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Studies of Polarized Ethylenes

Part VI.* Internal Rotations, Dipole Moments, and Ultraviolet Spectra of Nitroethylenes. Experimental Results and PPP Calculations

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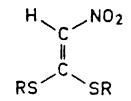
The barrier to rotation around the C=C bond in 1-methylthio-1-benzylthio-2-nitroethylene has been found to be *ca.* 28 kcal/mol by stereomutation. Considerably lower barriers to rotations around C=C and C–N bonds in the 1-methylthio-1-dimethylamino- and 1,1-bis-dimethylamino analogs have been determined by the NMR lineshape technique. Dipole moments and UV spectra have been measured and correlated with charge distributions and transition energies calculated by the PPP method.

The ^{1}H NMR spectrum of 1,1-bis-methylthio-2-nitroethylene (Ia) has been described by three groups of workers.[1–3] While Gompper and Schaefer[1] and Jensen *et al.*[2] observed a singlet for the *S*-methyl protons at ambient temperature, a doublet was observed below 0°C in deuteriochloroform ($\Delta\nu = 1.4$ Hz) and below −5°C in pyridine ($\Delta\nu = 2.3$ Hz, both at 60 MHz).[3] This observation was interpreted as the result of a hindered rotation around the C=C bond with $\Delta G^{\ddagger} = 14.8$ kcal/mol (from the coalescence temperature). However, later investigations showed that Ia gave a doublet at ambient temperature in benzene solution, which persisted when the temperature was raised. Furthermore, the benzyl analog Ib gave a doublet for the benzylic methylene protons also in deuteriochloroform solution,[2] and in *o*-dichlorobenzene solution this doublet persisted without exchange broadening to +180°C. It was therefore concluded that the barrier reported for Ia in Ref. 3 was questionable, and new attempts were made to determine this and analogous barriers. It has been observed that the barriers to rotation around the C=C bond in polarized ethylenes depend to a great extent on the character of the electron-donating groups, and for this reason the study has been extended to compounds III, IV, and V. The UV spectra have been recorded for compounds Ia, III, IV, and V, and the dipole

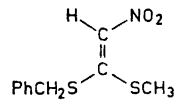
* Part V. Wennerbeck, I. *Acta Chem. Scand.* **27** (1973) 258.



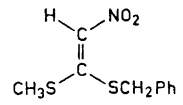
I, a. R = CH_3

b. R = CH_2Ph

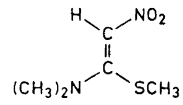
moments have been measured for Ia, IV, and V. These data have been correlated with the results of MO calculations by the Pariser-Parr-Pople (PPP) method.



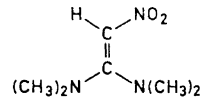
IIa



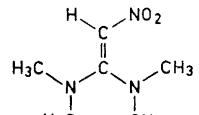
IIb



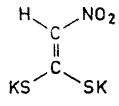
III



IV



V



VI

EXPERIMENTAL

Preparative part. The starting material, *d potassium 2-nitroethylene-1,1-dithiolate* (VI) was prepared according to Freund [4] from nitromethane, carbon disulphide, and potassium hydroxide in ethanolic solution. The dry crystals are labile and have detonated at room temperature on several occasions.

1,1-Bis-methylthio-2-nitroethylene (Ia) was prepared as described by Gompper and Schaefer [1] and gave the same physical data as reported by these authors.

1,1-Bis-benzylthio-2-nitroethylene (Ib) was prepared as described by Jensen *et al.*[2]

1-Methylthio-1-benzylthio-2-nitroethylene (II) was formed in two diastereomeric forms, here referred to as A and B. Methyl iodide (1.23 ml, 0.02 mol) in ethanol (20 ml) was added to a solution of VI (4.26 g, 0.02 mol) in water (20 ml). After 30 min a precipitate of Ia was removed by filtration, and benzyl chloride (2.3 ml, 0.03 mol) in ethanol (60 ml) was added. On the following day a precipitate of pale yellow crystals had formed, consisting according to the NMR spectrum of a mixture of A and B in the ratio 1:1. Variation of solvent ratios and order of addition of the alkylating agents gave different proportions of A and B. This result was in some cases observed even in parallel experiments under apparently identical conditions. In one experiment even a sample of pure isomer B was obtained, but this could never be repeated.

