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Rotational Barriers and Electronic Structures of Some 6,6-Diheterosubstituted Fulvenes

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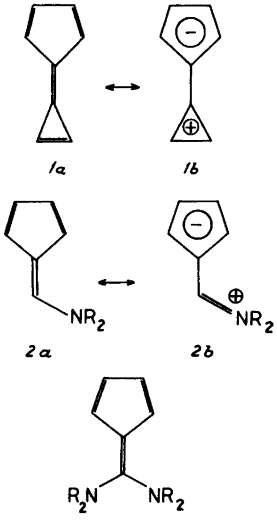
The title fulvenes with N, O, or S as heteroatoms were prepared by reaction of trifluoromethylcyclopentadiene with 2-mercaptoethanol, 2-hydroxyethyl-methylamine, N-methyl-N'-phenylethylenediamine and N-benzyl-N'-isopropyltrimethylenediamine. The free energy barriers to rotation about the fulvene C-1=C-6 bond were studied by ^{1}H NMR bandshape technique and were found to be: with O, S as heteroatoms >105 kJ mol^{-1}, with N, O 75.4 kJ mol^{-1}, and with N, N 41 kJ mol^{-1} or <30 kJ mol^{-1}, with the higher value for the *N*-phenyl compound.

The electronic charges, the dipole moments, and the energies of the initial and transition states of three model compounds with N,S (*4a*), N,O (*4b*) and N,N (*4d*) as heteroatoms were calculated by the CNDO/2 method, employing limited geometry optimization.

The free energy barrier of the N,O-substituted fulvene was strongly dependent on solvent polarity, and the effect could be explained by the reaction field theory. The calculated rotational barriers were much higher than the experimental ones and the difference was shown to be far too great to be explained by neglect of solvation in the calculations.

The tendency of the cyclopentadiene ring to accept electrons from exocyclic groups has been the subject of interest for a long time. As an example, fulvene was at one time regarded as an aromatic compound,[1] supported among other things by the high dipole moment directed towards the aromatic ring that resulted from calculations of the Hückel type.[2] The demonstration by microwave spectroscopy that the dipole moment of fulvene is in fact only 0.49 D[3] has shown that fulvene cannot be classed as an aromatic hydrocarbon on any grounds. Nevertheless, fulvenes with donor substituents on the exocyclic carbon atom have in many instances been defined as more or less aromatic. Without taking a stand to this diffuse and controversial quality one can safely conclude that the cyclopentadienylidene ring interacts strongly with donor groups, thereby approaching a cyclopentadienide ion. Pertinent examples are the calicenes (*1*),[4] 6-aminofulvenes (*2*)[5] and 6,6-diaminofulvenes (*3*).[6,7] The charge delocalization and the development of the electronic structure of a cyclopentadienide ion are evidenced by large dipole moments,[4,6] equalized C–C bond lengths in the ring[8,9] and high barriers to rotation about the C–N bond in *2*.[10–12]



1a *1b* *2a* *2b* *3*

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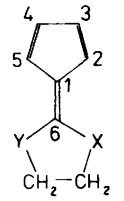
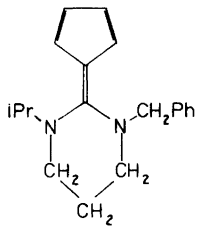


4a , X = O, Y = S

b , X = O, Y = NMe

c , X = PhN, Y = NMe

d , X = MeN, Y = NMe



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Compounds of types *1*[13] and *2*[11,12] have also shown exceptionally low barriers to rotation about the C-1 – C-6 double bond, which is readily explained by a good stabilization of the transition state, in which a cyclopentadienide ion is fully developed.

Our study was undertaken in order to investigate the delocalization of electrons and the barriers to rotation about the exocyclic double bond in some 6,6-dihetero-substituted fulvenes (*4a–4c*, *5*), in which the heteroatoms form part of a five- or six-membered saturated ring. The study has been performed by ^{1}H NMR bandshape analysis and by CNDO/2 calculations.

The stabilization of polar compounds in solution depends on the dipole moment of the solute and on the polarity and polarizability of the solvent. Since the dipole moment of the transition state to rotation about the exocyclic double bond is larger than that of the initial state, a study of the solvent effect on the rotational barrier has been performed with compound *4b*.

