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Electronic State of Push−Pull Alkenes: An Experimental Dynamic NMR and Theoretical ab Initio MO Study

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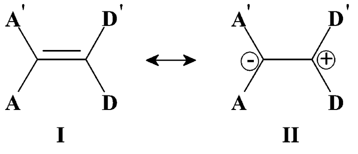
The ^1H and ^{13}C NMR spectra of a number of push−pull alkenes were recorded and the ^{13}C chemical shifts calculated employing the GIAO perturbation method. Of the various levels of theory tried, MP2 calculations with a triple-ζ-valence basis set were found to be the most effective for providing reliable results. The effect of the solvent was also considered but only by single-point calculations. Generally, the agreement between the experimental and theoretically calculated ^{13}C chemical shifts was good with only the carbons of the carbonyl, thiocarbonyl, and cyano groups deviating significantly. The substituents on the different sides of the central C═C partial double bond were classified qualitatively with respect to their donor (S,S < S,N < N,N) and acceptor properties ($C\equiv N$ < C═O < C═S) and according to the ring size on the donor side (6 < 7 < 5). The geometries of both the ground (GS) and transition states (TS) of the restricted rotation about the central C═C partial double bond were also calculated at the HF and MP2 levels of theory and the free energy differences compared with the barriers to rotation determined experimentally by dynamic NMR spectroscopy. Structural differences between the various push−pull alkenes were reproduced well, but the barriers to rotation were generally overestimated theoretically. Nevertheless, by correlating the barriers to rotation and the length of the central C═C partial double bonds, the push−pull alkenes could be classified with respect to the amount of hydrogen bonding present, the extent of donor−acceptor interactions (the *push−pull effect*), and the level of steric hindrance within the molecules. Finally, by means of NBO analysis of a set of model push−pull alkenes (acceptors: $-C\equiv N$, −CH═O, and −CH═S; donors: S, O, and NH), the occupation numbers of the bonding π orbitals of the central C═C partial double bond were shown to quantitatively describe the acceptor powers of the substituents and the corresponding occupation numbers of the antibonding π^* orbital the donor powers of the substituents. Thus, for the first time an estimation of both the acceptor and the donor properties of the substituents attached to the push−pull double bond have been separately quantified. Furthermore, both the balance between strong donor/weak acceptor substituents (and vice versa) and the additional influences on the barriers to rotation (hydrogen bonding and steric hindrance in the GSs and TSs) could be differentiated.

Introduction

Push−pull alkenes are derivatives of the type DD′C═CAA′ (**I**, Scheme 1) where D and A are electron-donating and electron-accepting functional groups, respectively.[1] These compounds, due to strong π-electron delocalization, are extremely polarized along the central alkenyl double bond and are effectively zwitterionic in structure (**II**). This has been confirmed experimentally quite recently where the electron distribution of the push−pull alkene 3-(1,3-diisopropyl-2-imidazolidinylidene)-2,4-pentanedione was determined by very low-temperature HR-X-ray diffraction analysis, and which indicated the molecule to be zwitterionic.[2]

SCHEME 1



The low barrier to rotation about this essentially partial C═C double bond can be readily determined in many cases by dynamic NMR spectroscopy[1,3] (DNMR) or 2-D EXSY NMR.[4] The strong polarization of the double bond is also readily discernible by ^{13}C NMR due to the extreme deshielded position of the alkenyl carbon on the donor side and the contrastingly shielded position of the

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carbon atom on the acceptor side of the push−pull alkene.[3] Both the barrier to rotation ($\Delta G^{\ddagger}$) about the double bond and the chemical shift difference ($\Delta\delta_{C=C}$) of the two sp^2-hybridized carbons constituting the double bond have been employed to quantify the *push−pull effect*. If the compounds compared are rather similar, e.g., aroylcyanoketene *S*,*S*-acetals with varying substitution on the phenyl ring,[3] then $\Delta G^{\ddagger}$ and $\Delta\delta_{C=C}$ can be linearly correlated[3] and $\Delta\delta_{C=C}$ can even be satisfactorily employed as a substitute for $\Delta G^{\ddagger}$ in cases where $\Delta G^{\ddagger}$ cannot be determined, for example, either because it lies outside the bounds set by the NMR time scale[3,5] or because it forms part of a ring.[6,7] The *push−pull effect* has been satisfactorily assessed by both these parameters in various classes of compounds including push−pull alkenes,[8−13] push−pull butadienes,[14] nitroenamines,[15] 1-methyl-4-(2′-methylthiovinyl)pyridinium iodide,[16] and push−pull enynes.[17] Other parameters that have been used to describe the *push−pull effect* include both the bond length and the π-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 due to steric hindrance, hydrogen bonding, and the abilities of the D and/or A substituents to stabilize/destabilize both the ground state (GS) and the transition state (TS) of the restricted rotation.[1] These facts, together with the generally observed nonaddibility of substituent influences on the *push−pull effect*,[5] encouraged us to extend our study of push−pull alkenes (see Scheme 2). In addition to the DNMR study of the restricted rotation about the C═C partial double bond (within the boundaries set by the NMR time scale), the ab initio MO calculation of the push−pull alkenes at the highest affordable level was the major aim of the present study in order to quantify the *push−pull effect* from a theoretical point of view.

The study of the electronic structure of push−pull diazenes[18] and push−pull dyes containing malononitrile dimer as acceptor[19] have previously been performed using ab initio HF calculations with a 6-31G* basis set. For the TSs of the push−pull alkenes studied here (cf. Scheme 2), 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 transition state is negligible for strongly polarized push−pull compounds.[9,10,20,21] However, if the barrier to rotation is too high to be studied by DNMR, then the rotational barrier cannot then, 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 multiconfigurational methods.[21] Alternatively, one can employ an extrapolation procedure which estimates the TS energy ($\theta = 90°$) from the HF energies calculated for conformations which are twisted to some degree ($\theta < 60°$).[22] For the push−pull compounds **1**−**29** examined here, the HF approach with correlation corrections made at the MP2 level of theory[23,24] was considered sufficient to provide reliable values for the internal rotation about the C(sp^2)−C(sp^2) bond.[21]

Results and Discussion

^{1}H and ^{13}C NMR Spectra. The signals in the ^{1}H NMR spectra of **1**−**29** were generally well dispersed, and consequently, they were easily assigned, as were the aromatic protons of the furanyl, thiophenyl, and phenyl substituents due to their scalar coupling patterns. The endocyclic location of C_9═C_{10} in **5**, **11**, **28**, and **29** was clearly implicated by APT spectra.[25] The corresponding ^{13}C NMR spectra of **1**−**29** were then assigned by HMQC and HMBC spectra.[25] The ipso carbons, C-5, were readily assigned as they displayed geminal C,H connectivities to the adjacent aromatic protons; the ^{13}C chemical shifts of the other quaternary carbons were also assigned via long-range C,H connectivities available from HMBC spectra. In particular, C-4 and C-1 displayed cross-peaks to H-6(6′) and H-9/10, respectively, while C-2 is, due to the *push−pull effect*, positioned at extremely high field (in a few cases long-range C,H couplings to H-6(6′) were also apparent for C-2). The cyano carbon atom C-3 was

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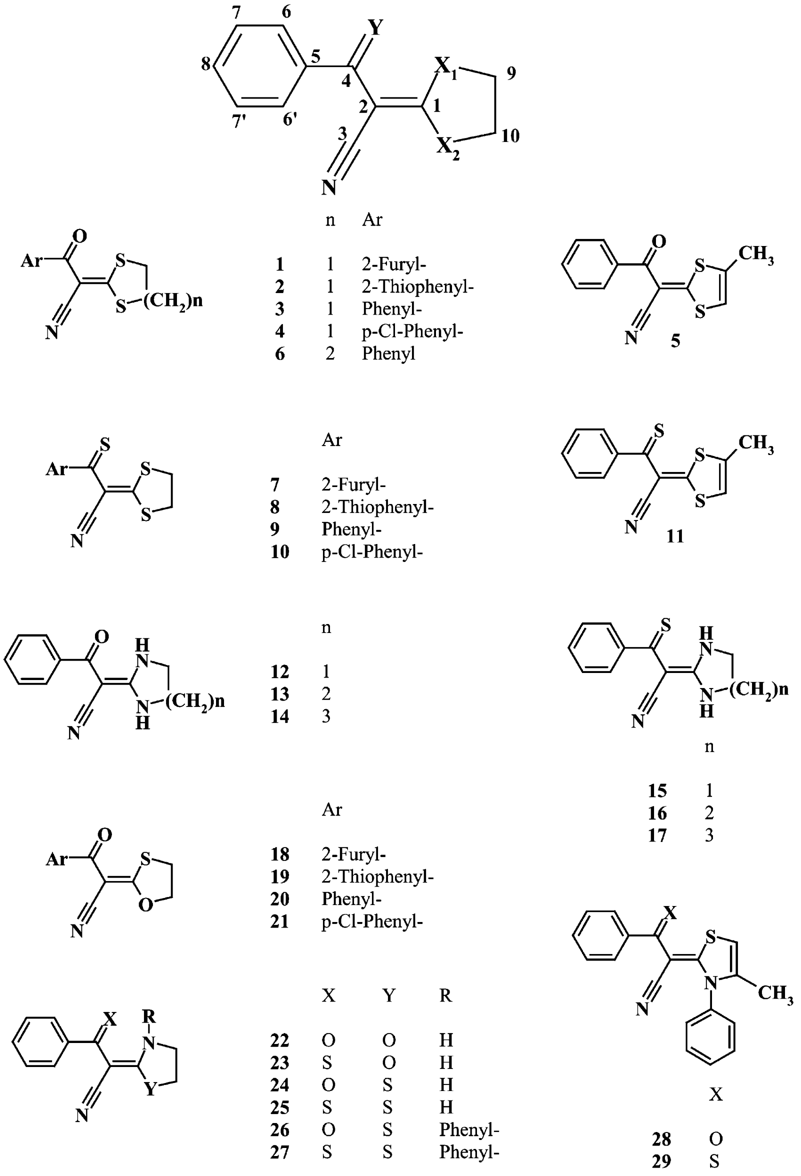
SCHEME 2



