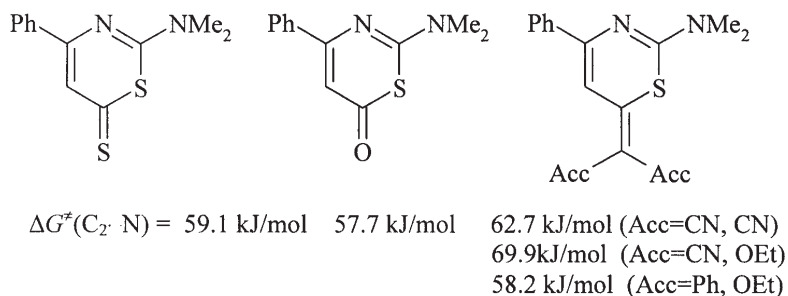
The *push-pull effect* is closely associated with the unusual properties of this class of compounds. Aside from large molecular dipoles, extremely high hyperpolarizabilities<sup>30,37–40</sup> and strong intramolecular charge-transfer absorption bands have also been measured.<sup>41</sup> On the whole, these properties render push-pull alkenes to be of great promise as materials for non-linear optical devices.<sup>37</sup> Here the required high first-order molecular hyperpolarizabilities [ $\beta(-2\omega, \omega, \omega)$  for second-order processes] proved to be dependent on the optimal donor/acceptor combination at the chromophore (in other words, on the *push-pull effect*). At present, there is an insufficient understanding of the corresponding effects of the substituents (number, positional isomerism, donor/acceptor strength and combination, preferred conformations and, finally, solution)<sup>42</sup> and more work is required be-

cause in this respect, there is generally only a singular combination of substituents that is most effective and the reason for this is not yet understood.

#### 4. PECULIARITIES OF PUSH-PULL ALKENES

##### 4.1. The pseudochalcogeno analogy principle

In the dynamic NMR study of compounds **3** (see Scheme 2), in addition to rotation about the C=C double bond, the barrier to rotation about the exocyclic partial C–N double bond was also studied. The values of  $\Delta G^\ddagger$  obtained for this latter rotation were compared with the corresponding barriers in their chalcogeno analogs (Scheme 6) and they were found to be of approximately the same size.<sup>11</sup> This observation suggests that there are very similar electronic effects for carbonyl, thiocarbonyl and the =C(Acc)<sub>2</sub> analogs present in compounds **3**, this is in line with the *pseudochalcogeno analogy principle*.<sup>43</sup> Consequently, the generality of the *pseudochalcogeno analogy principle*, which has been used successfully for the estimation of the reactivity of relevant compounds in partly anomalous reactions,<sup>43</sup> is hereby remarkably corroborated from another point of view.



Scheme 6. Pseudochalcogeno analogy principle.

The push-pull characters of compounds **3** have previously been assessed by the C=C barriers to rotation and the dependencies on the =C(Acc)<sub>2</sub> substituents were well understood by way of excellent correlations of  $\Delta G^\ddagger$  to the  $\sigma_p^-$  constants of the substituents on the acceptor moieties.<sup>11</sup> However, the influence of steric twist and/or the position of conformational equilibria (*E,E*, *E,Z* and *Z,Z* conformers) remained unclear. For this reason, compounds **3a** and **3b** (Scheme 7) were *ab initio* MO calculated and the various conformers compared energetically and the influence of the anisotropic effect of the carbonyl group on the <sup>1</sup>H chemical shift of H-5 determined quantitatively by *ab initio* calculation.<sup>44</sup> The following results were obtained:

(i) The *Z/Z* conformer proved to be the preferred one (see Fig. 5); the C=O *syn* to the ring sulfur is in-plane (polar interactions, see above) but the carbonyl group *syn* to H-5, however (obviously due to steric hindrance), was found to be strongly twisted away from the plane of resonance (dihedral angle  $\theta = 51^\circ$ ).

(ii) Energetically, the two *E/Z* conformers come next with respect to stability; the conformer with C=O *syn* to the ring sulfur was slightly less stable.

