Tetrahedron. Vol. 34, pp. 557 to 562. Pergamon Press 1978. Printed in Great Britain

A DIPOLE MOMENT STUDY OF N-TRIMETHYLAMMONIOBENZAMIDATES AND N-BENZOYLIMINODIMETHYLSULPHUR(IV)

H. Lumbroso* and Ch. Liégeois
Laboratoire de Chimie Générale, Université Pierre-et-Marie Curie, 4, place Jussieu,
75230 Paris Cedex 05, France

and

D. G. Morris and J. D. Stephen
Chemistry Department, The University, Glasgow G12 8QQ, Scotland

(Received in the UK 18 July 1977; Accepted for publication 16 August 1977)

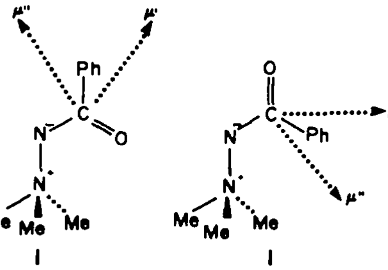
Abstract—Analysis of the dipole moments of N-trimethylammoniobenzamidates Me$_3$N–NCOC$_6$H$_4$X, with X = H, *p*-F, *p*-Cl or *p*-NO$_2$ and of N-aroyliminodimethylsulphur(IV) Me$_2$S=NCOC$_6$H$_4$X (X = H and *p*-NO$_2$) shows that, as solutes, these compounds exist in the *syn* conformation. Models are proposed for N-trimethylammonio-orthochlorobenzamidate and N-orthocyanobenzoyliminodimethylsulphur(IV). The (Me$_3\overset{+}{N}$–$\overset{-}{N}$) and (S=N) dipole moments, and the ($\overset{-}{N}$–C=O) and (S=N–C=O) mesomeric moments, are derived and discussed.

N-Trimethylammoniobenzamidates Me$_3\overset{+}{N}$–$\overset{-}{N}$COAr, also known as aminimides,[1,2] are isoelectronic with amine-oxides and also the closely related nitrogen ylides. As the N atom cannot use its 3*d* orbital in N-trimethylammoniobenzamidates, their N–N bond is quite polarized and these derivatives are to be distinguished from the ylides such as Ph$_3$P = CHCOAr and Ph$_3$As = CHCOAr in which some double bond character exists between the heteroatom and the adjacent trigonal C atom.[3,4]

N-Benzoyliminodimethylsulphur(IV) Me$_2$S=NCOPh also is a compound of great chemical interest having, like sulphur-ylides,[5] a tetracovalent S atom.

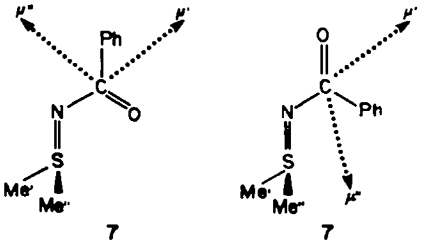
X-Ray diffraction structures of two N-trimethylammoniobenzamidates, with Ar = *p*-BrC$_6$H$_4$[6] and Ar = C$_6$H$_5$[7,8] and of N-benzoyliminodimethylsulphur(IV)[9] have been published showing that, in the solid phase, these compounds all exist in the *syn* conformation (Figs. 1 and 2).

^{1}H NMR spectra of various N-trimethylammonioimidates Me$_3\overset{+}{N}$–$\overset{-}{N}$COR, with R = H, Me, Ph and OMe, recorded in deuterochloroform are not diagnostic,[7] indicating either that the ylide system is locked in one unspecified conformation, or that rotation around the bond between N and the carbonyl C is extremely facile at low temperatures.



I I
Syn *Anti*

Fig. 1. Conformations *syn* and *anti* for N-trimethylammoniobenzamidates, and calculated vectors for their proper dipole moments.



7 7
Syn *Anti*

Fig. 2. Conformations *syn* and *anti* for N-benzoyliminodimethylsulphur(IV), and calculated vectors for their dipole moments.