The separation of isomers A and B was most advantageously performed in the following way. Glass rods were placed in a hot, dilute solution of the isomer mixture in cyclohexane. After several days isomer A had formed long needles on the rods, projecting into the solution, whereas isomer B formed plates, firmly adhering to the surface of the rods. The crystals could be separated manually, and the needles were recrystallized until the pure isomer A was obtained. The melting points are 120 – 123° (A) and 114 – 115.5° (B). (Found: C 49.0; H 4.58; N 5.64; S 26.3. $C_{10}H_{11}NO_2S_2$ (241.34) requires C 49.8; H 4.59; N 5.80; S 26.6.)

1-Dimethylamino-1-methylthio-2-nitroethylene (II). Ia (4.95 g, 0.03 mol) was added to a solution of dimethylamine (0.031 mol) in benzene (40 ml), and the solution was refluxed for 25 min. According to TLC on silica a mixture of Ia, III, and IV had resulted. Chromatography on silica gel and repeated recrystallizations from ethyl acetate gave pure III

(0.3 g, 6 % yield) as orange prisms, m.p. 59°C. (Found: C 37.2; H 6.28; N 17.2; S 19.7. $C_5H_{10}N_2O_2S$ (162.22) requires C 37.0; H 6.21; N 17.3; S 19.8.) The time of refluxing is critical, since on prolonged reaction time only Ia and IV are observed.

1,1-Bis-dimethylamino-2-nitroethylene (IV). Ia (4.95 g, 0.03 mol) was dissolved with dimethylamine (0.12 mol) in benzene (90 ml), and the mixture was allowed to stand for 24 h at room temperature. Evaporation and recrystallization twice from acetone gave pale yellow prisms (2.4 g, 50 % yield), m.p. 118°. (Found: C 45.1; H 8.25; N 26.3; O 20.3. $C_6H_{13}N_3O_2$ (159.19) requires C 45.3; H 8.23; N 26.4; O 20.1.)

1,3-Dimethyl-2-(nitromethylene)imidazolidine (V). *N,N'*-Dimethylethylenediamine (8.8 g, 0.1 mol) was added to a solution of Ia (16.5 g, 0.1 mol) in ethanol (300 ml), and the solution was refluxed for 2 h. Evaporation and repeated recrystallization from toluene gave light yellow prisms (4.2 g, 27 % yield), m.p. 120 – 121°. (Found: C 45.7; H 7.10; N 26.4; O 20.7. $C_6H_{11}N_3O_2$ (157.18) requires C 45.8; H 7.05; N 26.7; O 20.4.)

NMR Spectra were recorded on Varian A 60, HA-100, and/or XL-100 instruments, equipped with variable temperature probes and V-6040 temperature controllers.

Temperature measurements. In the majority of the isomerization experiments, the temperature was measured with the aid of an internal ethylene glycol capillary, previously calibrated against a copper-constantan thermocouple. In the other cases, the temperatures were recorded by the substitution technique, employing a precalibrated methanol or ethylene glycol sample. In the former case, the temperature readings are probably accurate to $\pm 0.3°$, in the latter to $\pm 2°$.

Isomerization experiments. The kinetics of the isomerization A $\rightleftharpoons$ B (IIa $\rightleftharpoons$ IIb) was studied by integration of the methyl and methylene signals of samples in *o*-dichlorobenzene solution (60 mg of substance in 0.5 ml of solvent) at different temperatures in the range 84 – 109°. The equilibrium ratio was 1:1 within the experimental accuracy in this temperature range. The evaluation of the rate constants was performed as described in Ref. 5, and the results are presented in Table 1.

Table 1. Rate constants and thermodynamic parameters for the isomerization IIa $\rightleftharpoons$ IIb.