	n	Ar
1	1	2-Furyl-
2	1	2-Thiophenyl-
3	1	Phenyl-
4	1	p-Cl-Phenyl-
6	2	Phenyl

5

	Ar
7	2-Furyl-
8	2-Thiophenyl-
9	Phenyl-
10	p-Cl-Phenyl-

11

	n
12	1
13	2
14	3

	n
15	1
16	2
17	3

	Ar
18	2-Furyl-
19	2-Thiophenyl-
20	Phenyl-
21	p-Cl-Phenyl-

	X	Y	R
22	O	O	H
23	S	O	H
24	O	S	H
25	S	S	H
26	O	S	Phenyl-
27	S	S	Phenyl-

	X
28	O
29	S

the only carbon without scalar C,H coupling in **1**–**29**; however, since it resonates in a very narrow range (115–128 ppm) and is quaternary, it is easily assigned. In the push–pull alkenes **26**–**29**, a second phenyl substituent was also present and consequently the proton resonances of these two phenyls strongly overlapped; however, the ^{13}C chemical shifts of the two phenyl substituents could be differentiated using HMQC–TOCSY experiments based on H-6(6′) which was unequivocally assigned via $^3J_{H6(6'),C4}$. The ^{13}C chemical shifts of compounds **1**–**29** are presented in Table S1 in the Supporting Information and the corresponding ^{1}H chemical shifts in Table S2 in the Supporting Information.

The ^{1}H and ^{13}C resonances for all the compounds examined fell well within the typical ranges anticipated; only C-1 and C-2, the carbons of the central C═C partial double bond, were obtained at extreme positions for sp^2-hybridized carbon atoms due to the *push–pull effect* whereby C-1 is strongly deshielded and C-2, on the other hand, is strongly shielded due to the bond polarization (cf. Scheme 1). Employing the bond polarization parameter $\Delta\delta$,[3] the substituents can be ordered with respect to both their acceptor and donor properties as follows:

$$\text{acceptors: C=O > C=S (e.g., } \Delta\delta_{C1,C2} = \text{93.0 ppm in } \mathbf{1} \text{ but 82.6 ppm in } \mathbf{7})$$

$$\text{donors: N,N > S,S (e.g., } \Delta\delta_{C1,C2} = \text{100.4 ppm in } \mathbf{12} \text{ but 89.8 ppm in } \mathbf{3}\text{), etc.}$$

However, a simple correlation to corresponding parameters does not exist[5] as additional effects (hydrogen bonding, steric hindrance in both GSs and TSs, etc.) need to be taken into account (vide infra).

Due to *E*/*Z* isomerism about C_1═C_2, two sets of signals were observed for some of the resonances of **5** and **11** in both the ^{1}H and ^{13}C NMR spectra. In each case, the chemical shift differences in the ^{1}H spectra were rather small, and consequently, differences in scalar couplings were ineffectual for assignment purposes. Unsurprisingly, both NOE difference and 2-D NOESY experiments failed to provide contacts between the two sides of these

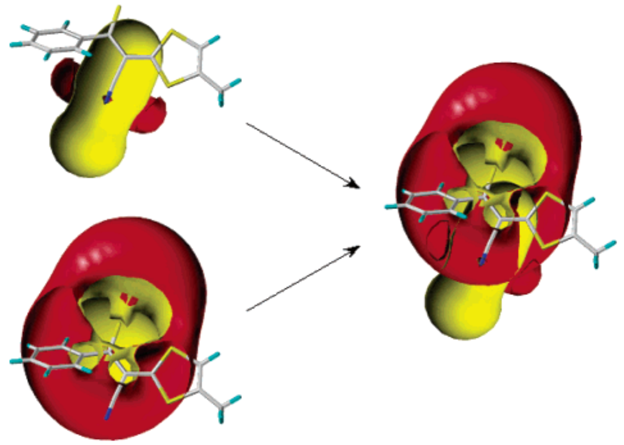


FIGURE 1. Anisotropic effects of the C≡N and C=S groups in **11**: separated (left) and as the combined anisotropic effect (right).

push–pull alkenes, and thus, these experiments were unable to afford assignment of the configurations of the interconverting species. Thus, first resort was made to the calculation of the anisotropic effects of the (thio)-carbonyl and cyano functional groups on the protons on the donor side of the push–pull alkenes to render identification.

Ab Initio MO Calculation of the Anisotropic Effect of C=S and C≡N in 11. The demonstrated effectiveness of the ab initio MO-calculated anisotropic effects for the cyano group in a number of cyanoimino quinoxalines[26] or the oxirane ring in 3-arylidine-1-thioflavan-4-one epoxides[27] to assign the corresponding *E*/*Z* isomers unequivocally (or even of the C–C single bond to differentiate axial and equatorial protons in cyclohexane[28]) prompted us to use these long-range anisotropic effects in these push–pull alkenes to effect solution of the *E*/*Z* isomerism question in compounds **5**, **11**, and **18**–**29**. Compound **11** was selected as an example, and the results are depicted in Figure 1. The anisotropic effect of the cyano group, however, was deemed to be too small (<0.01 ppm on H-10) to differentiate the two isomers. Though the effect of the C=S group on H-10 was calculated to be larger (for *E*, 0.06 ppm; for *Z*, 0.05 ppm), the experimental chemical shift difference of H-10 for the two isomers of **11** is much greater than this and thus it can be concluded that the anisotropic influence of the acceptor-side functional groups on the protons of the donor side is only minor and cannot account for the chemical shift differences. Indeed, the differences in the ^{13}C chemical shifts were observed to be even greater.

That the anisotropic effect calculations are not useless was easily demonstrated by calculation of the ring current effect of the *N*-phenyl moiety on the C-9 methyl protons and H-10 in compounds **28** and **29** in comparison to their corresponding S analogues **5** and **11**, respectively.

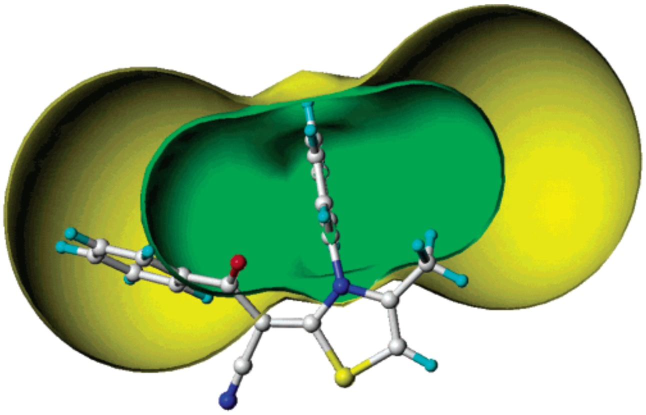


FIGURE 2. Ring current effect of the *N*-phenyl substituent in **28** (green, ICSS at −0.5 ppm; yellow, ICSS at −0.1 ppm).

Due to the anisotropic effect, the C-9 methyl protons were calculated to be shielded by −0.5 ppm and H-10 by −0.01 ppm (see Figure 2). This is precisely the chemical shift difference of the C-9 methyl protons and H-10 between **28** (**29**) and **5** (**11**), proving that the anisotropic influences can be correctly calculated. As previously stated, the anisotropic effects do not account for the Δδ values in the *E*/*Z* isomers; rather, they are dominated by the electronic donor/acceptor substituent effects at the central C=C double bond. Thus, it was left to the calculation of the ^{13}C chemical shifts to render a distinction between the *E* and *Z* isomers.

