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Studies of Polarized Ethylenes. Part XII.* Conformational Analysis of 2-Dimethylamino-2-methylthioethylenes

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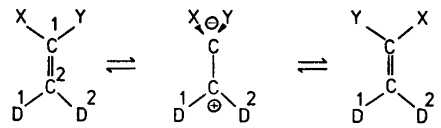
The conformations and rotational barriers in a series of push-pull substituted ethylenes with a variety of acceptor groups and with MeS and NMe_2 as donor groups have been studied by ^1H and ^{13}C NMR techniques. This donor combination is found more efficient than two NMe_2 groups in lowering the C=C barriers. On the other hand, the resonance stabilization of the planar initial state, as measured by infrared spectra and by the barriers to rotation of the NMe_2 and the acceptor groups, seems to be inferior to that in the bis(dimethylamino) analogues.

Attempts to correlate the barriers with different types of substituent constants have been unfruitful, showing that the interaction between donor and acceptor group across the double bond is highly dependent on the individual combinations of groups in a non-additive way.

Torsional barriers in push-pull ethylenes have been the subject of numerous investigations, aiming at an understanding of the effects of different donor and acceptor groups. The work up to 1971 has been reviewed by Kalinowski and Kessler,[1] and a more recent review is found in a textbook on dynamic NMR spectroscopy.[2] It is generally found that the barrier to rotation about the C=C bond is successively lowered by an increasing capacity of the acceptor groups to stabilize a negative charge and of the donor groups to stabilize a positive charge, in agreement with the generally accepted picture with a zwitterionic transition state to this rotation (Scheme 1). As in simple acylenamines, hindred rotation of the acceptor and donor groups is also often observed.[3,4]



Scheme 1.

A large variety of donor groups has been employed, including dimethylamino groups, methylthio groups, and groups that give rise to aromatic rings in the transition state, such as in calicenes [5] and 2- and 4-methylenedihydropyridines.[3,6,7] In the majority of the systems studied the rotational barriers fall within the range accessible to conventional NMR bandshape technique.

Shvo and Belsky [8] have studied a number of push-pull ethylenes with one dimethylamino group and one methylthio group as donors, using only methoxycarbonyl and cyano groups as acceptors. We have found it of interest to extend this study to other acceptor combinations and to work at lower temperatures in order to obtain a more complete picture of the conformational behavior of this class of compounds. The compounds studied in our investigation are denoted *1—13* (Scheme 2). Of these, *4* and *8* are treated in Ref. 8 as well. The preparations of compounds *1—13* were performed by methods *A—C* (Scheme 3). To make possible the assignment of the close-lying CH_3CO and CH_3S ^1H resonances, the trideuteriomethylthio analogues of *6*, *10* and *12* were prepared by method *C*.

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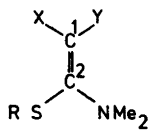


No.	X	Y	R
1	Ph	CN	CH_3
2	p-$O_2NC_6H_4$	CN	CH_3
3	CN	CN	CH_3
4	CH_3OCO	CN	CH_3
5	PhCO	CN	CH_3
6	Ph	$COCH_3$	CH_3
7	Ph	$COCH_3$	CD_3
8	CH_3OCO	CO_2CH_3	CH_3
9	CH_3CO	CO_2CH_3	CH_3
10	PhCO	$COCH_3$	CH_3
11	PhCO	$COCH_3$	CD_3
12	CH_3CO	$COCH_3$	CH_3
13	CH_3CO	$COCH_3$	CD_3
14	H	NO_2	CH_3

Scheme 2.

A 1-nitro analogue (*14*) has been studied previously, showing only slow rotation of the dimethylamino group down to low temperatures.[9] Its C-2–N barrier is included in Table 2 for comparison.

EXPERIMENTAL

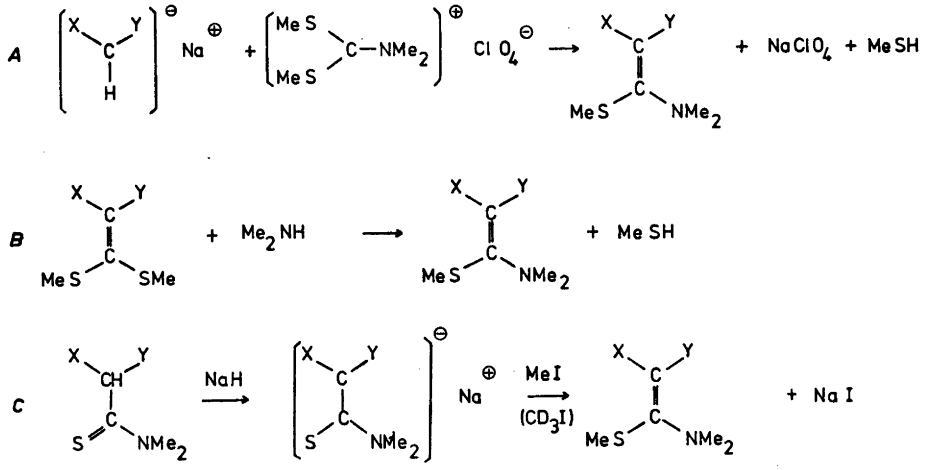
Preparations. The synthesis of compounds *1*,[10] *4*,[11] *9* [12] and *12* [13] was performed by published methods.