Isomer	T°C	$k \times 10^{-3}$ sec^{-1}	$\Delta G^{\ddagger}$ kcal/mol
A	92.0	0.40	27.7
A	102.0	0.71	28.0
B	84.9	0.066	28.4
B	90.0	0.122	28.5
B	91.4	0.182	28.2
B	95.0	0.230	28.3
B	97.5	0.268	28.4
B	109.0	0.63	28.7

$\Delta H^{\ddagger} = 24.0 \pm 2.7$ kcal/mol.
$\Delta S^{\ddagger} = -12 \pm 7$ e.u.

Lineshape determination of rotational barriers. The barrier to rotation around the C–N bond in III (see Results and discussion) was determined at the coalescence temperature by employing the approximate formula 1, obtained from the Eyring equation and the expression for the mean lifetime at coalescence.[6] In IV, one of the two barriers to rotation

$$\Delta G^{\ddagger} = 0.004573\ T_c\left(9.972 + \log \frac{T_c}{\Delta \nu_0}\right) \quad (1)$$

around C–N bonds and the one to rotation around the C=C bond were determined by a line-fitting procedure. Theoretical spectra were generated by a four-sites exchange program, utilizing the exchange scheme in Fig. 1 and the Bloch equations with exchange

terms as described in Ref. 7, and the chemical shifts and rate constants were varied to give the best visual fit between theoretical and experimental spectra. The results are presented in the discussion.

Dipole moment measurements were performed with a Dipolmeter Type DM 01 from WTW, Weilheim, D.B.R. The standardization was made with benzene (Merck, zur Analyse) and dibutyl ether (freshly distilled). The measurements were performed in benzene solution in a cell thermostated to 25.0°C, and the dipole moments were evaluated using the method of Hedestrand.[8] The slopes of the plots of dielectric constants and indexes of refraction *versus* weight fractions (a_ε and a_n) were obtained by the method of least squares. The results are given in Table 2.

Table 2. Dipole moment data.

Compound	Weight fraction range × 10^2	a_ε	a_n	μD
Ia	0.921 – 2.89	21.46	0.41	5.64 ± 0.02
IV	0.139 – 2.00	38.60	0.44	7.64 ± 0.01
V	0.0486 ± 0.491	38.39	0.38	7.39 ± 0.01

Compound V is rather slightly soluble in benzene and had to be measured in the weight fraction range $(0.5-5)\times10^{-3}$. However, measurements on IV in this range and in the range $(0.14-2.0)\times10^{-2}$ gave nearly the same result, and the value for V can be regarded as reliable.

Molecular orbital calculations were carried out with the SCF–MO–CI method according to Pariser and Parr [9,10] and Pople [11] with the parametrization developed by Roos *et al.*[12,13] Configuration interaction was performed between all singly excited states. The geometry

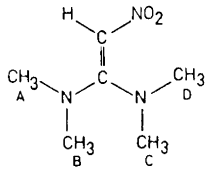
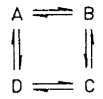


Fig. 1. Exchange diagram for rotation around the C=C and both C–N bonds in IV.



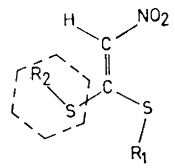


Fig. 2. Assumed time-average orientation of 1,1-bis-alkylthio-2-nitroethylene and benzene molecules.

of the nitroethylene part of the molecule was taken from the microwave study of Hess *et al.*[14] The geometry around carbon atom 1 was taken from an X-ray crystallographic investigation by Abrahamsson *et al.*[15] on 1,1-bis-methylthio-2-cyano-2-*p*-bromobenzoylethylene and 1,3-dimethyl-2-(cyano-*p*-bromobenzoylmethylene)imidazolidine.

RESULTS AND DISCUSSION

NMR Spectra and barriers. The NMR spectrum of Ia shows a doublet for the *S*-methyl protons in benzene up to 70°C, and in *o*-dichlorobenzene solution a sharp doublet persists up to 170°C. The behaviour in deuteriochloroform and in pyridine solution previously interpreted as a coalescence due to exchange [3] is instead due to a temperature-dependent chemical shift difference. This is demonstrated by the fact that the singlet splits into a doublet above +59°

in deuteriochloroform solution. In pyridine a similar behaviour is observed, with $\Delta\nu = 1.6$ Hz at $+98°C$ (60 MHz). This shows that great care must be exercised when barriers are obtained from exchange broadened doublets with small non-exchanging internal chemical shifts.