A large mesomeric effect in the ($\overset{-}{N}$–C=O) group of N-trimethylammoniobenzamidate is to be expected because the unit negative charge lowers, by 0.33,[10] the nitrogen electronegativity *x*(N) = 3.0; additionally N,N-dimethylamides are known to exhibit a rather high mesomeric moment.[11]

To our knowledge, the dipole moment of N-trimethylammoniobenzamidates and of N-benzoyliminodimethylsulphur(IV) have not been determined,[12,13] and this fact prompts us to make this study in order to elucidate the conformation of these compounds in (benzene) solution and to determine the mesomeric moments of the (N–C=O) and (S=N–C=O) groups.

DISCUSSION

Table 1 lists the dipole moments of the compounds studied in the present work.

It is well known that preferred conformations in dilute solution may differ, in some cases, from those found in the solid phase. For instance, 1,4-dimethoxybenzene as a (benzene) solute is an equimolecular mixture of planar

Table 1. Dipole moments of N-trimethylammoniobenzamidates and N-benzoyliminodimethylsulphur(IV)†

No.	Compound	μ(benzene), D
1	N-trimethylammoniobenzamidate	5.27
2	N-trimethylammonio-parafluorobenzamidate	6.58
3	N-trimethylammonio-orthochlorobenzamidate	5.34
4	N-trimethylammonio-metachlorobenzamidate	6.04
5	N-trimethylammonio-parachlorobenzamidate	6.62
6	N-trimethylammonio-paranitrobenzamidate	9.28‡
7	N-benzoyliminodimethyl-sulphur(IV)	4.51

†At 27.0°, and for $_EP + _AP = R_D$.
‡In dioxan at 27.0°.

cis and *trans* conformers,[14,15] whereas as a solid it exists in a planar *trans* conformation.[16]

The conformation in solution of N-*trimethylammoniobenzamidate*

From the NMR results in CDCl$_3$ (c = 10–15%), it is evident that N-trimethylammoniobenzamidate exists in an unique conformation (*syn* or *anti*) as the benzoyl-group rotational barrier around the ($\overset{-}{\mathrm{N}}$–CO) bond is presumably higher than the N-dimethylamino-group rotational barriers in N,N-dimethylbenzamide or N,N-dimethylformamide—known to be 16 and 21 kcal mol^{-1}, respectively[17,18]—on account of the influence of the unit negative charge formally on the N atom. Moreover, on the sole basis[19] of the dielectric permittivity of the medium, the population of the more polar conformer must decrease and, consequently, that of the less polar which is *syn*-shaped must increase, in passing from deuterochloroform (ϵ = 4.7) to benzene (ϵ = 2.3).

In the following, m is the mesomeric moment of benzaldehyde and m^* that of the benzoyl-group in N-trimethylammoniobenzamidate. Additional moment, due to the substituent, in p-substituted N-trimethylammoniobenzamidates p-XC$_6$H$_4$CO$\overset{-}{\mathrm{N}}$–$\overset{+}{\mathrm{N}}$Me$_3$, is designated by μ^*(Ph–X) whereas in p-substituted benzaldehydes it is μ'(Ph–X). Both μ^*(Ph–X) and μ'(Ph–X) figures can differ from the dipole moments of substituted benzenes, μ(Ph–X).

The assumption that $m^* = m$ and hence μ^*(Ph–CHO) = μ(Ph–CHO) implies no competition between ($\overset{-}{\mathrm{N}}$–C=O) and (Ph–C=O) mesomeric effects in N-trimethylammoniobenzamidate. This is improbable and, as the formyl group rotational barrier in benzaldehyde is ony 7.6 kcal mol^{-1},[20] m^* is likely to be markedly smaller than m. In this respect, it is interesting to note that N,N-dimethyl p-bromobenzamide[21] is not planar in the solid phase, and characterized by C–N and C$_{ar}$–C rotational angles of 9°18′ and 45°30′, respectively. Reduction of m to zero leads to the extreme solution μ^*(Ph–CHO) = μ(t-Bu–CHO) = 2.66D acting at 12°41′ to the CO bond.[22]

Since $0 < m^* < m$, μ^*(Ph–X) should lie between μ and μ' values as (X, O)-interaction moments parallel the actual m(Ph–CO) values.[23]

Taking μ(Ph–CHO) = 2.99D,[3] acting at 34° to the Ph–C bond,[14] analysis of the dipole moments of p-fluorobenzaldehyde (1.98D,[24] recalculated), p-chlorobenzaldehyde (2.04D[25]) and p-nitrobenzaldehyde (2.49D,[12] recalculated[3]) leads to μ'(Ph–X) = 1.41, 1.31 and 4.32D, for X = F, Cl or NO$_2$, to be compared with μ(Ph–X) = 1.48D[24] (recalculated), 1.59D,[12] and 3.98D in benzene, 4.04D in dioxan (Table 2).