EXPERIMENTAL

Syntheses. 2-Cyclopentadienylidene-1-thia-3-oxacyclopentane (4a). A solution of trifluoromethylcyclopentadiene, $CpCF_3$,[14] (3 mmol) in ether, was added to a slurry of 0.6 g (9 mmol) potassium hydroxide in 350 mg 2-mercaptoethanol. After vigorous stirring for 30 min, the reaction mixture was washed with several portions of water. Cyclohexane was added and the solvent was evaporated until the product precipitated as bright yellow crystals, m.p. 79–81 °C. Yield 195 mg (43 %). NMR ($CDCl_3$, 270 MHz, 298 K): δ 6.54 (1 H, m), 6.41 (1 H, m), 6.31 (2 H, m), 4.64 (2 H, t) and 3.42 (2 H, t). UV (ethanol): λ_{max} 310 nm (sh) log ε 4.33, 320 nm log ε 4.43 and 332 nm (sh) log ε 4.30. MS (34 eV): *m/e* 152 (55 %, M^+) and 92 (100). Abs. mass 152.032; calc. for C_8H_8OS 152.030.

N-*Methyl-2-cyclopentadienylidene-1-aza-3-oxacyclopentane* (4b), was prepared as described for *4a* from 2-(hydroxyethyl)-methylamine, in 78 % yield as colourless crystals, m.p. 163–164 °C. NMR ($CDCl_3$, 270 MHz, 298 K): δ 6.74 (1 H, m), 6.65 (1 H, m), 6.40 (1 H, m), 6.33 (1 H, m), 4.52 (2 H, t), 3.82 (2 H, t) and 3.35 (3 H, s). UV (ethanol): λ_{max} 310 nm log ε 4.50. MS (34 eV): *m/e* 149 (100 %, M^+), 122 (13), 93 (48) and 92 (34). Abs. mass 149.083; calc. for $C_9H_{11}NO$ 149.084.

N-*Methyl*-N′-*phenyl-2-cyclopentadienylidene-1,3-diazacyclopentane* (4c), was prepared as described for *4a* from *N*-methyl-*N*′-phenyl-ethylenediamine, in 52 % yield as pale gray crystals, m.p. 148–150 °C. NMR ($CDCl_3$, 270 MHz, 298 K): δ 7.10–7.40 (5 H, m), 6.09 (4 H, s), 3.93 (2 H, t), 3.76 (2 H, t) and 3.40 (3 H, s). UV (ethanol): λ_{max} 266 nm log ε 4.08 and 333 nm log ε 4.24. MS (34 eV): *m/e* 224 (61 %, M^+), 223 (100), 207 (15), 107 (22) and 106 (23). Abs. mass 224.131; calc. for $C_{15}H_{17}N_2$ 224.131.

N-*Benzyl*-N′-*isopropyl-2-cyclopentadienylidene-1,3-diazacyclohexane* (5), was prepared as described for *4a* from *N*-benzyl-*N*′-isopropyl-trimethylenediamine, in 43 % yield, m.p. 132–135 °C. NMR ($CDCl_3$, 270 MHz, 298 K): δ 6.95–7.15 (5 H, m), 6.03 (2 H, m), 5.95 (2 H, m), 4.90 (1 H, septet), 4.71 (2 H, s), 3.03 (2 H, t), 2.99 (2 H, t), 1.75 (2 H, quintet) and 1.01 (6 H, d). UV (ethanol): λ_{max} 249 nm log ε 4.10, 267 nm log ε 4.08 and 332 nm log ε 4.22. MS (34 eV): *m/e* 280 (100 %, M^+), 279 (46), 265 (22), 238 (19), 237 (39), 189 (10), 146 (9), 98 (29) and 91 (39). Abs. mass 280.194; calc. for $C_{19}H_{24}N_2$ 280.194.

The variable temperature ^{1}H NMR spectra were recorded on *ca.* 0.5 M solutions in solvents given in Tables 1 and 2, on a JEOL Model MH-100 NMR spectrometer with standard variable temperature probe and temperature controller.