*1-Cyano-2-dimethylamino-2-methylthio-*p*-nitrostyrene (2).* (Method *A*). *p*-Nitrophenylacetonitrile (4.4 g, 0.03 mol) in DMF (50 ml) was added dropwise with stirring to a suspension of sodium hydride (3 g, 0.06 mol) in dry benzene (150 ml) during 0.5 h. The mixture was then kept at +50 °C for another 0.5 h, and a solution of dimethylamino-bis(methylthio)-methylium perchlorate [13] in DMF (50 ml) was added. The mixture was left overnight and then poured into water (200 ml). Work-up of the benzene layer gave a yellow solid (3.4 g, 43 % yield), m.p. 112 °C after recrystallization from ligroin (b.p. 60–80 °C). Anal. $C_{12}H_{13}N_3O_2S$: C, H, N, S.

1,1-Dicyano-2-dimethylamino-2-methylthioethylene (3). (Method *B*). A solution of 1,1-dicyano-2,2-(bismethylthio)ethylene (5.1 g, 0.03 mol) and dimethylamine (1.35 g, 0.03 mol) in ethanol (30 ml) was refluxed for 4 h and evaporated. The crystalline residue (3.2 g, 64 % yield) crystallized from absolute ethanol as colourless prisms, m.p. 75–76 °C (lit.[13] 76–77 °C).

1-Benzoyl-1-cyano-2-dimethylamino-2-methylthioethylene (5) was prepared by method *B*, starting from 1-benzoyl-1-cyano-2,2-(bismethylthio)ethylene.[14] Colourless prisms in 73 % yield, m.p. 121–122 °C after recrystallization from toluene–ligroin (1:1 v/v). Anal. $C_{13}H_{14}N_2OS$: C, H, N, S.

1-Acetyl-2-dimethylamino-2-methylthiostyrene (6). (Method *C*). A solution of *N*,*N*-dimethyl-α-acetyl-α-phenylthioacetamide[15] (1 g, 0.045 mol) in DMF (10 ml) was added dropwise with stirring to a suspension of sodium hydride (0.13 g, 0.005 mol) in dry benzene (25 ml), followed by methyl iodide (1 ml, 0.015 mol). Extraction of the benzene solution with several portions of water followed by evaporation gave a liquid residue, which with picric acid (1.2 g, 0.005 mol) in ethanol (10 ml) gave a crystalline



Scheme 3.

picrate (1.6 g, 77 % yield), m.p. 159–160 °C. Anal. $C_{19}H_{20}N_4O_8S$: C, H, N, S. The pure compound *6* used in the NMR experiments was obtained by decomposition of a weighed quantity of the picrate with an excess of 1 N NaOH followed by extraction with benzene, drying with magnesium sulfate and evaporation.

Methyl 2-methoxycarbonyl-3-dimethylamino-3-methylthioacrylate (8) was prepared by method *B*, starting from methyl 1-methoxycarbonyl-2,2-(bismethylthio)acrylate.[16] The reaction required heating to 120 °C for 24 h in a sealed tube. Yield 27 %, m.p. 74–75 °C (lit.[13] 75 °C) after recrystallization from toluene–ligroin (1:1, v/v).

1-Acetyl-1-benzoyl-2-dimethylamino-2-methylthioethylene (10) was prepared by method *B* in a smooth reaction between 1-acetyl-1-benzoyl-2,2-(bismethylthio)ethylene[14] and dimethylamine in ethanol at +10 °C. Yield 77 %, pale yellow prisms, m.p. 94–96 °C after recrystallization from toluene–ligroin (1:2, v/v). Anal. $C_{14}H_{17}NO_2S$: C, H, N, S. This compound is hygroscopic, and *12* even more so.