According to whether μ^*(Ph–X) is taken as equal to μ or μ', the angle (designated as θ or θ') that the dipole moment of N-trimethylammoniobenzamidate makes with the C–Ph bond axis is 31, 36.2 or (0°), 21°, 20° or 29°, as calculated from the dipole moments of p-fluoro-, p-chloro- and p-nitrobenzamidates (Table 1). From these results, the best value for the angle is between 33 and 25°, say $\theta^* = 30 \pm 5°$. Hence, the dipole moment of N-trimethylammoniobenzamidate is directed as μ'_s or μ''_s, μ'_t or μ''_t (Fig. 1).

μ_s and μ_t vectors can be expressed as

$$\mu = \mu(\mathrm{Me_3\overset{+}{N}{-}\overset{-}{N}}) + \mu(\mathrm{Me{-}\overset{-}{N}}) + \mu^*(\mathrm{Ph{-}CHO}) + \mathrm{M},$$

where M is the ($\overset{-}{\mathrm{N}}$–C=O) mesomeric moment.

Knowledge of the directions of M and the gross vector μ, and of the pertinent geometrical parameters,[8] allows both $\mu(\mathrm{Me_3\overset{+}{N}{-}\overset{-}{N}})$ and M to be determined. Taking $\mu(\mathrm{Me{-}\overset{-}{N}}) = \mu(\mathrm{Me_3N}) = 0.86\mathrm{D}$,[12] μ^*(Ph–CHO) = μ(Ph–CHO), one evaluates†

(a) $\mu(\mathrm{Me_3\overset{+}{N}{-}\overset{-}{N}}) = +7.5 \pm 0.1\mathrm{D}$, $M = 1.4 \pm 0.3\mathrm{D}$, if $\mu = \mu'_s$,

(b) $\mu(\mathrm{Me_3\overset{+}{N}{-}\overset{-}{N}}) = +7.3 \pm 0.1\mathrm{D}$, $M = -(3.7 \pm 0.3)\mathrm{D}$, for $\mu = \mu''_s$;

(c) $\mu(\mathrm{Me_3\overset{+}{N}{-}\overset{-}{N}}) = -17\mathrm{D}$, $M = -11\mathrm{D}$, if $\mu = \mu'_t$,

(d) $\mu(\mathrm{Me_3\overset{+}{N}{-}\overset{-}{N}}) = -14\mathrm{D}$, $M = -5\mathrm{D}$, for $\mu = \mu''_t$.

Since both $\mu(\mathrm{Me_3\overset{+}{N}{-}\overset{-}{N}})$ and M must be *positive*, the only acceptable solution is that written in (a), showing that N-trimethylammoniobenzamidate exists, as a benzene solute, in the conformation *syn*. Similar dipole moment analysis has shown that, as benzene solutes, benzoylmethylene triphenylphosphorane[3] and triphenylarsenane[4] also exist in the *syn* conformation.

Taking μ^*(Ph–CHO) as μ(t-Bu–CHO) leads to $\mu(\mathrm{Me_3\overset{+}{N}{-}\overset{-}{N}}) = 6.9\mathrm{D}$, $M = 0.8\mathrm{D}$, for $\mu = \mu'_s$.

The M mesomeric moment (1.4 ± 0.3D) is in rough agreement with that in N,N-dimethylformamide, 1.7D as obtained by comparing the dipole moments of N,N-dimethylformamide (3.86D) and formaldehyde (2.34D).[11]

N-*Trimethylammonio o-chloro- and m-chlorobenzamidates*

o-Chloro- and m-chlorosubstituted N-trimethylammoniobenzamidates can exist in a number of sub-conformations characterized by a phenyl rotational angle around the Ph–CO bond axis, among which the (O, Cl)-

---

†Some moment reduction is likely to occur in passing from μ(Me–N) to $\mu(\mathrm{Me{-}\overset{-}{N}})$, but it would be compensated by the nitrogen hybridization moment being 0.14D greater when N is trigonally hybridized.[26,27] Being small, the C–N ionic moment is not subject to marked increase.[26]

cis and (O, Cl)-*trans* planar conformations benefit from full (Ph–C=O) conjugation energy.