The rate constants for *4b* and *4c* were obtained by visual comparison of the experimental spectra with spectra calculated with the DNMR 3 program.[15] The slow exchange limit for *4c* is below –100 °C, and no well-resolved spectrum could be obtained because of extensive bandbroadening at this temperature. The spectra were therefore calculated with coupling constants that are averages of those derived by Mannschreck and Kölle[16] for 6-dimethylaminofulvene. Exchange-broadened ^{1}H NMR spectra for *4c* could be recorded over a 40° interval, but unfortunately, the sensitivity of the spectrum to changes in the rate constant was rather low in the region of fast exchange. This is because the chemical shifts of H-2 and H-5 ($\delta\nu$ = 90.8 Hz) are symmetrically disposed with respect to those of H-3 and H-4 ($\delta\nu$ = 22.5 Hz), and the averaged spectrum lacks completely AA'BB' structure and

Table 1. Rate constants and free energy barriers for *4c* in dichlorofluoromethane solution.[a]

T/K	k/s^{-1}	$\Delta G^{\neq}$/kJ mol^{-1}
175.0	4.0	40.1
189.2	22.5	40.7
193.8	33	41.1
197.7	55	41.2
201.7	75	41.5
211.3	200	41.8

[a] Spectral parameters (in Hz): ν_1 544.4, ν_2 575.9, ν_3 598.4, ν_4 635.2. J_{12} 4.57, J_{13} 1.64, J_{14} 2.10, J_{23} 2.48, J_{24} 1.64 and J_{34} 4.57.

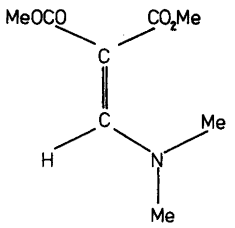
appears as a singlet in the fast exchange limit. Therefore, no attempt was made to calculate activation enthalpy or entropy, but the free activation energies recorded in Table 1 increase with temperature, indicating a negative activation entropy, as expected for this type of compound.[17]

The ^{1}H NMR spectrum of *4a* in DMSO-d_6 showed no effects of exchange below +150 °C, indicating a free energy barrier >105 kJ mol^{-1}, since a rate constant >1 s^{-1} should have caused an observable broadening.

The free energy barriers of *4b* in toluene-d_8, acetonitrile-d_3 and in two mixtures of these solvents are found in Table 2. No effects of slow rotation could be observed in the spectrum of *5* down to −130 °C.

The temperatures[18] and the transverse relaxation times[19] were measured as previously described, the NMe signal in the spectra of *4b* and *4c* serving as resolution standard.

The CNDO/2 calculations were performed by the standard program[20] (without *d*-orbitals for S) on the initial states (assumed planar) and the transition states (twisted 90° around the C-1−C-6 bond) of compounds *4a*, *4b* and *4d*. The latter structure was chosen as a model for *4c* in order to limit the computational work and also because the steric effects



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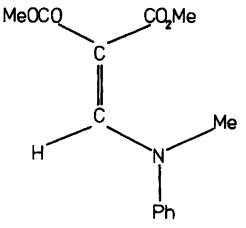

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in *4c* were not expected to be adequately treated in the CNDO/2 calculations. The barrier to rotation about the C-1−C-6 bond is certainly higher in *4c* than in *4d*. An upper limit to the difference of *ca.* 14 kJ mol^{-1} may be obtained by a comparison between compounds *6* and *7*,[21] but the difference is probably smaller since the steric hindrance to coplanarity is stronger in the initial state of *4c* than in that of *7*.

The geometry of the cyclopentadiene ring in the initial state was taken from an X-ray crystallographic study of 6-dimethylaminofulvene,[8] which differs very little from that of 6,6-bis(dimethylamino) fulvene.[9] This geometry was also first employed in the 90° twisted state, but a regular pentagon with a C−C bond length of 1.403 Å was found to give ca. 13 kJ mol^{-1} lower energy in *4b* and was employed throughout. The C-1−C-6, C-6−S, C-6−O and C-6−N bond lengths were optimized, and the final values are found in Table 3. The remaining bond lengths and angles in the rings containing the donor atoms were standard values and were not optimized, since they were not expected to undergo important changes during the rotational process. Only small changes in the ring angles at the heteroatoms (X, Y) were performed in order to keep the other bond lengths constant when the C-6−X (C-6−Y) bond lengths were varied. The calculated energies and dipole moments are found in Table 3.