Theoretical Calculation of the ^{13}C Chemical Shifts in 1–29. The ^{13}C chemical shifts of compounds **1**–**29** were theoretically calculated at the highest level that was affordable, and carefully scrutinized with respect to their correlation with the experimentally determined values, and especially with respect to the assignment of the *E*/*Z* isomers. The chemical shifts were calculated using the GIAO perturbation method,[29–31] the basis for these calculations being high level ab initio MO structures. Because the level of theory is important for good agreement between experimental and theoretical values, both the method (HF, MP2, and B3LYP) and the size of the basis set (3-21G, 6-31G*, 6-311G*, 6-31+G**, and 6-311++G**) were evaluated. The results of the corresponding ab initio calculations, employing compound **20** as a test case, are provided in the Supporting Information. The implication of these preliminary calculations was that the push–pull alkenes **1**–**29** can be sufficiently described by MP2 calculations employing the triple-ζ-split basis set; enlargement to diffuse functions resulted in enormous increases in CPU time but with only slight, indeed negligible, improvements to the results. The agreement (vide infra) between experimental and theoretical calculations was poorest for the carbons of the acceptor functional groups (C=O, C=S, and C≡N) even with the largest basis set tried, 6-311G**, and obviously this means that even this basis set is still insufficient. However, application of a mixed basis set-6-311G** for oxygen and 6-31G* for the rest of **20** led to notable

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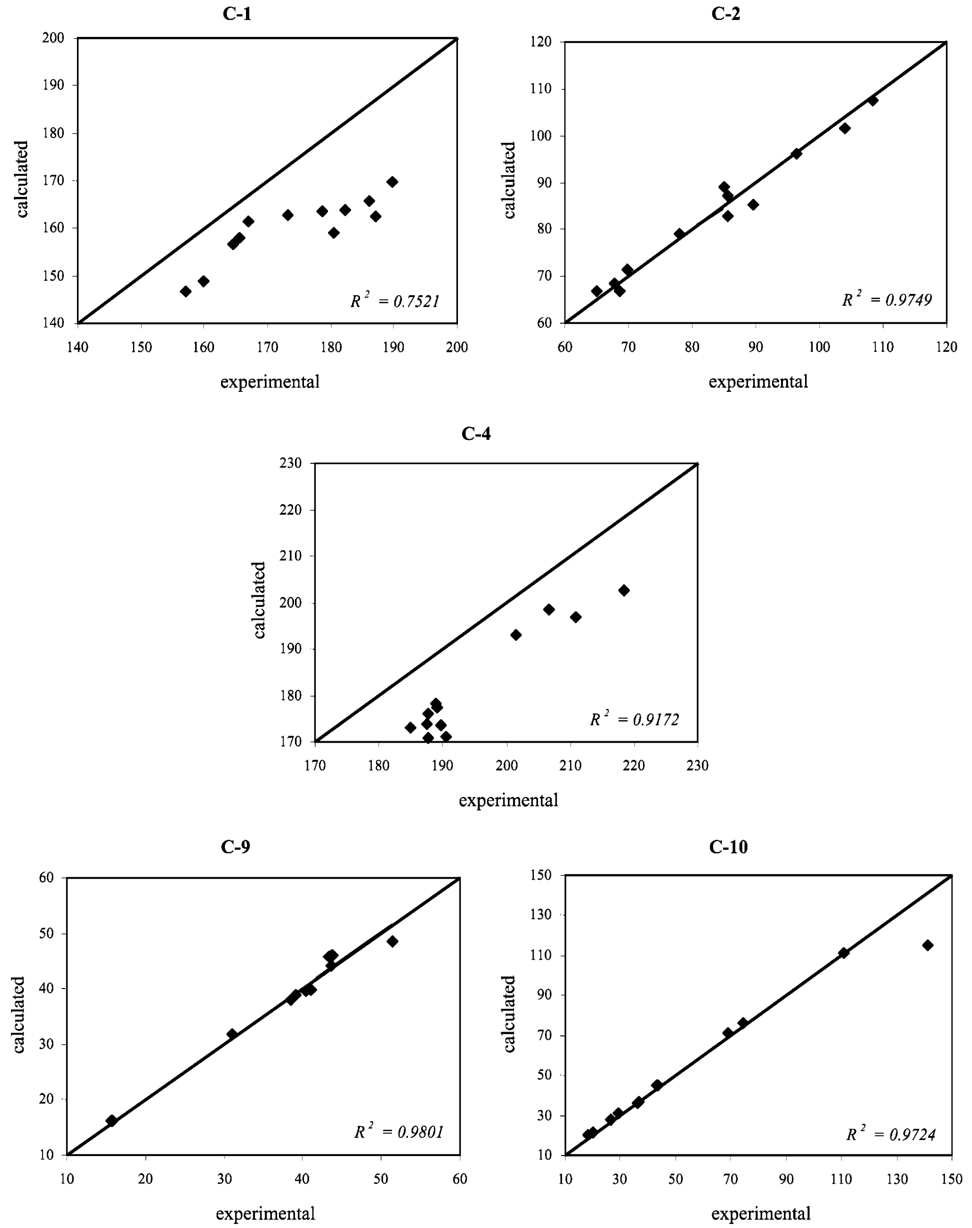

FIGURE 3. Correlation of the experimental and theoretically calculated ^{13}C chemical shifts of the push−pull alkenes **3**, **5**, **9**, **11**−**16**, **20**, **22**, and **24**.

improvements for the calculation of $\delta_{C=O}$ and $\delta_{C\equiv N}$ while leaving the remaining carbons essentially unchanged (see the Supporting Information). Because the influence of the solvent employing the SCI−PCM method[31] cannot be utilized by the GIAO method within the Gaussian 98 program,[32] only gas-phase calculations were employed for this type of calculation. The results of these calculations for **3**, **5**, **9**, **11**−**16**, **20**, **22**, and **24** are presented in Table S3 (Supporting Information) (all compounds **1**−**29** were also calculated at the HF/6-311G** level of theory; see the Supporting Information).

The best agreement between experimental and theoretical ^{13}C chemical shifts of the push−pull relevant carbons were obtained for carbons C-2, C-9, and C-10 (see Figure 3); correlation coefficients better than 0.98 were obtained, and significant deviations from the line of identity do not occur. The calculated values of δ for C-1 and C-4 still correlate with the experimental values, but are overestimated. On the other hand, $\Delta\delta$ values between the different compounds are quite well reproduced (R^2 = 0.74 for C-1 and 0.85 for C-4). Since C-3 shows no correlation whatsoever, it is excluded from consideration for the following conclusions. It is clear though, particularly when based on carbons C-9 and C-10, that sufficient agreement between experimental and calculated values has been achieved to warrant identification of the *E* and *Z* isomers for compounds **5**, **11**, and **18**−**29**.

For compounds **1**−**4** and **6**−**10** with two sulfur atoms within the donor ring moiety, two different ^{13}C signals for C-9 and C-10 were expected and observed, similarly for the ring protons. The difference of the two *E*/*Z* positions (i.e., C-9 and C-10) with respect to thiocarbonyl is ca. 4 ppm. The calculated chemical shift difference of these carbons is in the same range leading readily to the correct assignment of C-9 and C-10 in **1**−**4** and **6**−**10**; C-9, *Z* to C=S, is shielded with respect to C-10.

TABLE 1. Barrier to Rotation, $\Delta G^{\ddagger}$ (kJ mol^{-1}), about the Central C=C Partial Double Bond in Push−Pull Alkenes 1−29

	toluene		CD_2Cl_2 or $C_2D_2Cl_4$		acetone		DMF		DMSO	
	T_C (K)	$\Delta G^{\ddagger}$	T_C (K)	$\Delta G^{\ddagger}$	T_C (K)	$\Delta G^{\ddagger}$	T_C (K)	$\Delta G^{\ddagger}$	T_C (K)	$\Delta G^{\ddagger}$
1			>380	>84.8					[a]	
2−**4**			[a]						[a]	
5			>380	>85.4					>380	>84.9
6			>380	>78.8					>380	>78.4
7			370	93.3			380	85.5	375	87.4
8			390	95.3			390	90.3	380	87.9
9, **10**			[a]						[a]	
11			354	76.6			325	70.2	[b]	
12	360	75.5	345	72.8	295	62.9				
13	345	61.1	315	58.6	288	51.5				
14	330	68.8	345	61.5	298	53.0				
	370	65.5								
15	293	55.1	263	54.2[c]	203[c]	41.6[c]				
			298	52.5[d]	233[d]	41.4[d]				
16	243	41.7	238	41.2	<193					
17	218	45.3	238	41.4	<193					
	258	44.7								
18−**21**			[e]						[e]	
22			[e]				[e]		370	65.7
23			[e]		[e]		[e]			
24			>380	>76.9			330	67.2	335	68.2
							345	64.4	360	67.7
25			345	69.1	288	57.2	263	51.1		
					293	53.8	288	51.0		
26−**29**			[e]		[e]				[e]	

[a] Acetal protons not dispersed. [b] Methyl signal overlapped with solvent. [c] C(9,10)H_2 protons. [d] NH protons. [e] Signals of the second isomer not observed.

In the ^{13}C NMR spectra of the N,N-donor compounds **12**−**17** at room temperature, only one signal is observed for the two ring carbons adjacent to nitrogen. Thus, rotation about the central C_1=C_2 bond is too fast at room temperature to observe the two expected signals. Again, the quantum chemical calculations imply that the more shielded carbon is *Z* to C=S, while the *E*-positioned carbon is deshielded. This provided the assignment of the low-temperature spectra where two signals were observed.