Evidently, the normal lineshape method is not suited for measuring the barriers in Ia and Ib. Instead, the stereomutation of an unsymmetrical analog was investigated by the integration technique. As described in the experimental part, two diastereomers, A and B, of the general structure II could be prepared. The assignment of structures IIa and IIb to these diastereomers could be made with the aid of the shifts induced by aromatic solvents (ASIS). It is generally conceded that dipolar solute molecules and aromatic solvent molecules form loose collision complexes, in which the aromatic molecules are oriented on the time-average as far away from the negative ends of the solute dipoles as possible.[16] In the case of compounds II, the time-average orientation should be as in Fig. 2. The benzylic methylene protons in IIa should show a larger upfield shift than those in IIb on going from deuteriochloroform to benzene solution or on increasing the dilution in a pure benzene solution. In the same way, the *S*-methyl proton signal in the spectrum of IIb should show larger upfield shifts than that in the spectrum of IIa under the same conditions.

Table 3. Chemical shifts of methyl and benzylic methylene protons in A and B at large dilution.

Compound	Group	ν_{CDCl_3} Hz	$\nu_{C_6H_6}$ Hz	$\Delta\nu$ [a] Hz
A	CH_3	149	105	44
B	CH_3	149	79	70
A	CH_2Ph	248	190	58
B	CH_2Ph	255	230	25

[a] $\Delta\nu = \nu_{CDCl_3} - \nu_{C_6H_6}$

The shift values listed in Table 3 show that, provided the above assumptions are correct, compound A has structure IIa and compound B structure IIb.

The negative activation entropy is in qualitative agreement with the negative entropies observed for 1-benzylthio-1-methylthio-2-carbomethoxy-2-cyanoethylene ($\Delta S^{\ddagger} = -24.0 \pm 2.9$ e.u.) and 1,1-bis-methylthio-2-benzoyl-2-cyanoethylene ($\Delta S^{\ddagger} = -16.5 \pm 1.6$ e.u.).[17] For these compounds, as well as for compounds I and II, a polar transition state is assumed for the rotation around the C=C bond. The negative $\Delta S^{\ddagger}$ values indicate that this transition state is also more strongly solvated than the initial state. Unfortunately, the uncertainty in $\Delta S^{\ddagger}$ in the present case precludes a more detailed analysis of this effect.

The barrier measured for II is considerably lower than for simple ethylenes, but it is higher than for the majority of ethylenes with push-pull substituents studied in Ref. 17. In these, two electron-attracting groups contribute to the stabilization of the negative charge in the polar transition state, whereas in II there is only one, although a rather efficient one. The σ_R-value for the

nitro group, 0.64, is less than the sum of those for, *e.g.*, the cyano and carbomethoxy groups (+0.77),[18] which may be qualitatively correlated with the $\Delta H^{\ddagger}$ values for the rotation in II (24.0 kcal/mol) and in 1-methylthio-1-benzylthio-2-carbomethoxy-2-cyanoethylene (14.7 and 15.0 kcal/mol for forward and reverse reactions).

At ambient temperature, the NMR spectrum of III in deuteriochloroform consists of singlets for the methylthio, dimethylamino, and vinyl protons at δ=2.58, 3.33 and 6.80 ppm, respectively.

The same general appearance is observed in dichlorofluoromethane solution, but at −99°C the dimethylamino signal splits into a symmetrical doublet ($\Delta\nu_0$=12.2 Hz). Since neither the *S*-methyl nor the vinyl proton signals show broadening or doubling indicative of exchange down to *ca.* −115°C, it is evident that the doubling of the dimethylamino signal is due to a slow rotation around the C–N bond. For this rotation, $\Delta G^{\ddagger}$ = 8.9 kcal/mol at the coalescence temperature is calculated by formula (1). The rotation around the C=C bond may be fast at −115°, but the absence of exchange broadening of the vinyl and *S*-methyl proton signals at this temperature may also be due to the existence of one strongly preferred conformation with respect to the C=C bond. If this is the reason, steric factors indicate the *Z* conformation as the most likely one (nitro and *S*-methyl groups on the same side of the double bond).[19]