Table 2. Solvent effects on the chemical shifts, rate constants and free energy barriers for *4b*.

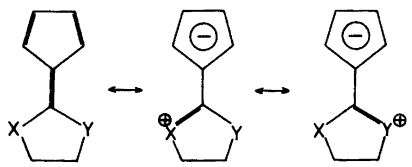
Solvent	Molar ratio	Chemical shift/Hz H-1	H-2	H-3	H-4	T/K	k/s^{-1}	$\Delta G^{\neq}$/kJ mol^{-1}
Toluene-d_8	–	697	660	~660	~660	362	100	75.4
Toluene-d_8 − acetonitrile-d_3	1.59:1	691	668	652	645	329	50	70.1
Toluene-d_8 − acetonitrile-d_3	0.81:1	685	668	646	637	315	38	67.8
Acetonitrile-d_3	–	658	668	626	613	281	17	62.0
		658	668	627	613	284	24	61.9
		658	669	628	613	288	35	62.0
		658	670	628	613	299	70	62.6

Table 3. Bond lengths, energies (E), rotational barriers (ΔE), and dipole moments, calculated by the CNDO/2 method.

Molecule	Optimized bond length/Å C-1–C-6	C-6–N	C-6–O	C-6–S	E/a.u.	ΔE/kJ mol^{-1}	μ/D
4a							
Initial state	1.390	–	1.360	1.755	−91.74154	173.6	5.24
Transition state	1.410	–	1.350	1.730	−91.67539		9.98
4b							
Initial state	1.375	1.375	1.360	–	−102.26196	125.9	6.38
Transition state	1.405	1.360	1.350	–	−102.21399		10.28
4d							
Initial state	1.390	1.380		–	−104.94954	95.8	6.15
Transition state	1.415	1.365		–	−104.91306		10.28

RESULTS AND DISCUSSION

The barriers to rotation about the C-1–C-6 bond in *4b*, *4c* and *5* are much lower than the barrier in a simple ethylene, which is 260 kJ mol^{-1} for 1,2-dideuterioethylene[22] and 251 kJ mol^{-1} for *cis*- to *trans*-2-butene.[23] The barrier differences are determined by the delocalization energies in the initial state (*8a*–*8c*), by the stabilizing interaction



8a *8b* *8c*

of the heteroatoms X and Y with the carbocation in the transition state (*9*), and by the delocalization energy in the cyclopentadienide ion. The first effect is barrier-raising and the second and third ones are barrier-lowering.

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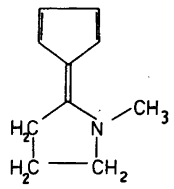
The energies of interaction of heteroatoms as electron donors with unsaturated groups and with carbocations have been much discussed in recent years, and PMO arguments supported by *ab initio* calculations show that the energy of interaction, ΔE, with a carbocation is much greater than with a double bond.[24] In the PMO model with neglect of overlap, ΔE is determined by the energy gap between the "lone pair" orbital of the donor (n_x) and the lowest empty orbital of the acceptor (π^*) and by the matrix element, H_{ij}, between these orbitals (eqn. (1)).[25] The variation in H_{ij} is normally much smaller than that in the energy gap, and ΔE is in

$$\Delta E \approx \frac{2H_{ij}^2}{E(\pi^*)-E(n_x)} \qquad (1)$$

most cases determined by the latter quantity. Thus the low barriers in compounds *4b*, *4c*, and *5* are explained by the good stabilization of the negative charge in the transition state in the cyclopentadienide ion and of the positive charge in the heteroatom-substituted carbocation. The order of these barriers and also the higher barrier in *4a* is determined by the order of n_X, n_Y energies, which fall off in the series X, Y = N, S, O as indicated by the vertical ionization potentials of Me_2NH (8.24 eV), MeSH (9.44 eV) and MeOH (10.85 eV).[26] Since π^* is always higher than n_x, the energy gap increases and ΔE decreases in the above sequence. The high barrier of *4c* as compared to *5* is probably largely due to the phenyl ring, which diminishes the donor capacity of the attached nitrogen atom in *4c*.