The ^1H NMR spectra were recorded on a JEOL Model MH-100 NMR Spectrometer, equipped with standard variable temperature probe and temperature controller. *The ^{13}C NMR spectra* were recorded on a JEOL Model FX-60 FT NMR spectrometer operating at 15.03 MHz, also with standard variable temperature equipment.

The solvent for the ^1H NMR spectra was dichlorofluoromethane unless otherwise stated, and the samples were *ca.* 0.8 M in this solvent. Tetramethylsilane was added to provide the internal lock signal. The samples were thoroughly degassed by several cycles of freeze-thawing before being sealed off.

The samples for the ^{13}C spectra contained 20 % of hexadeuterioacetone for the internal lock in addition to dichlorofluoromethane.

The signals below −100 °C were in general quite broad, and the linewidth increased rapidly with decreasing temperature. This may be due to association of the strongly polar solute molecules leading to large, slowly tumbling aggregates with short transverse relaxation times (T_2). This made the determination of T_2 very uncertain and it was not considered advisable to use complete bandshape methods to evaluate the rate constants. The rotations about the C-2–NMe_2 bonds, which give rise to symmetrical uncoupled two-site exchange systems, were treated by the well-known coalescence approximation [eqn. (1)].[17]

$$k_c = \frac{\pi \Delta \nu_0}{\sqrt{2}} \qquad (1)$$

The unequally populated exchange systems arising by rotation about the C-1=C-2 and C-1–X (C-1–Y) bonds were treated by the approximation described by Shanan-Atidi and Bar-Eli.[18] Thus only free energies of activation are obtained, and since they are determined at different temperatures and the activation entropies probably are not negligible, the comparisons made in the discussion are open to criticism. However, as discussed by Shvo *et al.*,[7] it is unlikely that the relative order of the barriers would change if all free activation energies could be measured at one temperature, and the discussion is probably qualitatively correct.

The chemical shifts pertinent to the discussion are found in Table 1, and the C-1=C-2, C-2–N and C-1–X rotational barriers in Tables 2–4. The infrared spectra were recorded as described in Ref. 14, and they are collected together with those of some comparison compounds in Table 5.

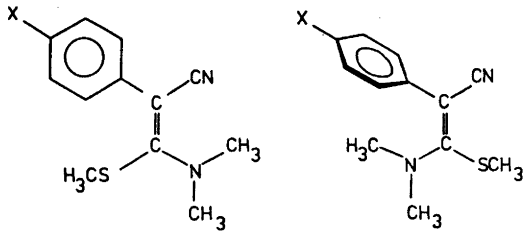
RESULTS

In 1-cyano-2-dimethylamino-2-methylthiostyrene (*1*) the rotation about the C=C bond is slow on the NMR timescale at −20 °C. The SMe ^1H resonance appears as one signal at δ 1.97 and one at 2.39 with the intensity ratio 0.15:0.85. The corresponding signals for the NMe_2 groups appear at δ 3.25 and δ 2.81 in the same intensity ratio. Below −89 °C the major *N*-methyl signal splits into a symmetrical doublet due to slow rotation about the C–N bond. No splitting of the minor *N*-methyl signal was observed down to −150 °C.

Two conformations, *1A* and *1B*, are possible for this compound, corresponding to the weak and strong SMe and NMe_2 signals observed at −20 °C. The assignment of conformation *1B* to the major conformer is made with aid of the high-field position of its NMe_2 signal and the low-field position of its SMe signal. It has been observed in similar systems[4] that a phenyl ring on C-1 exerts a strong shielding effect on a neighbouring dimethylamino group on C-2, and particularly on the nearest *N*-methyl group (Scheme 4).

This is ascribed to a sterically induced twist of the phenyl ring out of the plane of the double bond, which places the NMe protons in the shielding region of the magnetic field caused by the ring current. The cyano group, on the other hand, is deshielding in all directions perpendicular to the CN bond.

The dominance of *1B* over *1A* is not expected when considering steric effects alone. It is possible, however, that the conjugation is more efficient in *1B* where the strongest donor and



Scheme 4.

the strongest acceptor groups are *trans* related. Furthermore, *1B* certainly has the larger dipole moment, which will increase the relative stabilization of this conformer in a polar solvent. The importance of the dipole moment is shown by the decrease of the *1A*:*1B* ratio to 0.12:0.88 in trideuterioacetonitrile as solvent ($t = -25$ °C).

The barrier to rotation of the dimethylamino group in *1B* is 36.7 kJ mol^{-1}. No splitting of the dimethylamino resonance in *1A* could be observed. It has not been possible to decide if this is due to a small non-exchanging chemical shift difference or to a low barrier.