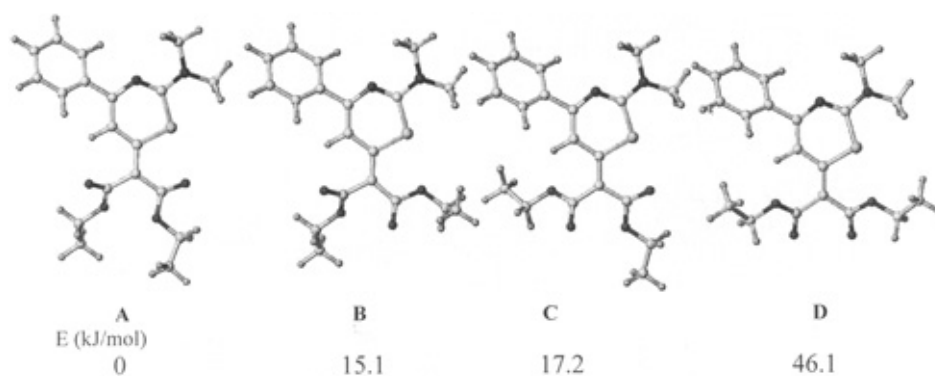
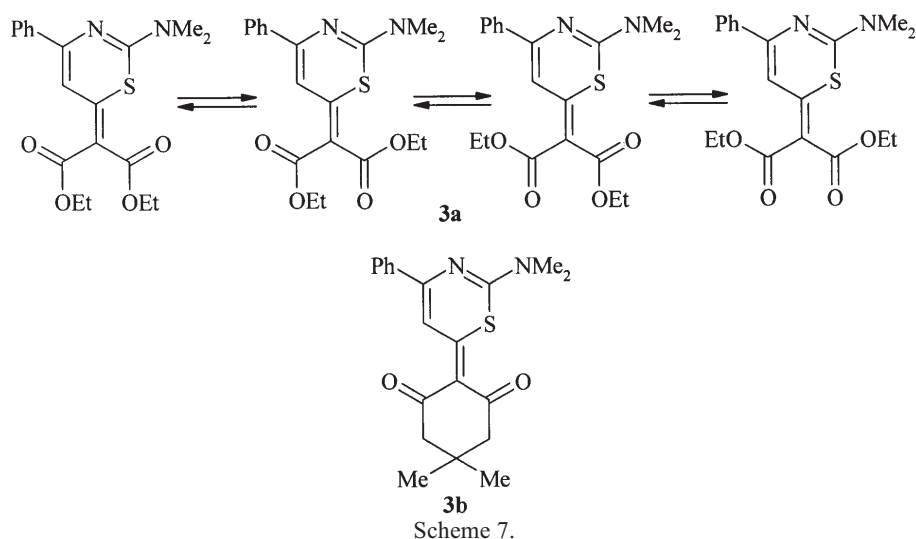


Fig. 5. Preferred conformers of **3a** together with their relative stabilities.

(iii) The *E/E* conformer was the least stable conformer by 46 kJ/mol. Obviously repulsion between the ester  $sp^3$  oxygen lone pairs and the lone pairs at the ring sulfur destabilize this conformation.

(iv) For the anisotropic effect of the carbonyl group in **3b**<sup>44</sup> which is fixed in this Meldrum's acid derivative, Fig. 6 clearly visualizes the position of H-5 in the shielding zone of the carbonyl anisotropy (a shielding of  $-0.3$  ppm was theoretically calculated). This is in strong opposition to the experimental finding:  $\Delta\delta = +1.83$  ppm (low-field shift). Thus, the strong deshielding of H-5 in **3b** is not the result of carbonyl anisotropy as might be anticipated, but is a result of steric compression. This is another example of the overestimation of anisotropic effects in tandem with an underestimation of steric effects in  $^1\text{H}$  NMR spectroscopy, as has been demonstrated in the comparison of phenanthrene and ethynylphenanthrene where the same discrepancy was encountered.<sup>45</sup>

#### 4.2. Thioamide/vinylogous thioamide “resonance”

In a previous study,<sup>46</sup> the stereochemistry and dynamic behavior of a number of aminosubstituted thioacrylamides **9** (Scheme 8) were examined where it was de-