The free energy barrier of *4b*, 76 kJ mol^{-1} in toluene-d_8, is similar in magnitude to that of 6-methyl-6-dimethylaminofulvene, 73 kJ mol^{-1}, in deuteriochloroform[11] and that of the analogue *10*, 82 kJ mol^{-1}, in acetone.[12] This is in harmony with the fairly poor donor capacity of the oxygen atom. The barrier of *4b* is harder to reconcile with the observation by Downing *et al.*[11] that the analogue *11* shows an averaged (AA'BB') spectrum down to



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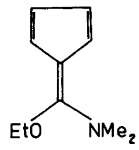
−60 °C. The explanation may be an accidental isochrony of H^2 with H^5 and of H^3 with H^4, rather than a low barrier, and it could be worth while to reinvestigate *11* in a variety of solvents, considering the strong solvent effect on the spectrum of *4b*.



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Several authors[17,27-29] have observed that rotational barriers in push-pull ethylenes are successively lowered by increasing solvent polarity. This is in good agreement with the proposed mechanism for the rotation with a dipolar transition state that is more stabilized by a polar solvent than the less polar initial state. The influence of solvent polarity on the free energy barrier of *4b* is unusually large, (Table 2) with a lowering of 12 kJ mol^{-1} from toluene-d_8 to acetonitrile-d_3. This effect can be semiquantitatively treated by the reaction field model.[30] The reaction field is created by a point dipole in a polarizable medium, and its strength at the position of the dipole is given by eqn. (2). The direction of the field in this point is the same as that of the dipole, and the energy of interaction between dipole and field is given by eqn (3). In eqns. (2) and (3), ε is the dielectric constant

$$R = \frac{K(\varepsilon-1)}{2\varepsilon+1}\frac{\mu}{a^3} \qquad (2)$$

$$\Delta E = R\mu = \frac{K(\varepsilon-1)}{2\varepsilon+1}\frac{\mu^2}{a^3} \qquad (3)$$

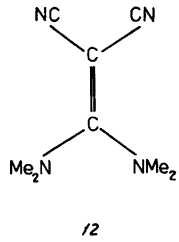
of the medium, μ is the dipole moment of the solute, and a is the radius of a cavity, assumed spherical, which contains the molecule. If a is given in Å, μ in D, and E in kJ mol^{-1}, K has the value 60.23.

For liquid compounds, a is calculated by eqn. (4), where M is the molecular weight, N is Avogadro's number, and ρ is the density of the pure liquid. For the compounds used in this study, the density in the

$$4\pi a^3/3 = M/N\rho \qquad (4)$$

liquid state is not known, but from comparisons with similar compounds, values between 1.0 and 1.1 seem reasonable for *4b* and *4d*. This gives $a = 3.77-3.89$ Å for *4b* and $3.88-4.00$ Å for *4d*.

The dipole moments of the initial and the transition states are also required in order to calculate the solvent effect on the rotational barrier. These moments are available from the CNDO/2 calculations. Previous experience shows that such calculations reproduce the experimental dipole moments of push-pull ethylenes reasonably well.[31] The calculated initial state moment for *4d* is 6.15 D, and it can be compared with that for 6,6-bis(dimethylamino)fulvene (*3*, R = CH_3), 5.4 D.[6] The moment for the latter compound is expected to be lower because of steric hindrance to coplanarity of the dimethylamino groups but this probably does not explain the whole discrepancy. The dipole moments for two similar compounds, *12* and *13*, are



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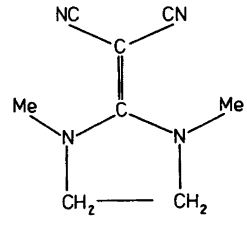

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7.84 D and 7.93 D, to be compared with the calculated values of 6.32 D and 7.86 D, respectively.[31]

The solvation energies for the initial state (ΔE_{is}) and the transition state (ΔE_{ts}) have been calculated by eqn. (3) for acetonitrile (ε36.2) and toluene (ε2.38). The solvent effect, $\delta\Delta E$, is given by eqn. (5). It depends greatly on the value chosen for a, and instead of fixing this value we have traced the