The *p*-nitro analogue *2* shows a similar behaviour, though the C=C barrier is lowered and the C–N barrier in the major rotamer is raised. Thus, below −70 °C the SMe resonance appears as a doublet with the intensity ratio 0.17:0.83 with the major signal at δ 2.50 and the minor at δ 2.13. In the same temperature region the NMe resonance appears as two signals, at δ 2.70 and 3.31 in the intensity ratio 0.83:1.17. On the low-field side of the down-field signal a shoulder appears, which is due to the *N*-methyl resonance of the minor rotamer. The use of other solvents and solvent mixtures did not lead to improved resolution in this spectral region. In the aromatic region a splitting of the upfield part of the AA'BB' spectrum into two multiplets with the same intensity ratio as above occurs in the same temperature region. These observations show that the rotations around the C-1=C-2 bond and around the C-2–N bond in the major rotamer are slow on the NMR timescale below −70 °C ($\Delta G^{\ddagger}$ = 37.2 and 41.7 kJ mol^{-1}, respectively). No splitting of the *N*-methyl resonance of the minor rotamer is observed at lower temperatures, but below −110 °C the upfield part of the AA'BB' spectrum of the major rotamer is split into two multiplets with the same intensities, corresponding to a slow rotation of the *p*-nitrophenyl ring with $\Delta G^{\ddagger} = 32.3$ kJ mol^{-1}.

The assignment of the two rotamers to the structures *2A* and *2B* can be made as for *1*, leading to *2B* as the major form. In 3 only the C-2–NMe_2 barrier can be measured by ^{1}H NMR, but the C-1=C-2 barrier was readily measured by monitoring the temperature-

Table 1. Chemical shifts of ^{1}H resonances.[a]

Compound	*T*/K	δ SMe	δ NMe_2	δ (X)
1	253	2.39; 1.97	2.81; 3.25	–
2	203	2.50; 2.13	3.4 (2.70; 3.31)[b]	–
3	184	2.70	(3.33; 3.35)	–
4	145	2.72; 2.55	(3.17; 3.44)	3.72
5	205	2.68	(3.13; 3.45)	–
6	149	1.74; 1.76; 2.15; 2.31	3.30; 3.16; 2.93	1.94; 1.87; 2.09; 2.53
8	135	2.49	(3.31; 3.44)	3.63; 3.73
9	203	2.44	(3.33; 3.41)	2.40; 3.60
10	143	2.60; 2.22	3.15;[c] (3.42; 3.51)	2.52; 1.69
12	150	2.51	3.54; 3.48; 3.43	2.44 (1.87; 2.46)

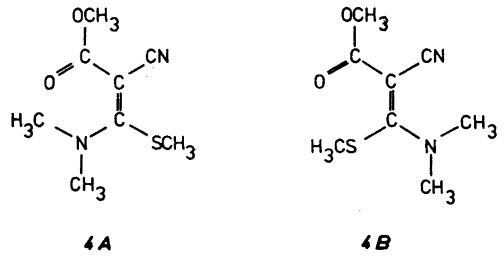
[a] In ppm downfield from TMS, and in order of decreasing rotamer population. [b] Values in parentheses, symmetric doublet. [c] Doublet ($\Delta\nu = 3.8$ Hz) below 200 K, but the splitting disappears due to bandbroadening at lower temperatures.

dependent ^{13}C NMR spectrum of the CN carbon atoms. This appeared as a doublet with $\Delta\nu$ = 18.2 Hz below −15 °C.

The ^1H NMR spectrum of *4* shows singlets corresponding to OMe, NMe_2 and SMe at ambient temperature. At −68 °C the NMe_2 resonance shows decoalescence into a symmetrical doublet, and below −115 °C the high-field components of this as well as the SMe group appear as unsymmetrical doublets with the intensity ratio 0.12:0.88 with the smaller signals on the high-field side. This splitting may be due to the rotation about the C-1=C-2 or the MeOCO−C-1 bonds becoming slow. Since both the SMe and one NMe signal are affected, whereas the OMe signal remains a singlet, the former explanation seems more acceptable. It is also supported by the similarity of the SMe proton chemical shift of the major conformer with that in *3* and in the minor conformer with that in *8* (Table 1).

The high-field NMe signal of the major rotamer was much more broadened than the low-field on decreasing temperature, but down to −140 °C no further splitting was observed.