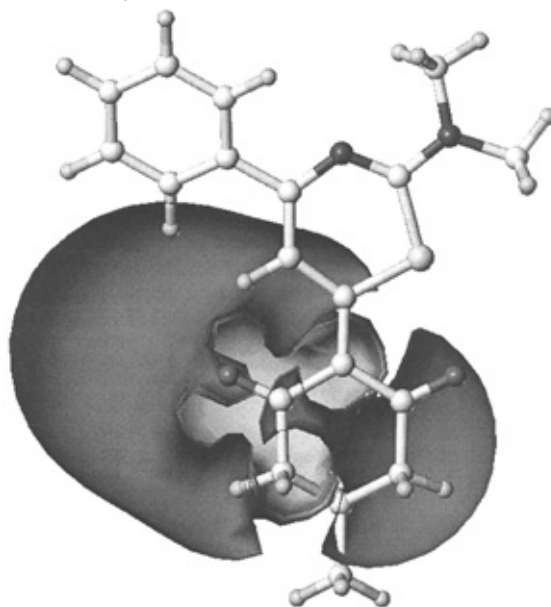


Fig. 6. Anisotropic effect of the carbonyl group *syn* to H-5 in **3b** as calculated by NICS analysis (shielding surface at  $-0.1$  ppm, dark area; deshielding surface at  $+0.1$  ppm, light area); the chemical shieldings within the environment of the molecules were calculated as described in reference 44a. Within the *SYBYL* contour file, the anisotropy effects of the carbonyl groups under investigation were visualized as iso-chemical-shielding surfaces (ICSS) enabling appreciation of the spatial extension of the anisotropy to particular protons.

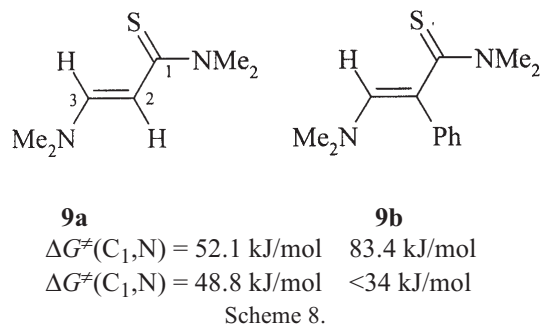
termined that the compounds prefer *s-trans/s-cis* conformation/configurations and, interestingly, display similar barriers to rotation about the two partial C–N double bonds, *i.e.*, the same amount of thioamide and vinylogous thioamide “resonance” was concluded. If, however, C-2 is substituted by a voluminous substituent (phenyl in **9b**), then the entire resonance is restricted to the thioamide moiety, though this results in the C<sub>3</sub>–N barrier to rotation no longer being measurable on the NMR timescale (Scheme 8). Both structures **9a** and **9b** were *ab initio* MO calculated (there was no experimental proof for any steric twist except for the effect on the two barriers to rotation)<sup>46</sup> and, in addition, the occupation numbers of the various molecular orbitals of both the bonds and lone pairs in the compounds were assessed by NBO analysis.<sup>33</sup> The GSs of **9a** and **9b** are portrayed in Fig. 7 and the results of the NBO analysis are collected in Table II. These results provide two points of note:

(i) Structural expectations<sup>46</sup> proved to be well-founded. In **9a** the entire molecule is completely flat thereby affording the opportunity of full “resonance” within

TABLE II. Occupation of characterizing bonding/antibonding and N lone pair orbitals together with related bond lengths in **9**

Compound	$\Pi(C_2=C_3)$	$\pi^*(C_2=S_3)$	$\pi^*(C_1=S)$	LP N-3	LP N-1	$\Delta G_c^\ddagger$ (C <sub>1</sub> -N)	$\Delta G_c^\ddagger$ (C <sub>3</sub> -N)	$p(C_3-N)$	$p(C_2-C_3)$	$p(C_1-C_2)$	$p(C_1-N)$	$p(C_1-S)$
<b>9a</b>	1.85463	0.20511	0.42210	1.73049	1.68527	59.5 <sup>a</sup> /53.2 <sup>b</sup>	55.3 <sup>a</sup> /51.5 <sup>b</sup>	1.344	1.351	1.455	1.341	1.698
<b>9b</b>	1.91418	0.11959	0.25990	1.85046	1.65584	<34 <sup>a</sup> /19.7 <sup>b</sup>	83.4 <sup>a</sup> /45.6 <sup>b</sup>	1.392	1.336	1.501	1.332	1.677

<sup>a</sup>Experimental values (kJ/mol). <sup>b</sup>Calculated values (kJ/mol).



the molecule. In **9b**, steric hindrance precludes the 3-NMe<sub>2</sub> moiety from “resonance” and thereby limits the contribution of the “resonance” to the thioamide fragment, which nevertheless remains in-plane for conjugation.