The low temperature NMR spectrum of IV in dichlorofluoromethane showed splittings indicative of slow exchange, but a detailed analysis was precluded by the small internal chemical shifts. In a 1:1 (v/v) mixture of fluorobenzene and dichloromethane a singlet was observed at ambient temperature, but this broadened from *ca.* −40° and split at −53° into a doublet with the intensity ratio 3:1 (Fig. 3). At −63° the low field signal split into a 2:1 doublet, and from

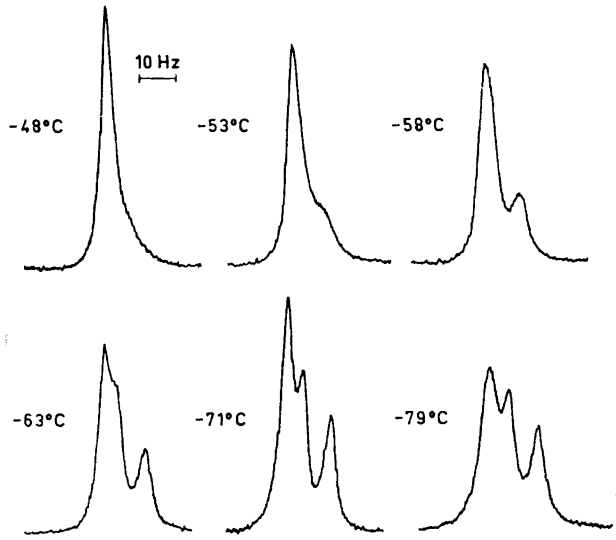


Fig. 3. 60 MHz ^{1}H NMR spectra of the dimethylamino groups in IV in a solution in fluorobenzene and dichloromethane (1:1, v/v).

about $-80°$ the low field component of this was further broadened, but at still lower temperatures crystallization of the solute precluded further measurements. An analysis as described in the experimental part shows that the upfield doublet below $-63°$ is due to one dimethylamino group and the downfield singlet to the other. At $-71°$ $\Delta G^{\ddagger}$ for rotation around the C=C bond is found to be 10.7 kcal/mol, and for rotation around one of the C–N$(CH_3)_2$ bonds 11.8 kcal/mol. The barrier for the other C–N$(CH_3)_2$ bond is probably lower than 10 kcal/mol. The NMR spectrum of V in dichlorofluoromethane shows singlets for the *N*-methyl protons and the ring protons down to $-125°$.

Dipole moments. The dipole moments have been recorded for Ia, IV, and V in order to get an idea of the π-electron distribution in these molecules. The dipole moments have been treated as vector sums of π and σ moments, and the σ moments have been taken from Ref. 20, with the exception of that for the nitro group. The σ moment for this group was obtained from nitromethane. A PPP calculation on the nitro group gave a π moment of 2.9 D, which was subtracted together with the methyl group moment (0.4 D) from the nitromethane gas phase value of 3.46 D [21] to give a σ moment for the nitro group of 0.2 D, directed from the nitrogen towards the oxygen atoms along the symmetry axis.

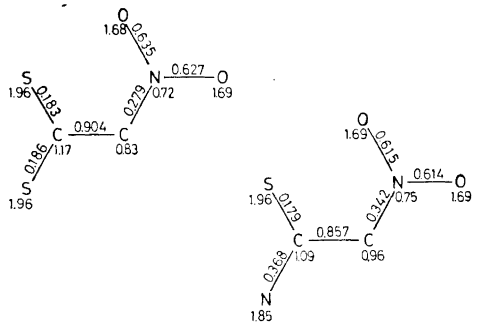
In Ia, the methyl groups are assumed to be oriented as in Fig. 2 to avoid steric interferences. The group moment for the SCH_3 group, 1.4 D,[20] is assumed to bisect the  angle and to be directed as indicated by the arrow. In IV, the CN bond moments in the dimethylamino group are assumed to cancel, which is an approximation, since the carbon atoms have different states of hybridization.