Shvo and Belsky [8] have proposed that *4A* (Scheme 5) is the dominating conformer, based

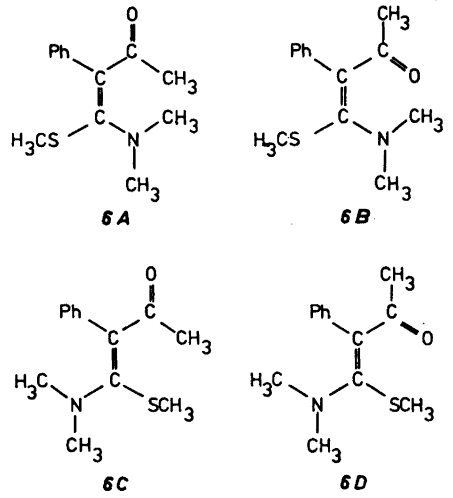


Scheme 5.

on the chemical shifts in *3* and *4*. This conclusion is supported by the above-mentioned similarity of the MeS proton shifts in the minor conformer of *4* and in *8*.

In *5* hindered rotation about the C-1=C-2, C-2−NMe_2, and PhCO−C-1 bonds could be expected, but only the C-2−NMe_2 rotation gave rise to a splitting (t_c −41 °C) above −144 °C. This may be due to the presence of one strongly preferred conformation.

The ^1H NMR spectrum of *6* at ambient temperature displays sharp singlets for the NMe_2, SMe, and MeCO protons. At lower temperatures all signals broaden, and in the temperature region below −110 °C the NMe_2 signal splits into four signals, and the COMe and SMe resonances appear as altogether seven resolved signals. This behaviour is in agreement with the rotations around the C-1−COMe and C-1=C-2 bonds becoming slow in the same temperature region. The spectrum at −124 °C (Fig. 1) shows the four different conformations *6A* to *6D* (Scheme 6), but no clear indication



Scheme 6.

of slow rotation around any of the C-2−NMe_2 bonds. However, this event could happen in one or more of the four conformers with rates

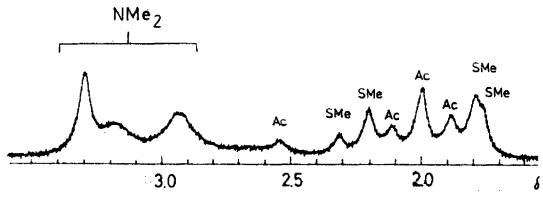
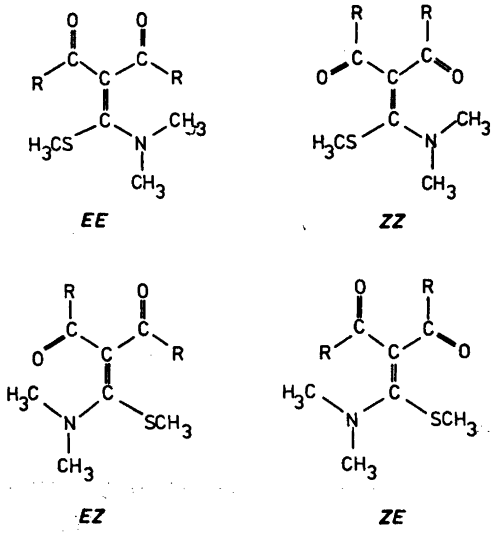


Fig. 1. ^1H NMR spectrum of *6* in $CHCl_2F$ at −124 °C.

similar to those pertaining to the C-1 – COMe and C-1 = C-2 rotations, and the insufficient number of resolved NMe signals could be due to overlap, a possibility, which is difficult to eliminate because of the broadness of the NMe signals. The splitting of the SMe and COMe proton signals, however, definitely proves the existence of the four rotamers *6A* to *6D*, interconverting slowly below −120 °C.

The 1,1-bis(methoxycarbonyl) compound *8* shows OMe, NMe_2, and SMe singlets down to −74 °C, when the NMe_2 signal splits into a symmetrical doublet due to slow rotation about the C-2 – NMe_2 bond. At −130 °C the OMe signal also splits into an unsymmetrical doublet due to slow rotation about the CO – C-1 bond. In the ^{13}C spectrum the CO, C-1 and C-2 resonances remain sharp down to −130 °C, whereas all methyl carbon resonances show strong broadening without further splitting. Thus, though four rotamers are possible for this compound (Scheme 7), there is no evidence



8, R = OCH_3

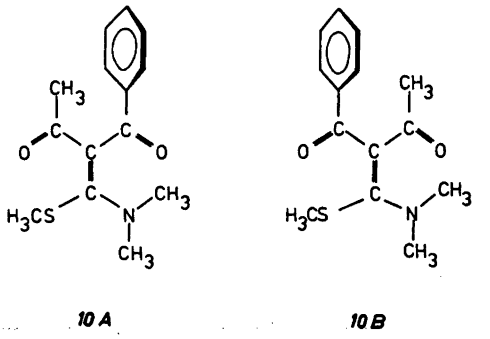
12, R = CH_3

Scheme 7.

for slow rotation about the C-1 = C-2 bond. The unsymmetrical splitting of the OMe resonance indicates slow exchange between one or two symmetrical forms, probably only the *ZZ* form (*vide infra*) and one or two unsymmetrical forms.