(ii) The effects on the barriers to rotation can be derived from the corresponding occupation differences in the relevant molecular orbitals (see Table II). For one aspect the results were fruitful: the reduced barrier about C<sub>3</sub>–N is correctly reproduced by the calculations of the barrier to rotation as well as the corresponding orbital occupations and relevant bond lengths. The barrier is strongly reduced and correspondingly, the occupation of N-3 is increased and its donation of  $\pi$ -electron density into

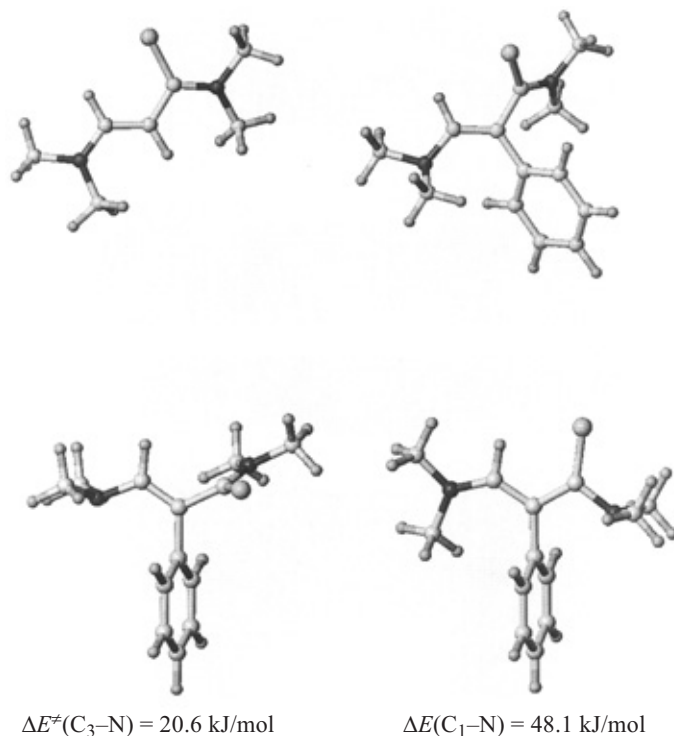


Fig. 7. Depiction of the GS of **9a** and both the GS and TSs for restricted rotations about partial C–N double bonds in **9b**; barriers to rotation are also given.

the conjugated systems lowered. The C<sub>3</sub>-N bond length is increased accordingly. On the other hand, both the corresponding barrier to C<sub>1</sub>-N rotation is calculated to be far too low and moreover, the occupation of the relevant orbitals do not corroborate the present experimental findings; only the occupation of N-1 lone pair is reduced, as expected, and the corresponding C<sub>1</sub>-N bond length shortened.

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## ИЗВОД

## PUSH-PULL АЛКЕНИ: СТРУКТУРА И π-ЕЛЕКТРОНСКА РАСПОДЕЛА

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Push-pull алкени су супституисани алкени са једном или две електрон-донорске групе на једном крају C=C везе, и са једном или две електрон-привлачне групе на другом крају. Због π-електронске делокализације централна C=C веза постаје поларизованија и са повећањем push-pull карактера, ред π-везе се смањује, а супротно томе, одговарајући ред π-веза C-Дон и C-Асс се повећава. Овај *push-pull ефекат* битно утиче, како на динамичко понашање, тако и на хемијску реактивност ове класе једињења и стога је од посебног интереса одређивање и квантификовање поменутог ефекта. У ту сврху одређиване су ротационе баријере за C=C, C-Дон и/или C-Асс везе, које поседују делимични карактер двоструких веза (на бази  $\Delta G^\ddagger$  вредности добивених применом динамичке NMR спектроскопије), или разлике <sup>13</sup>C хемијских помака поларизоване двоструке везе ( $\Delta\delta_{C=C}$ ). Међутим, ови параметри имају озбиљна ограничења, јер у неким случајевима баријере (уколико су сувише високе или ниске) не могу бити одређене на бази NMR временске скале, или се добивају неадитивне  $\Delta\delta_{C=C}$  вредности када се узимају у обзир могуће комбинације четири супституента. Према томе, општи параметер за квантификовање *push-pull ефекта* још није доступан. *Ab initio* MO израчунавања примењена на серији једињења, у комбинацији са NBO анализом, дала су корисне информације које се тичу структуре, енергије веза, електронске заступљености и везивних/антивезивних интеракција. Осим  $\Delta G^\ddagger_{C=C}$  вредности (било експериментално одређених или теоријски израчунатих) и  $\Delta\delta_{C=C}$ , дужина парцијалних C=C веза је такође проучавана и на основу тога је доказано да она представља поуздан параметар за квантификовање *push-pull ефекта*. Слично томе, однос бројева заузетости антивезивних и везивних π орбитала централне парцијалне C=C везе ( $\pi^*_{C=C}/\pi_{C=C}$ ) може такође бити искоришћен у ту сврху.

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