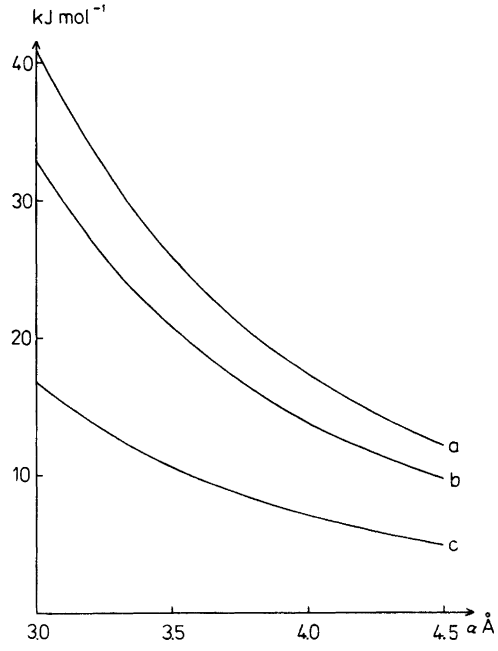

Fig. 1. Calculated difference in solvation energy between acetonitrile and toluene for *4b*. (a), $\mu_{is}=6.38$ D and $\mu_{ts}=10.84$ D; (b), $\mu_{is}=5.70$ D and $\mu_{ts}=9.70$ D; (c), Calculated solvation energy for *6* in dichloromethane for $\mu_{is}=4.30$ D and $\mu_{ts}=6.03$ D.

$$\delta\Delta E=(\Delta E_{ts}-\Delta E_{is})_{acetonitrile}-(\Delta E_{ts}-\Delta E_{is})_{toluene} \quad (5)$$

dependence of $\delta\Delta E$ on a in the range $a=3.0-4.5$ Å. The calculations were performed with the CNDO/2 dipole moments $\mu_{is}=6.38$ D and $\mu_{ts}=10.84$ D (Table 3), but also with the perhaps more realistic moments $\mu_{is}=5.70$ D and $\mu_{ts}=9.70$ D. These values were obtained by introducing a scaling factor for all the calculated moments, which gives *4c* the value 5.5 D, 0.1 D larger than that for *3*, $R=CH_3$ corresponding to the difference between *12* and *13*. The results are shown in Fig. 1.

It is obvious that the calculated solvent effect is somewhat larger than the experimental one of 12 kJ mol^{-1}. In view of the uncertainties in a and the dipole moments it is not very meaningful to discuss the reason for the discrepancy. In any case, the reaction field model accounts for the observed solvent effect in a semiquantitative way, and the large effect can be ascribed to an unusually large difference between μ_{ts} and μ_{is}.

The CNDO/2 calculations give the rotational barriers in the gaseous state, $E_{ts}-E_{is}$. The calculated barrier for *4b* is 125.9 kJ mol^{-1}, to be compared with the experimental free energy barrier of 76.0 kJ mol^{-1} (in toluene). The activation enthalpy is more appropriate for a comparison than the free energy barrier, but it is not known for *4b* though it is certainly lower than 76.0 kJ mol^{-1}. Shvo *et al.*[32] found the activation anthalpy to rotation around the C=C bond in *6* to be 34.7 kJ mol^{-1} in dichloromethane, to be compared with 145.6 kJ mol^{-1} calculated by the INDO method. The corresponding values for the rotation about the C–N bond were in much better agreement, 54.0 and 37.2 kJ mol^{-1}. The large difference between the experimental and calculated barriers to rotation about the C=C was mainly ascribed to the solvent effect, though no attempt was made to quantity this hypothesis. This can be made using the reaction field model. For *4c*, the increase in stabilization from gas phase to toluene solution is the same as the solvent effect from acetonitrile to toluene, since $(\varepsilon-1)/(2+1)$ for acetonitrile is by chance precisely twice the value for toluene. Clearly, the experimental value of 12 kJ mol^{-1} vastly underestimates the difference of 57 kJ mol^{-1} between the calculated and experimental barriers.