In *9* only slow rotation of the dimethylamino group could be observed (t_c −49 °C). No further splittings were observed above −145 °C. This may be due to the presence of one strongly preferred conformation.

The 1-benzoyl-1-acetyl derivative *10* showed splitting of the NMe_2 resonance at −70 °C. The acetyl resonance and the SMe resonance appeared below −115 °C as doublets in the ratio 0.11:0.89. In the same temperature region the NMe_2 resonance is split in the same intensity ratio. Bandshape analysis as well as the similar intensity ratios indicates that all groups are exchanged by the same process, which may be rotation around the C = C bond or rotation of the carbonyl groups. The large shift difference between the acetyl signals and the extreme high-field position (δ 1.69) of the minor signal indicates that the latter explanation is the correct one and that the minor rotamer has the conformations *10A* + *10B* (Scheme 8) with the acetyl methyl shielded by the phenyl ring and the rotation around the C = C bond still being fast. This assignment is supported by the low-field position of the NMe_2 signal in the



Scheme 8.

minor rotamer (δ 3.42 and 3.51), this group being in the deshielding region of the carbonyl groups in both rotamers.

The diacetyl analogue *12* has the same conformational possibilities as *8*, as indicated in Scheme 7. In the 1,1-bis(dimethylamino) analogue, only the *EZ* conformer has been observed,[4] but in some analogues, which are permanently twisted about the double bond, both the *EZ* and the *ZZ* forms are found in

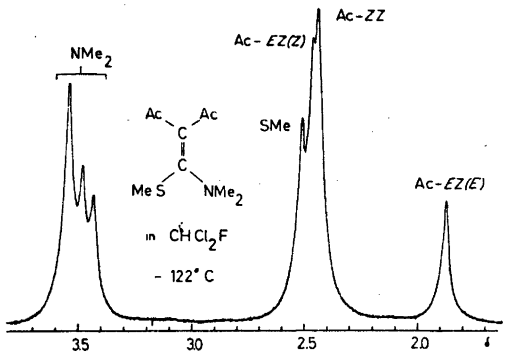


Fig. 2. ^{1}H NMR spectrum of *12* in $CHCl_2F$ at −122 °C.

ratios varying from 0.40:0.60 to 0.83:0.17.[19] No *EE* form has been observed, and calculations of dipole-dipole repulsion energies indicate that this form should be strongly disfavoured.[20] Detailed bandshape analysis shows that the *EZ* ⇌ *ZE* exchange goes *via* the *ZZ* form but in some cases also *via* the unobserved *EE* form.[19]

With decreasing temperature, first a normal decoalescence of the NMe_2 resonance is observed at −42 °C. In the temperature region −80 °C to −120 °C all signals broaden and emerge at −120 °C as (from low to high field) one group of three partly overlapping NMe_2 signals, one group of three signals due to Ac and SMe protons, and an isolated Ac singlet at rather high field (δ 1.87) (Fig. 2). Bandshape analysis shows that two rotamers exist, which are exchanged by a process with a free activation energy of 33.5 ± 1.0 kJ mol^{-1}. Since the rotation about the C=C bond cannot affect the ^{1}H NMR spectrum of the SMe and NMe_2 groups unless the acetyl groups are locked in the *EZ* conformation, two alternatives exist for the interpretation of the observed temperature effects: (1) The C=C barrier is higher than or equal to the Ac−C-1 barrier, and both rotations are slow at −120 °C. In that case the observed spectrum may be explained by the existence of only the *ZZ* and one *EZ* form (Scheme 7) in the ratio 0.42:0.58. This combination requires four NMe_2 signals, two SMe signals and four COMe signals. The lower number of observed signals in this version has to be explained by accidental magnetic equivalence. (2) The rotation about the C=C bond is fast in the whole temperature region studied, and the observed effects are due only to slow acetyl group exchange. If only the *EZ* form exists, this model cannot explain the three NMe_2 and the two SMe signals. If an equilibrium between the *EZ* and the *ZZ* form in the ratio 0.58:0.42 is assumed, four NMe_2, two SMe, and three COMe signals should result, and also in this case some accidental equivalence is necessary.