For compounds **26**−**29**, only one set of ^{13}C signals was observed due to the one isomer as the energy difference between the two possible isomers is too large and only the more stable isomer is present. The calculations imply that the chemical shift differences are in the same range as for the compounds discussed above, however, the preferred isomer was assigned based on the calculated energy differences (vide infra).

Barrier to Rotation about the Central C=C Partial Double Bond. In **1**−**29**, two donor and two acceptor substituents are attached to the central double bond, thus, due to the *push*−*pull effect*, the barrier to rotation about this bond, which in alkyl substituted ethylenes is still >230 kJ mol^{-1},[33] is lowered sufficiently to be studied within the range set by the NMR time scale (if steric influences are only minor) and the barrier to rotation can be evaluated by DNMR as free energies of activation ($\Delta G^{\ddagger}$).[34] Due to the different coalescence temperatures (T_c) and solubility of the compounds studied, the DNMR measurements were made in various solvents and the free energies of activation were determined at T_c[34] (in cases of differing populations of the rotamers, the approximation of Shanan-Atidi and Bar-Eli[35] was applied). Both the T_c values and the corresponding barriers to rotation $\Delta G^{\ddagger}$ for compounds **1**−**29** are presented in Table 1, conditions permitting (e.g., strong preference of one isomer, barrier too high or too low, etc.). The following points are noted concerning the experimentally determined barriers to rotation: (i) The effect of the solvent is very significant; the more polar the solvent, the lower the corresponding barrier to rotation. This result is completely in line with TS stabilization which is more polar than the GS due to charge separation.[1] (ii) With respect to electron-withdrawing capability, only C=S and C=O can be compared qualitatively as acceptor substituents [**12** (C=O): $\Delta G^{\ddagger}$ (CD_2Cl_2), 72.8 kJ mol^{-1}; **15** (C=S): $\Delta G^{\ddagger}$ (CD_2Cl_2), 54.2 and 52.5 kJ mol^{-1}. As expected, C=S was, in comparison to C=O, the stronger acceptor substituent. (iii) The donor substituent combinations S,S, S,N and N,N can be compared with respect to the properties of sulfur and nitrogen, respectively (**7** (S,S), $\Delta G^{\ddagger}$ ($C_2D_2Cl_4$), 93.3 kJ mol^{-1}; **25** (S,N), $\Delta G^{\ddagger}$ (CD_2Cl_2), 69.1 kJ mol^{-1}; **15** (N,N), $\Delta G^{\ddagger}$ (CD_2Cl_2), 54.2 and 52.5 kJ mol^{-1}.

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TABLE 2. Calculated Barriers to Rotation [Δ*G*, Δ*E* (kJ mol^{-1})] about the Central C═C Partial Double Bond in Push−Pull Alkenes 1−29

	HF level of theory				MP2 level of theory	
	6-31G*		6-311G**		6-31G*	6-311G**
	Δ*E*	Δ*G*	Δ*E*	Δ*G*	Δ*E*	Δ*E*
1	171.5	169.4	163.6	161.7	177.9	170.2
2	168.3	166.9	161.2	159.7	176.4	169.5
3	173.3	171.0	166.1	164.0	177.6	170.7
4	169.5	167.3	162.4	160.4	173.8	167.2
5	144.5	143.6	135.6	135.2	128.8	118.8
6	175.3	172.2	168.2	165.7	174.2	167.9
7	117.0	115.3	111.4	109.9	114.2	107.8
8	114.8	115.6	111.0	112.7	110.7	103.8
9	121.4	120.5	115.1	114.6	112.6	107.6
10	118.8	118.0	112.5	111.9	112.9	107.8
11	97.7	99.0	88.7	90.2	102.8	90.4
12	103.7	100.9	99.0	96.8	112.6	107.5
13	87.1	87.4	82.0	82.9	94.3	89.5
14	100.1	98.9	95.1	93.8	113.2	109.4
15	63.5	63.7	59.1	59.8	82.7	78.6
16	45.9	48.9	42.4	45.9	65.6	60.8
17	55.4	55.8	51.6	53.3	80.5	77.4
18	155.9/137.1	153.9/136.7	149.9/132.6	148.3/132.4	168.9/146.8	162.1/141.7
19	153.7/133.9	151.6/134.3	148.0/130.6	146.4/131.0	167.5/144.4	161.1/140.4
20	155.0/139.6	152.1/139.0	149.5/135.9	147.1/135.7	167.3/147.3	161.6/143.7
21	153.9/135.0	151.0/134.8	148.2/130.7	145.9/130.9	165.1/142.6	159.1/138.4
22	119.4/88.1	117.1/88.1	115.3/84.9	113.2/85.2	129.5/95.9	125.0/93.7
23	79.2/50.3	80.7/53.3	75.6/47.1	77.2/50.3	97.2/66.8	94.2/63.5
24	129.3/118.8	127.6/117.7	123.9/113.9	122.7/112.7	142.8/132.1	136.3/126.5
25	84.7/72.0	85.5/72.9	80.0/65.4	81.4/67.0	108.5/97.2	105.1/90.8
26	76.6/69.6	76.6/71.1	72.7/67.7	72.6/68.9	*a*	*a*
27	27.9/18.1	31.0/19.8	24.6/16.6	27.5/17.6	*a*	*a*
28	64.9/46.3	67.0/49.2	60.5/44.1	62.1/46.4	*a*	*a*
29	18.2/4.0	21.5/7.1	13.8/2.9	17.3/5.6	*a*	*a*

[a] Too many heavy atoms for the MP2 level of theory.

As expected, nitrogen was the stronger donor in comparison to sulfur. (iv) The ring size of the donor structural fragments on the barrier to rotation runs in the sequence: five-membered ring (**12**, $\Delta G^{\ddagger}$ ($C_2D_2Cl_4$), 72.8 kJ mol^{-1}) > seven-membered ring (**14**, $\Delta G^{\ddagger}$ ($C_2D_2Cl_4$), 61.5 kJ mol^{-1}) > six-membered ring (**13**, $\Delta G^{\ddagger}$ ($C_2D_2Cl_4$), 58.6 kJ mol^{-1}). This is identical to the sequence in amides/thioamides,[36] which was shown to be determined by steric hindrance in the GS.[37]

However, the conclusions to be drawn from these experimental results are somewhat limited. In more than half of the cases, the rate constants of the restricted rotation could not be measured on the NMR-time scale for various reasons and in the cases experimentally accessible, leaving the compounds to be directly compared with respect to the *push−pull effect* limited. In addition, the relative energies of both the GSs and TSs of the rotation about the C═C partial double bond are not available, only the difference of the two are, but both are characteristically contributing to the charge separation. For this reason, the global minimum energies and structures of both the GSs and TSs of this dynamic process in **1**−**29** were determined by theoretical calculations at the ab initio level of theory.

Theoretical Calculation of the Barriers to Rotation about the Central C═C Partial Double Bond in Push−Pull Alkenes 1−29. In Table 2, the calculated barriers to rotation are presented; in the case of **26**−**29**, the more extended MP2 level of theory could not be employed as too many heavy atoms were present.

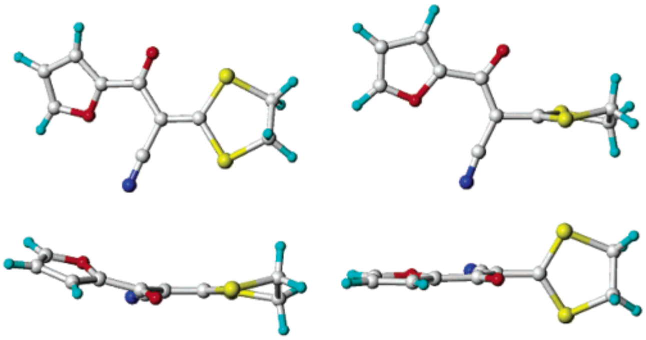

FIGURE 4. Both the GS (left pair of structures) and TS (right pair of structures) of the restricted rotation about the central C═C partial double bond in **1** (molecule shown from two directions perpendicular to each other for both depictions).