The PPP calculations gave a π-electron moment of 3.74 D for Ia and 6.18 D for IV. Vector addition of the σ moments gave a total moment of 4.15 D for Ia and 6.75 D for IV. The calculated moments are 1.5 D and 0.7 D too low, which is not discouraging in view of the uncertainties in the σ moments. The calculated π-electron distributions in the ground and first excited states and the π bond orders in the ground state are shown in Fig. 4.

The close similarity of the moments of IV and V is surprising in view of the large differences in barriers to rotation around the C=C bond observed for analogs of IV and V with the same set of electron-attracting substituents.[7,22] Since the analogs of V have the lowest barriers, they would be expected to show the largest initial state polarizations. An explanation may be found in different degrees of twisting around C-amino and C-nitro bonds. However, a detailed discussion of this effect will have to await the results of a more extensive investigation of dipole moments of polarized ethylenes, which is at present underway.

The π-electron densities on C_2 in Ia (0.83), III (0.96), and IV (1.03) show a rough correlation with the chemical shifts of the vinyl protons, 7.12, 6.80, and 6.38 ppm, respectively, in deuteriochloroform solution. In this case, however, the anisotropy effects of the neighbouring groups must also be taken into account.

Ultraviolet spectra have been recorded for compounds Ia, III, IV, and V



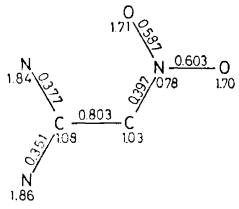


Fig. 4a. Calculated charge distributions and bond orders in the ground states of Ia, III, and IV.

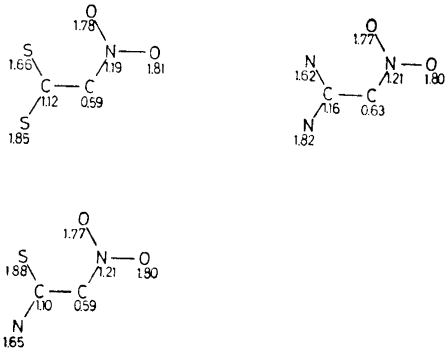


Fig. 4b. Calculated charge distributions in the first excited states of Ia, III, and IV.

in heptane (with 0.3 % dichloromethane for solubility reasons) and absolute ethanol solutions. The experimental and theoretical λ_{max} values, experimental log ε values, and experimental and theoretical oscillator strengths (f) are found in Table 4. Since λ_{max} for nitroethylene is 203 nm with a shoulder at 242 nm,[23] the electron-donating substituents have considerable bathochromic effects. The strongest bathochromic effect is observed in III with one dimethylamino and one methylthio group, whereas the other three compounds have rather similar spectra in heptane solution. This effect is not reproduced by the PPP calculations, which give λ_{max} values increasing in the series I, III, and IV.

Table 4. Experimental and theoretical ultraviolet spectra.

Compound	Experimental					Theoretical	
	Ethanol		Heptane				
	λ_{max} nm	log ε	λ_{max} nm	log ε	f	λ_{max}	f
I	291	3.78					
	355	4.17	335	4.12	0.221	298.1	0.318
III	370	4.28	348	4.09	0.232	308.0 [a]	0.484
IV	345	4.33	333.5	4.21	0.296	328.3	0.459
V	333.5	4.22	332 [b]	4.19 [b]	—	—	—

[a] *Z* conformation.
[b] In heptane with 0.6 % dichloromethane.

The calculated oscillator strengths are 1.5 – 2 times as large as the experimental ones, but this is a general feature of the PPP method.

Changing the solvent from heptane to ethanol causes considerable bathochromic shifts for Ia, III, and IV, but only a small one for V. Such large shifts are generally interpreted as consequences of increased polarization during the electronic transition. The charge distribution in the first excited state of compounds I, III, and IV (taking configuration interaction into account) is given in Fig. 4. The excited state dipole moments are 11.5 D, 10.6 D, and 11.6 D, respectively, nearly parallel with the ground state dipole moments. Evidently, the excitation causes strong increases in the dipole moments in the same direction as that of the ground state moments, and this is in very satisfactory agreement with the observed solvent shifts.

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