The decision between these two alternatives can be made with the aid of the ^{13}C NMR spectrum. At −120 °C the carbonyl carbon resonance is split into a triplet in the ratio 3:4:3, and the C^2, the SMe, and the two NMe_2 resonances appear as doublets (the three latter only partly resolved) in ratios of *ca* 0.4:0.6. The COMe resonance also appears as a triplet, but due to partial overlap with the $(CD_3)_2CO$ septet the intensities cannot be estimated. The multiplicity of the ^{13}C spectrum at −120 °C is, however, in precise agreement with version 2, and it is thus evident that the C=C rotation is still fast at this temperature.

Table 2. Free energy barriers to rotation about the C-1=C-2 bond.

Compound	T/K	$\Delta\nu$/Hz	P (major)	$\Delta G^{\ddagger}$/kJ mol^{-1} [a]	$\Delta G^{\ddagger}$/kJ mol^{-1} [b]	$\Delta G^{\ddagger}$/kJ mol^{-1} [c]
1	315	41.2	0.85	59.3	>105	84.2
2	203	39.0	0.83	37.2	>105	62.8
3	258	18.2	–	55.0 [d]	–	–
4	163	26.3	0.88	30.9	104	58.6
6	153	12	0.35 [e]	28 ± 2	86.2	41.0
8	130	–	–	<25 [f]	–	–
10	130	–	–	<25 [f]	75.3	39.3
12	130	–	–	<25 [f]	–	<25

[a] Major → minor. [b] The 2,2-bis(methylthio) analogues.[14] [c] The 2,2-bis(dimethylamino) analogues.[4] [d] From ^{13}C spectra. [e] The major of four rotamers. [f] Calculated assuming $T_c < 130$ K, P_{major} 0.7 and $\Delta\nu$ 10 Hz.

DISCUSSION

One of the aims of this study was to compare the donor capacity of one SMe and one NMe_2 group with that of two SMe groups and of two NMe_2 groups. An inspection of the data in Table 2 reveals that the barriers to rotation about the C-1 = C-2 bond are considerably lower in the $=C(SMe)NMe_2$ compounds than in any of the other donor group combinations when compounds with the same acceptor groups are compared. This shows that in these compounds the $MeS-C-NMe_2$ group is more efficient in stabilizing a positive charge in the zwitterionic transition state than either of the $(MeS)_2C$ and $(Me_2N)_2C$ groups. This is contrary to all σ scales,[21] which rate NMe_2 as a much better donor than SMe. The explanation is probably a steric interaction in the 2,2-bis(dimethylamino)ethylenes, which forces the NMe_2 groups to rotate out of the plane of the double bond. In this conformation the NMe_2 groups cannot exert their full donor capacity, and the $(Me_2N)_2C$ group is surpassed by the $MeS-C-NMe_2$ group. This interpretation is supported by the observation that the barrier to rotation about the C=C bond is still lower in push-pull ethylenes where the donor nitrogen atoms form part of a five- or six-membered ring.[22,23] Here only molecules with comparatively poor acceptor groups (analogues of *1*) show "normal" behaviour with free energy barriers to rotation about the C=C bond of the order of 28 to 35 kJ mol^{-1}, whereas molecules with more efficient acceptor groups are permanently twisted about the double bond.

It has been found [7,8] that the barriers to rotation about the C=C bond are correlated by the Taft σ_R^- constants for the acceptor groups, and in the series of 2,2-bis(methylthio)-ethylenes a reasonable correlation was obtained with $\sum\sigma_R^-$.[24] This is also observed for com-

Table 3. Free energy barriers to rotation about the C-2 – NMe_2 bond.

Compound	T_c/K	$\Delta\nu$/Hz	$\Delta G^{\ddagger}$/kJ mol^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1} [a]
1	184	65.1	36.7 [b]	51.0; 54.6
2	208	62.1	41.8 [b]	58.2
3 [c]	225	31.2	46.6	43.1
4	209	24.2	43.6	60.3
5	232	32.2	48.1	57.3
6	–	–	< 37 [d]	63.6
8	200	14.4	42.5	58.6
9	224	7.5	49.1	64.9
10	203	3.8	45.4	68.6
12	231	7.5	51.7	62.8
14	174	12.3	37.0 [e]	49.4 [e]

[a] The 2,2-bis(dimethylamino) analogues.[4] [b] The major rotamer. [c] In toluene-d_8 – $CDCl_3$ (1:1). [d] No splitting observed. [e] From Ref. 9.

Table 4. Free energy barriers to rotation about the C-1 – X bond.