Geometries of the Ground and Transition States. In the GS, the four substituents attached to the central C═C partial double bond are in the plane of the double bond and the global minimum results from the lowest steric hindrance between the remaining parts of the molecule. In the TS, the acceptor and donor moieties are at an angle of 90° (i.e., the plane containing the two donors and C-1 is at a 90° angle to the plane containing the two acceptors and C-2). The most characteristic feature that is distinct between the geometries of the two states is the length of the central C═C partial double bond (which is actually a C−C single bond in the TS)

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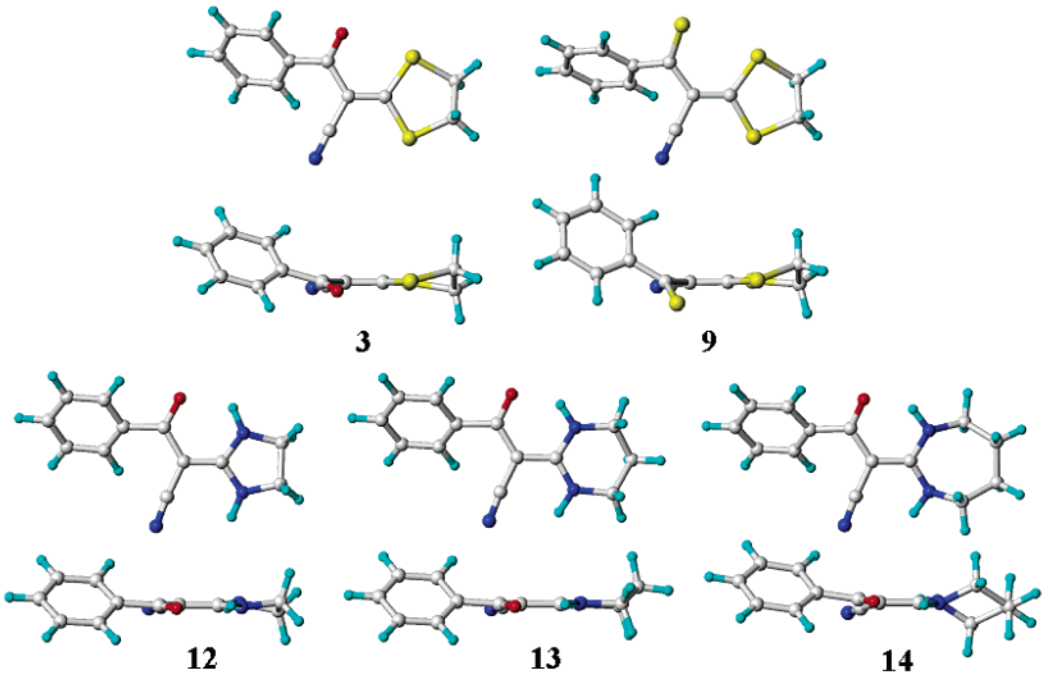

FIGURE 5. Ground states of the restricted rotation about the central C=C partial double bond in **3**, **9**, and **12**−**14** (molecules shown from two directions perpendicular to each other).

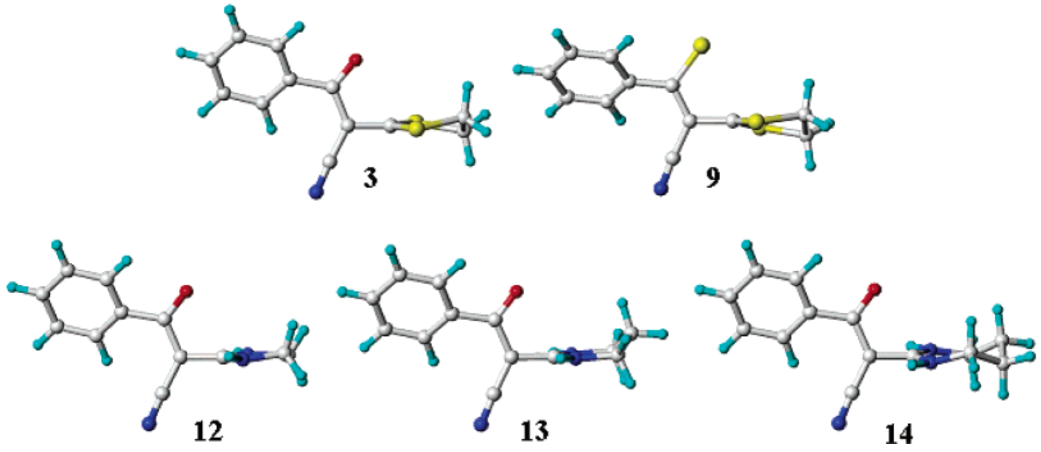

FIGURE 6. Transition states of the restricted rotation about the C=C partial double bond in **3**, **9**, and **12**−**14**.

and of those bonds involving the donor and acceptor substituents (see the Supporting Information). As an example, in Figure 4 both the GS and TS of the restricted rotation about the central C=C partial double bond of **1** are depicted.

While in the GS the donor heteroatoms (S,S, S,N, and N,N) are generally in-plane with the central C=C partial double bond (due to the heterocyclic ring present in **1**−**29**, the remaining ring carbons are either in-plane or twisted slightly; see the Supporting Information), the acceptor moieties proved to be slightly twisted with respect to the donor moieties of **1**−**29** due to steric hindrance. The *push*−*pull effect* and the hydrogen bonding between the two sides of the molecules are significant: e.g., S=CPh in **9** proved to be more twisted than O=CPh in **3** (cf. Figure 5) and the hydrogen bonding C=X···H−N forces the two groups X = CPh to be in-plane (cf. **12**−**14** in Figure 5). All these effects are interrupted in the TS where steric hindrance is reduced due to the longer C_1−C_2 bond and the expanded bond angles C_1−C_2−C_4, C_2−C_4−O(S,) and C_2−C_4−C_5. Furthermore, the aryl substituents become nearly coplanar with the acceptor moiety of the push−pull alkenes (cf. Figure 6).

Barriers to Rotation. The energy differences between the GSs and the TSs, as calculated for all push−pull alkenes **1**−**29**, can be considered as theoretical measures for the barriers to rotation (cf. Table 2). In comparison to the experimentally determined barriers, there was qualitative agreement as both the electron-withdrawing properties of the acceptor substituents (C=S > C=O) and the electron-donating properties of the donor substituents (N,N > N,S > S,S) were correctly reproduced. However, the theoretically calculated barriers are overestimated. Basis set extension led to a reduction of the resulting calculated values, but this was offset when using the MP2 level of theory which inflates them due to overvaluation

TABLE 3. Effect of Different Solvents on the Barrier to Rotation [ΔG (kJ mol^{-1})] about the Central C=C Partial Double Bond in Push−Pull Alkenes 8 and 12

	vacuum	$C_2D_2Cl_4$		DMF		DMSO	
	$\Delta G^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta E_{LM}{}^{a}$	$\Delta G^{\ddagger}$	$\Delta E_{LM}{}^{a}$	$\Delta G^{\ddagger}$	$\Delta E_{LM}{}^{a}$
8 experimental		95.3		90.3		87.9	
HF/6-31G*	114.8	100.5	14.3	97.8	17.0	97.7	17.1
HF/6-311G**	111.0	95.1	15.9	92.5	18.5	92.3	18.7

	vacuum	toluene		CD_2Cl_2		acetone	
	$\Delta G^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta E_{LM}{}^{a}$	$\Delta G^{\ddagger}$	$\Delta E_{LM}{}^{a}$	$\Delta G^{\ddagger}$	$\Delta E_{LM}{}^{a}$
12 experimental		75.5		72.8		62.9	
HF/6-31G*	103.7	85.6	18.1	77.7	25.9	70.6	33.1
MP2/6-31G*	112.6	92.2	20.5	78.6	34.1	74.7	37.9

[a] Solvent effect on barrier to rotation.

of the extended π-electron delocalization, i.e., additional GS stabilization (see Table 2).

To account for the different solvents used in the DNMR experiments, the SCI−PCM method[31] was employed and single-point calculations of both the GSs and TSs of **8** and **12** were performed (cf. Table 3). The results headed in the right direction as the barriers calculated were lowered and relatively correct sequences were obtained [e.g., **8**: $\Delta G^{\ddagger} = 95.3$ kJ mol^{-1} (CD_2Cl_2) > $\Delta G^{\ddagger} = 90.3$ kJ mol^{-1} (DMF) > $\Delta G^{\ddagger} = 87.9$ kJ mol^{-1} (DMSO)]. However, both the solvent polarity and, especially, the effect of hydrogen bonding on the barrier to rotation was accounted for insufficiently by the SCI−PCM method and the subsequent correlation coefficient was not improved substantially. Obviously, polarized continuum models are insufficient to correctly describe these highly polar compounds.[38]

Thus, the barriers to rotation of the push−pull alkenes **1**−**29** calculated in a vacuum were employed to draw possible conclusions about the electron distribution as the correlation to the available experimental values (in CD_2Cl_2) was considered sufficient ($R^2 = 0.8294$, cf. Figure 7) as the line of best fit (without taking into consideration the influence of the solvent) is almost parallel to the line of identity and thus reliable conclusions regarding the donor/acceptor substituents on the push−pull double bond can be expected. The following points are worth noting: (i) The combinations of S,S and N,N donor substituents can be extended to oxygen and analogous N,O and N,S compounds and the following sequence of decreasing activity of the donor moiety in **1**−**29** was obtained: N,N (**15**: $\Delta G^{\ddagger} = 54.2$ kJ mol^{-1}) < N,O (**25**: $\Delta G^{\ddagger} = 69.1$ kJ mol^{-1}) < N,S (**24**: $\Delta G^{\ddagger} < 76.9$ kJ mol^{-1}) < S,S (**7**: $\Delta G^{\ddagger} = 93.3$ kJ mol^{-1}). (ii) The additional double bond within the donor ring of **5** and **11** decreases the barrier to rotation and obviously additional resonance stabilization of the conjugated five-membered ring in both the GSs and TSs is more active in the TS. (iii) The larger electron-withdrawing property of C=S compared with C=O is corroborated with a larger number of cases (e.g., 54.2 kJ mol^{-1} in **15** vs 72.8 kJ mol^{-1} in **12**); the acceptor property of cyano cannot be estimated in this series of compounds as it is present in each compound.