No experimental solvent effect is available for *6*, but an approximate calculation of the difference in stabilization energy between the gas phase and dichloromethane solution can be made by eqn. (3), using $\mu_{is}=4.30$ D and $\mu_{ts}=6.03$ D from the INDO calculations.[32] Values for the cavity radius a from 4.06 to 4.19 Å are obtained under the same assumptions as for *4b*. The $\delta\Delta E$ values are shown by the lowest curve in Fig. 1, and it is obvious that the solvent effect is quite small, and that the calculated rotational barrier for *6* is even more off the mark than that for *4b*. Thus, the discrepancies between experimental and calculated barriers cannot be ascribed to neglect of solvent stabilization but must be due to the approximations in the methods of calculation. All valence electron calculations with total neglect of differential overlap sometimes have given quite good agreement with experimental barriers,[33,34] but that has been when a group rotates that is small compared to the rest of the molecule, and the effect of the rotation is only a small perturbation of the total energy of the molecule. This is not the case with rotations about the C=C bond in compounds like *4b* and *6*, and calculation of barriers to such processes evidently requires more advanced methods.

Table 4. Calculated formal charges (π-electron charges in parentheses).

Molecule	q_1	q_2[a]	q_3[a]	q_6	q_N/q_S	q_O
4a						
Initial state	−0.1154	−0.0460	−0.0442	+0.3014	−0.1002	−0.2080
	(−0.2005)	(−0.0855)	(−0.0648)	(+0.1920)	(+0.2318)	(+0.1254)
Transition state	−0.1595	−0.0698	−0.0867	+0.4048	−0.0853	−0.1881
	(−0.3038)	(−0.1791)	(−1.4002)	(+0.3711)	(+0.3109)	(+0.1807)
4b						
Initial state	−0.1107	−0.0453	−0.0404	+0.3375	−0.1487	−0.2114
	(−0.1928)	(−0.0879)	(−0.0589)	(+0.1917)	(+0.2355)	(+0.1228)
Transition state	−0.1590	−0.0641	−0.0849	+0.4403	−0.1208	−0.1905
	(−0.3092)	(−0.1757)	(−0.1374)	(+0.3889)	(+0.3370)	(+0.1743)
4d						
Initial state	−0.1231	−0.0476	−0.0483	+0.2872	−0.1502	–
	(−0.2165)	(−0.0899)	(−0.0733)	(+0.1925)	(+0.2255)	–
Transition state	−0.1566	−0.0771	−0.0889	+0.3671	−0.1263	–
	(−0.2970)	(−0.1837)	(−0.1432)	(+0.3505)	(+0.2991)	–

[a] q_4 and q_3, like q_5 and q_2, are quite similar. X is the atom with lowest atomic number of X and Y.

The calculated barrier for *4d* is 95.8 kJ mol^{-1}. The experimental barrier is not known, but it is in all likelihood somewhat lower than that of *4c*, 42 kJ mol^{-1}, and higher than that of *5*, which has 30 kJ mol^{-1} as an estimated upper limit. A reasonable estimate for *4d* is 35 kJ mol^{-1} and it is evident that no realistic solvent effect can explain the difference of *ca.* 60 kJ mol^{-1} between the experimental and calculated barriers. However, even if the CNDO/2 calculations are unable to give good rotational barriers for these compounds, some comfort can be taken from the fact that the barriers of *4a*, *4b* and *4d* fall in the right order, and that the calculated difference between *4b* and *4d*, 37.4 kJ mol^{-1}, does not differ much from the estimated difference between their free energy barriers of *ca.* 40 kJ mol^{-1}.

The calculated charge distributions for the initial and transition states are shown in Table 4. The effects are similar to those found in previous calculations on push−pull ethylenes.[31] The donor atoms (N,O,S) lose π-electrons but are more than compensated through their inductive attraction for σ-electrons. The electron density on C−1 is high and that on C−6 is low with respect to both π- and σ-electrons. The cyclopentadiene ring attracts electrons in the initial state, but the polarization is much increased in the transition state.

The charge density on C−1 and C−6 is reflected in the chemical shifts of the corresponding ^{13}C resonances. While C−2 to C−5 fall in the range of δ113−120, the C−1 resonance falls at *ca.* δ 100 and that of C−6 at *ca.* δ 160, in agreement with data from other push−pull ethylenes.[35]

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