Compound	X	T/K	$\Delta\nu$/Hz	P (major)	$\Delta G^{\ddagger}$/kJ mol^{-1} [a]	$\Delta G^{\ddagger}$/kJ mol^{-1} [b]
2	$p-O_2N-C_6H_4$	163	64	–	32.4	48.5
6	Ac	153	7.0	0.35 [c]	28 ± 3	54.0
8	CO_2Me	143	10	0.67	30.5	33.9
10	Bz/Ac	163	38	0.89	33.1	–
12	Ac/Ac	168	59	0.58	33.5 [d]	42.7

[a] Major→minor. [b] The 2,2-bis(dimethylamino) analogues.[4] [c] The major of four rotamers. [d] The $EZ \rightleftharpoons ZE$ exchange in the *EZ* form (Scheme 7).

Table 5. Infrared frequencies of

X	Y	ν_{CN}/cm^{-1}			$\nu_{C=O}$/cm^{-1}			$\nu_{C=C}$/cm^{-1}		
		a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
Ph		2199	2150	2165	—	—	—	1505	1525	1590
p-$O_2NC_6H_4$	CN	2199	2150	2165	—	—	—	1520	1525	1585
NC	CN	2209	2170, 2190	2190	—	—	—	1425	1525	1530
NC	CO_2Me	2204	2170	2175	1709	1665	1670	1455	1520	1525
PhCO	CN	2199	2150	2170	1635	1595	1595	1410–1445	1550	1570
Ph	COMe	—	—	—	1610	1565	1640	1410–1440	1500	1590
MeOCO	CO_2Me	—	—	—	1705–1720	1625	1660	1530	1510–1540	1520
MeCO	CO_2Me	—	—	—	1710, 1660	1650	1650	1490	1570	1430
PhCO	COMe	—	—	—	1655	1580	1520, 1585	1445	1550	1435
MeCO	COMe	—	—	—	1655	1560	1550	1480	1505	1495

[a] $D^1=D^2=SMe$.[14] [b] $D^1=D^2=NMe_2$.[4] [c] $D^1=SMe$, $D^2=NMe_2$.

pounds *1* to *12*, though the correlation is far from good (the correlation coefficient $R=0.90$).

One should expect that low C=C barriers should indicate strong conjugative interaction also in the planar initial state. This, however, is not manifested in high barriers to rotation of the Me_2N or the acceptor groups. As can be seen in Tables 3 and 4, these barriers are considerably lower in compounds *1–12* than in their 2,2-bis(dimethylamino) analogues. This is even more against expectations considering that the C-2–N and C-1–X barriers in the latter group of compounds are probably more lowered by steric strain in the initial state than in the 2-methylthio-2-dimethylamino analogues.

Based on a comparison of the C-2–N barriers in *4* and *8* Shvo and Belsky [8] proposed that these barriers were determined by inductive rather than by resonance effects. This hypothesis, however, is not supported by the results of the present study. The diacetyl compound *12* has the highest C-2–N barrier, and the acceptor capacity of the acetyl group is rated as inferior to that of the cyano group both in the σ_I and the σ_P^- scales, but not in the σ_R^- scale. Attempts to correlate the C-2–N barriers with $\sum\sigma_R^-$ leads to a correlation that is even worse than that for the C=C barriers, R being 0.86.

It has previously been observed that polarization of the π-electrons in push-pull ethylenes has a strong influence on the infrared frequencies.[4,14,25] Double bonds in donor groups show diminished frequency, and groups like CN and CO_2Me, which are comparatively slightly affected by coupling with the C-1=C-2 bond, may be used as convenient probes for the polarization of the planar initial state, whereas the MeC=O and C-1=C-2 stretching vibration frequencies, being more affected by coupling, are more uncertain measures of the polarization.

The data in Table 5 on the whole support the picture that compounds *1–12* are intermediate in polarization between the bis(methylthio) and bis(dimethylamino) analogues.

Smith and Taylor [16] have proposed increments for calculation of $\nu_{C=C}$ in enaminoketones and analogues with oxygen and sulfur as donor atoms. It is worth noticing that the use of their increments for N ($-65/-85$ cm^{-1}) give reasonably good values for $\nu_{C=C}$ in the bis(dimethylamino)ethylenes. The experimental

values for the bis(methylthio) analogues are considerably lower than the calculated values (increments $-20/-65$ cm^{-1}) and also lower than the values for the dimethylamino analogues. It is highly unlikely that this is due to a stronger conjugation in the $C=C(SR)_2$ compounds but may be explained by a weaker coupling in this group than in the $C=C(NR_2)_2$ group, which leads to a lower frequency for the antisymmetric combination vibration.

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