(iv) From the calculations, the lengths of the central C=C partial double bond in the GS are available (cf. Table S4 in the Supporting Information). This geometric parameter should, together with the barrier to rotation, also characterize the π-electron distribution.[39] These two parameters for **1**−**29** are correlated in Figure 8a and though qualitative dependence is discernible, good linear dependence is not afforded (the bond length $C_1{=}C_2$ is a GS property, the barrier to rotation is dependent on both the GSs and TSs). If, however, the compounds are classified with respect to the acceptor substituents C=S

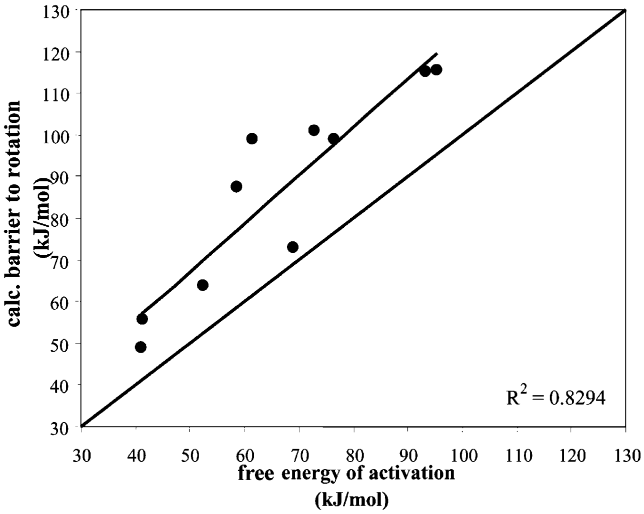

FIGURE 7. Correlation of experimental barriers to rotation in **7**, **8**, **11**−**17**, and **25** (solvent CD_2Cl_2) and the theoretical values as calculated in a vacuum.

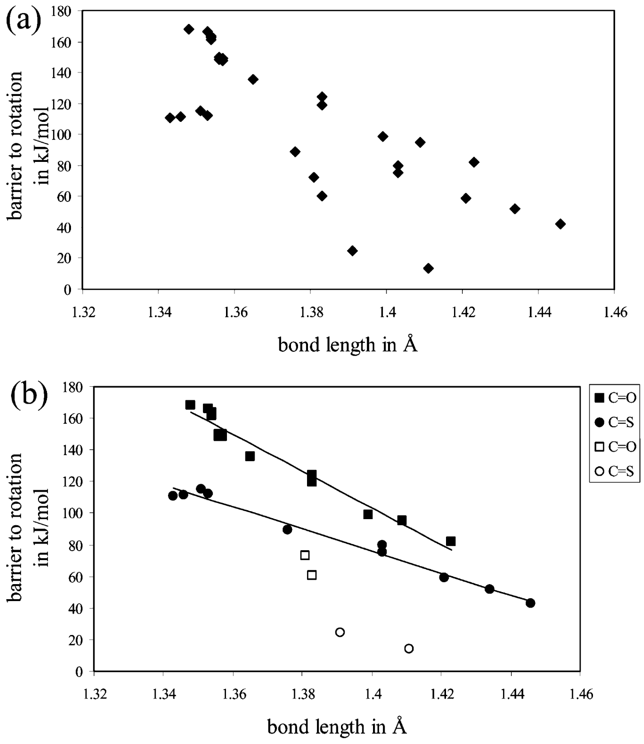

FIGURE 8. Correlation of calculated barriers to rotation about $C_1{=}C_2$ and the corresponding bond length of $C_1{=}C_2$ in **1**−**29**.

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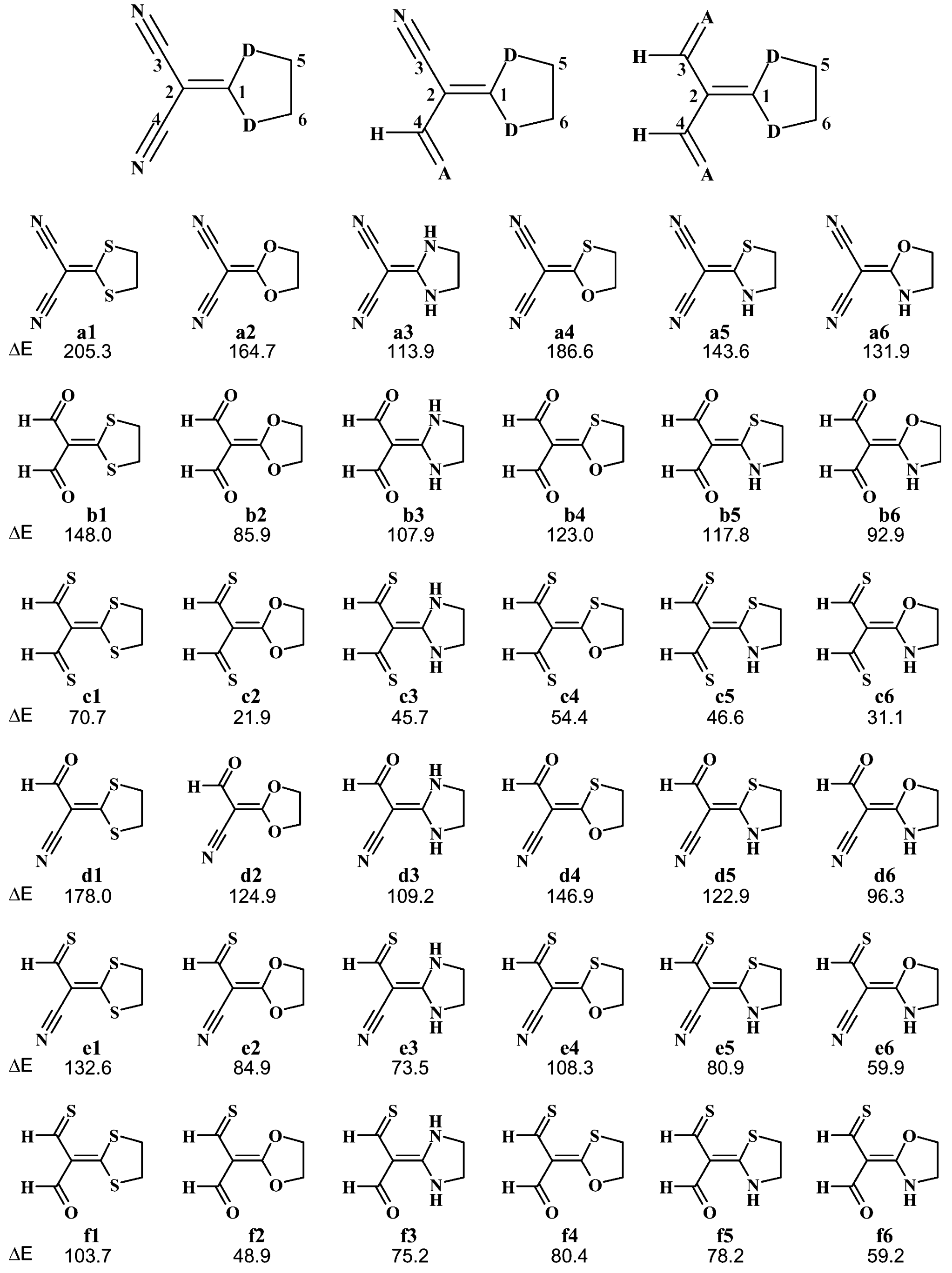
CHART 1



and C═O, much better linear dependencies can be observed (cf. Figure 8b, only **26**−**29** are deviating significantly where the phenyl substituent at N-1 alters the GSs dramatically due to additional steric hindrance). This result is of 2-fold interest: first, the stronger electron-withdrawing power of C═S compared with C═O is corroborated, and second, the slopes of the two correlation lines are different. Obviously, the steric hindrance of the thiocarbonyl group in these push−pull alkenes destabilizes the GSs more (dependent on the *push−pull effect*) and additionally reduces π-delocalization, thereby lengthening the $C_1{-}C_2$ bond in the GS and reducing the barriers to rotation correspondingly.

To draw firmer conclusions regarding these influences, a number of model compounds were also ab initio MO-calculated.

Model Compounds. To eliminate the steric influences on both the barrier to rotation and the $C_1{=}C_2$ bond length, the C-3 aryl group was replaced by H, otherwise all possible combinations of acceptor substituents (C═S, C═O, C≡N) and donor atoms (NH, S, O) were included in the ab initio calculations at the HF/6-31G* level of theory. The collection of 36 model compounds **a1**−**f6** are displayed in Chart 1.

In all model compounds, the GS was shown to be completely planar and there is no longer any steric

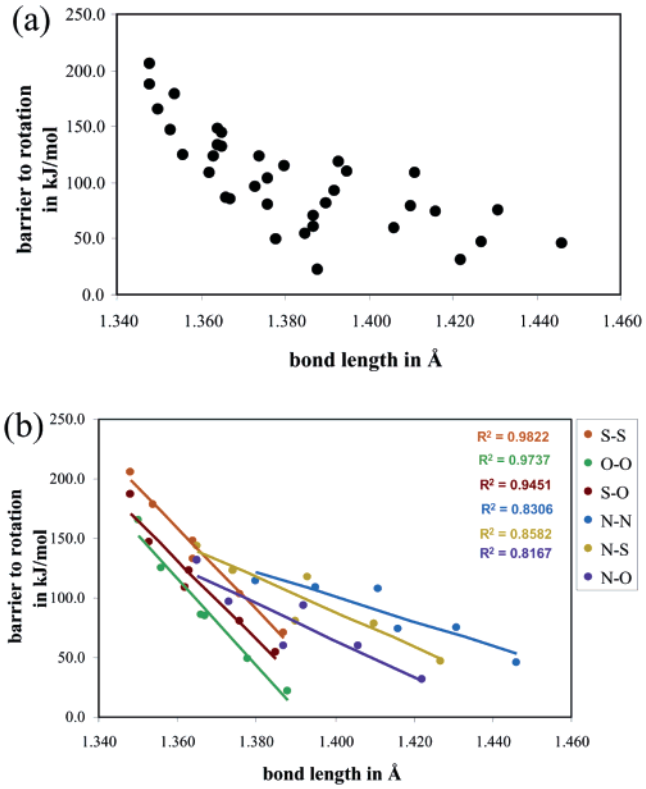


FIGURE 9. Correlation of calculated barriers to rotation about $C_1{=}C_2$ and the corresponding bond lengths of $C_1{=}C_2$ in model push–pull alkenes **a1**–**f6**.

hindrance present in the acceptor moiety of **a1**–**f6**. As expected, in the TS the two moieties are at an angle of 90° to each other and are also free of steric hindrance (barriers to rotation and GS bond lengths are presented in Table S5 in the Supporting Information). In addition to the aforementioned observations, both the donor and acceptor moieties of the model compounds **a1**–**f6** could be classified as follows:

$$\text{acceptors: } (C{\equiv}N,C{\equiv}N) < (C{\equiv}N,C{=}O) < (C{=}O,C{=}O) < (C{\equiv}N,C{=}S) < (C{=}O,C{=}S) < (C{=}S,C{=}S)$$

$$\text{donors: } (S,S) < (S,O) < (O,O) < (S,N) < (O,N) < (N,N)$$

The two sequences are only truly valid within the series of model compounds **a1**–**f6**; other combinations of AA′C=CDD′ could well exhibit donor/acceptor sequences different to this but in the present context they correlate well with the experimentally obtained results (vide supra).

The dependence of the barrier to rotation vs the bond length of $C_1{=}C_2$ was also examined for **a1**–**f6** (see Figure 9a). Upon initial inspection there appears to be a lack of correlation, similar to the plot in Figure 8a, but again as previously, if only model compounds with the same donor moieties are compared (cf. Figure 9b), good correlations result. The correlation lines for the donors (S,S), (S,O), and (O,O) are displaced with respect to one another but possess similar gradients. (Due to the different acceptor/donor combinations, the dependence of $\Delta G^{\ddagger}$ vs bond length ($C_1{=}C_2$) proved to be distinct for the electron acceptors but identical with respect to the electron-donating effect of the donor moieties of the model push–pull alkenes.) The gradients of the correlation lines are flatter in the cases of (S,N) and (O,N) and flattest for (N,N). In the latter case, two NH protons are available for hydrogen bonding (stabilizing additionally the GS);[40] in the former cases, (S,N) and (O,N), only one NH moiety is available for the same stabilization. Thus, the GS stabilizing effect of hydrogen bonding can be truly gauged and quantitatively classified.

NBO Analysis of Model Compounds a1–f6. Thus, correlations of the barrier to rotation and the length of the central $C_1{=}C_2$ partial double bond were employed to quantify the influence of steric hindrance and hydrogen bonding on the *push–pull effect*; however, the *push–pull effect* as a general quantifiable parameter has as yet not been available. For this reason, the model compounds were studied further by an NBO analysis.[41] By NBO analysis the occupation of the various molecular orbitals of both bonds and lone pairs in the compounds were assessed and the different donor/acceptor combinations compared accordingly. These occupancies are provided in Table 4.

If the compounds are compared with respect to the activity of both donor and acceptor substituents, the following two molecular orbital interactions are revealed as the most significant: the lone pairs of the donor substituent with the antibonding π^* orbital of the central partial C=C double bond and the antibonding orbital of the C-3(4)-acceptor bonds with the π orbital of the central partial C=C double bond (cf. Scheme 3). These can thus be employed to quantify the *push–pull effect* as electron density is shifted from the donor lone pairs into π^* of the $C_1{=}C_2$ bond and from the π orbital of this bond into the π^* orbitals of the adjacent bonds in the acceptor groups. The $C_1{=}C_2$ bond thus facilitates the transport of electron density from the donor to the acceptor groups and is therefore active as both an acceptor and a donor simultaneously and can readily be described as a conduit for the electron flow.

Applying these considerations, from the occupancy of the π^* of acceptors and the lone pairs of the donors, the corresponding sequence of activities were determined:

$$\text{acceptors: } C{=}S > C{=}O > C{\equiv}N$$

$$\text{donors: } N > S > O$$

More interesting, however, are the net balances that result when strong and weak donors/acceptors are combined and the following can be noted: (i) A strong electron donor combined with a weaker donor substituent decreases the donor activity of the latter and increases its own one accordingly, e.g., N in **a5** LP = 1.761 but N in **a3** LP = 1.789; S in **a5** LP = 1.859 and in **a1** LP = 1.847. (ii) Similar results were obtained for the electron-withdrawing groups as strong electron acceptors increased their activity when combined with weaker ones

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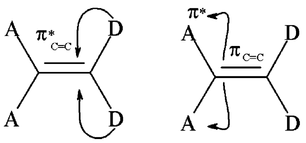
TABLE 4. Occupation Numbers of the Various Orbitals in the Model Compounds a1−f6 as Obtained by NBO Analysis

	π $C_1{-}C_2$	π^* $C_1{-}C_2$	π^* C_3A	π^* C_4A	LP D	LP D
a1	1.886	0.272	0.061	0.061	1.847	1.847
a2	1.863	0.263	0.072	0.072	1.851	1.851
a3	1.819	0.366	0.098	0.098	1.789	1.789
a4	1.874	0.261	0.069	0.064	1.854	1.850
a5	1.850	0.331	0.073	0.056	1.859	1.761
a6	1.840	0.318	0.081	0.089	1.854	1.781
b1	1.816	0.292	0.108	0.108	1.818	1.818
b2	1.788	0.271	0.114	0.114	1.837	1.837
b3	1.672	0.424	0.181	0.181	1.746	1.746
b4	1.799	0.274	0.102	0.122	1.832	1.832
b5	1.729	0.384	0.164	0.143	1.695	1.840
b6	1.721	0.361	0.176	0.131	1.726	1.840
c1	1.734	0.336	0.163	0.163	1.796	1.796
c2	1.676	0.307	0.178	0.178	1.818	1.818
c4	1.699	0.313	0.189	0.155	1.808	1.814
d1	1.859	0.276	0.092	0.067	1.824	1.848
d2	1.834	0.263	0.099	0.078	1.841	1.851
d3	1.752	0.394	0.169	0.104	1.748	1.786
d4-1	1.849	0.259	0.087	0.076	1.839	1.855
d4-2	1.840	0.267	0.105	0.070	1.849	1.835
d5-1	1.807	0.342	0.126	0.063	1.754	1.841
d5-2	1.792	0.363	0.145	0.060	1.712	1.858
d6-1	1.804	0.322	0.115	0.096	1.777	1.844
d6-2	1.777	0.349	0.156	0.089	1.736	1.852
e1	1.818	0.302	0.152	0.062	1.807	1.841
e2	1.779	0.283	0.166	0.074	1.828	1.844
e3	1.647	0.433	0.302	0.091	1.716	1.769
e4-1	1.803	0.280	0.145	0.072	1.828	1.847
e4-2	1.789	0.289	0.174	0.065	1.843	1.817
e5-1	1.738	0.373	0.216	0.062	1.733	1.826
e5-2	1.702	0.404	0.263	0.081	1.669	1.850
e6-1	1.735	0.348	0.200	0.090	1.758	1.833
e6-2	1.679	0.385	0.279	0.080	1.699	1.845
f1	1.769	0.318	0.178	0.100	1.800	1.810
f2	1.726	0.292	0.193	0.106	1.824	1.829
f4-1	1.747	0.296	0.170	0.114	1.820	1.823
f4-2	1.740	0.297	0.203	0.093	1.824	1.814
f5-2	1.657	0.413	0.243	0.151	1.673	1.827
f6-2	1.654	0.383	0.223	0.160	1.711	1.831

SCHEME 3



at the expense of the electron-withdrawing capability of the weaker electron acceptor, e.g., C═S in **f2** $\pi^* = 0.193$ but C═S in **c2** $\pi^* = 0.178$; C═O in **f2** $\pi^* = 0.106$ and in **b2** $\pi^* = 0.114$). (iii) The electron-donating activities can be directly correlated to the corresponding electron-accepting activities of the corresponding substituents: stronger electron-accepting activity strengthens the donor activity of the corresponding substituents in the same molecule and vice versa.

The conclusion to be drawn from these theoretical calculations is that the acceptor activity in push−pull alkenes can be characterized best by the occupancy of the π orbital and the corresponding donor activity by the occupancy of the π^* orbital of the $C_1{=}C_2$ partial double bond. Both parameters are of decisive influence on the corresponding $C_1{=}C_2$ bond length and for this reason the quotient of the two occupancies was correlated with the $C_1{=}C_2$ bond length (cf. Figure 10). The correlation is clear: strong donors increase π^* orbital occupation, thereby increasing the bond length, and strong acceptors reduce π orbital occupation thereby also lengthening the $C_1{=}C_2$ bond.

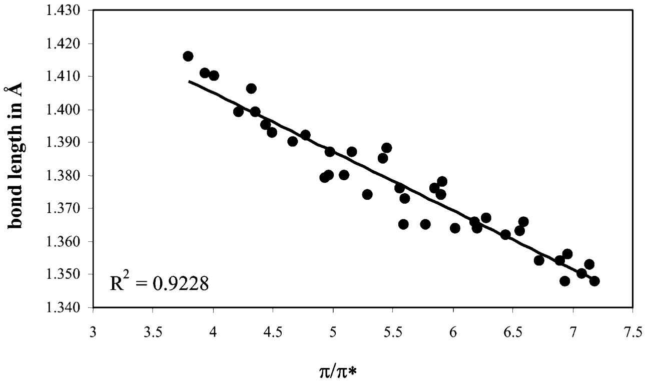


FIGURE 10. Correlation of the lengths of the central $C_1{=}C_2$ partial double bond with the quotient of the electron occupancies of the π and π^* orbitals of this bond.

It is clearly evident therefore that the length of the central C═C partial double bond of push−pull alkenes is the one, simple characterizing parameter for the *push−pull effect*. The separate, quantified donor/acceptor properties of the substituents can be ascertained from the corresponding occupancy numbers of the π and π^* orbitals of this bond where both steric destabilization of the GS and stabilization of the GS by intramolecular hydrogen bonding are included.

Conclusions

A series of push−pull alkenes **1**−**29** was studied with respect to π electron distribution. Two donor substituents on the one side and two acceptor substituents on the other one of the C═C double bond characteristically change both the electronic and spectroscopic properties of these compounds and the central $C_1{=}C_2$ double bond is strongly polarized. Consequently, the ^{13}C chemical shift difference of these two carbons, $\Delta\delta_{C1,C2}$, increases and the barrier to rotation about this bond can often be measured by DNMR. These two parameters characterize the push−pull character of these compounds, but only in a qualitative manner as they are actually dependent on the particular combination of the four substituents present. Although a general parameter to quantify the *push−pull effect* has previously not been available, nevertheless, both the electron-withdrawing effect of acceptor substituents and the electron-donating effect of donor substituents could be evaluated by employing these two parameters despite the GS influencing effects of hydrogen bonding and steric hindrance. By NBO analysis of a number of model compounds, **a1**−**f6**, a linear dependence of the length of the $C_1{=}C_2$ partial double bond on the quotient of the occupation numbers of the bonding π and antibonding bonding π^* orbitals of this bond was obtained where the occupation of the bonding π orbital characterizes quantitatively the acceptor power and the occupation of the antibonding π^* orbital characterizes quantitatively the donor strength of the substituents present. Thus, it is the *length of the central C═C partial double bond* that has now been proven to be the only sole parameter able to generally quantify the *push−pull effect* in push−pull alkenes, including special GS influencing effects such as hydrogen bonding and steric hindrance. Low occupation of π and high occupation of π^* is typical for strong acceptor substitution (C═S > C═O > C≡N); high occupation of π and low occupation of π^* is typical for strong donor substitution (NH > O > S). However, there is a conundrum: strong acceptors (donors) reduce the electron-withdrawing (electron-donating) effect of weaker acceptors (donors). On the other hand, substitution by strong donors increases the effect of acceptors and vice versa. Since both the barrier to rotation about the $C_1{=}C_2$ double bond and the ^{13}C chemical shift differences of C-1 and C-2 are determined by all of the influences of both the donor and acceptor substituents on both the GSs and TSs, they adequately characterize the *push−pull effect* only in special cases.

Experimental Section

Compounds **1**, **2** (yield: 63%; mp 151−153 °C), **3**, **4**, **5** (yield: 42%, mp 176−178 °C), and **6** were prepared by dithiocarboxylation of acylacetontriles and subsequent alkylation with α,ω-dihaloalkanes or propargyl bromide.[42]

Cyclic thioacylcyanoketene acetals **7** (yield: 59%, mp 197−199 °C), **8** (yield: 63%, mp 175−176.5 °C), **9** (yield: 61%, mp 170−172.5 °C), **10** (yield: 47%, mp 187−188 °C), **11** (yield: 69%, mp 183−185 °C), **15**−**17**, **23**, **25**, **27**, and **29** (yield: ca. 90%, mp 265−267.5 °C) were prepared by sulfuration of corresponding acyl compounds with Lawesson's reagent.[43]

Cyclic acylketene *N*,*N*-acetals **12**, **13** (yield: 6−70%, mp: 185−187 °C), **14** (yield: 54%, mp 194−195 °C), O,S-acetals **18** (yield: 92%, mp 192−193 °C), **19** (yield: 93%, mp 153−154 °C), **20** (yield: 97%, mp 128−129.5 °C), **21** (yield: 77%, mp 164−165 °C), *N*,*O*-acetal **22**, and *N*,*S*-acetal **24** were available by reaction of acylketene *S*,*S*-acetals with α,ω-diaminoalkanes, 2-mercaptoethanol, ethanolamine, and cysteamine, respectively.[44]

Thiocarbamoylation of benzoylacetonitrile and subsequent alkylation with 1,2-dibromoethane led to substituted 3-phenylthiazolidine **26** (yield: 33%, mp 244−245 °C); 4-methyl-3-phenyl-thiazoline **28** was prepared in the same way using propargyl bromide for alkylation.[45]

The ^{1}H and ^{13}C NMR spectra were acquired at 11.75 (operating at 500 and 125 MHz for ^{1}H and ^{13}C, respectively) and 7.05 T (operating at 300 and 75 MHz for ^{1}H and ^{13}C, respectively), generally with $CDCl_3$ as the solvent at room temperature except for the DNMR experiments where other solvents and temperatures were used as indicated. Determination of the actual probe temperature was made using standard NMR thermometers (uncertainties in temperature measurement ±1 K). Toluene-d_8, $C_2D_2Cl_4$, DMF-d_7, and DMSO-d_6 were used as solvents for high-temperature experiments and toluene-d_8, CD_2Cl_2, acetone-d_6, and DMF-d_7 for low-temperature experiments. ^{13}C spectra were acquired using a 10 s repetition time and proton broadband decoupling. All ^{1}H and ^{13}C chemical shifts were referenced using TMS as an internal standard (= 0 ppm for both nuclei). NMR spectra were assigned using APT and 2-D techniques such as gs-HMQC,[46] HMQC-TOCSY[46] and gs-HMBC[46] using standard vendor-supplied software.

The free energies of activation were calculated by means of eqs 1 and 2:[47,48]

$$k_c = \frac{\pi \Delta \nu}{\sqrt{2}} \tag{1}$$

$$\Delta G_c = 19.14 T_c \left[10.32 + \log\left(\frac{T_c}{k_c}\right)\right] \tag{2}$$

Quantum chemical calculations were performed on SGI Octane R12000 and SGI Origin workstations using the Gaussian 98 software package. The molecules were optimized at different levels of theory using the keyword *opt*, optimization of transition states of the rotation about the central double bond using *opt = ts* and *calcfc*. ΔE of the barrier to rotation was concluded from the total energy difference between GS and TS; ΔG is the similar difference corrected by zero-point energy correction. TSs are indicated by having only one imaginary frequency for the rotation around the central double bond, while GSs have no imaginary frequencies. 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[49] was used linked to the Gaussian 98 program package[32] 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. The results were illustrated using the program SYBYL.[50]

The chemical shieldings in the surrounding of the molecules were calculated as described in ref 26a. Within the SYBYL contour file, the anisotropy effect of the functional groups under investigation were visualized as iso-chemical-shielding surfaces (ICSS) enabling appreciation of the spatial extension of the anisotropy effect to particular protons.

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Supporting Information Available: Detailed description of experimental procedures and characterization of compounds **2**, **5**, **11**, **13**, **14**, **18**−**21**, **26**, and **29**. Discussion and tables of the ab initio calculations of the ^{13}C NMR chemical shifts of compound **20** comparing various levels of theory, various basis sets, the extension of the basis set for the carbonyl oxygen, the inclusion of the solvent and the effect of varying the bond length of the carbonyl oxygen; the ^{13}C NMR chemical shifts of compounds **1**−**29** calculated at the HF/6-31G* level of theory; and depiction of the ground and transition states (for restricted rotation about the central C═C partial double bond) in compounds **2**, **4**−**8**, **10**, **11**, and **15**−**29**. This material is available free of charge via the Internet at http://pubs.acs.org.

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