From μ(Ph–Cl) = 1.59D,[3] and μ = 5.27D acting at 30 ± 5° to the C–Ph bond, one obtains:

o-Chloroderivative: $\mu(cis) = 5.5 \pm 0.1$D, $\mu(trans) = 4.0 \pm 0.1$D;
m-Chloroderivative: $\mu(cis) = 6.7 \pm 0.1$D, $\mu(trans) = 5.5 \pm 0.05$D.

Unexpectedly, since *o*-chlorobenzaldehyde exists in the conformation *trans*,[14] N-trimethylammonio-*o*-chlorobenzamidate appears to prefer the *cis* conformation since its dipole moment is 5.34D. The calculated moment for the orthogonal conformation is as high as 6.1 ± 0.1D. Of course some rotation of the phenyl group around the C–Ph axis is not precluded, but the Cl atom prefers to lie near the O atom. This may be due to the (Cl, O)-*trans* conformer being disfavoured by strong ($\bar{\text{N}}$, Cl) repulsive potential.

The dipole moment of N-trimethylammonio-*m*-chlorobenzamidate (6.04D) is consistent with a mixture of planar *cis*- and *trans*-conformers, existing in the conformational ratio $(trans)/(cis) = (57 \pm 5)/(43 \mp 5)$. *m*-Chlorobenzaldehyde is a mixture of both conformers with the *trans* the more stable (56%).[14]

The conformation in solution of N-*benzoyliminodimethylsulphur*(*IV*)

In the solid phase, N-benzoyliminodimethylsulphur(IV) is characterized by the following features (Me′–S=N–C) = 168.6°, (Me″–S=N–C) = 87.4°; Me′SMe″ = 101° (that is near MeSMe angle in Me_2S = 100°),[28] Me′SN ~ Me″SN (99.5 and 104.2°).

With the assumption that $\mu^*(Ph\text{–}NO_2)$ equals $\mu(Ph\text{–}NO_2)$ = 3.98D or $\mu'(Ph\text{–}NO_2)$ = 4.32D (see p. 558), dipole moment analysis of N-*p*-nitrobenzoyliminodimethylsulphur(IV), 7.7D,[29] shows the electric moment of N-benzoyliminodimethylsulphur(IV), 4.51D, to act at 49.3 or 58.6° to the C–Ph bond axis (Fig. 2). In the subsequent calculations, the angle adopted is $\theta^* = 55 \pm 5°$, and $\mu(Me_2S\text{=}NCOPh)$ was assumed to lie in the Me′SNCO plane since μ(Me″–S) . sin (180°–102°) is certainly much less than the resultant μ(S=N) + μ(Me′–S) + [μ(Me″–S) . cos (180°–102°)] . v.

μ(Me′–S) and μ(Me″–S) are equal to $\mu(Me_2S)/(2\cos 50°) = 1.13$D. Thus, the plane component of the gross vector is $\mu_{pl.} = 4.37$D, at nearly 55° to the C–Ph bond axis.

The $\mu_{pl.}$ vector can then be expressed as

$$\mu_{pL} = \mu(\text{Me}'\text{–S}) + [\mu(\text{Me}''\text{–S}) \cdot \cos 78°] \cdot \mathbf{v} + \mu(\text{S=N}) \\ + \mu(\text{Me–N}) + \mu(\text{Ph–CHO}) + M(\text{S=N–C=O}),$$

where **M** denotes the mesomeric moment of the (S=N–C=O) group. Taking μ(Me–N) = 0.86D, μ^*(Ph–CHO) = μ(Ph–CHO), one derives:

(*a*) $\mu(\text{S=N}) = 3.6 \pm 0.2$D, $M = 2.2 + 0.2$D, if $\mu = \mu'_a$,
(*b*) $\mu(\text{S=N}) = 8.6 \pm 0.3$D, $M = -6.1 \pm 0.3$D, for $\mu = \mu''_a$;
(*c*) $\mu(\text{S=N}) = -12.0 \pm 0.5$D, $M = 10.6 \pm 0.2$, if $\mu = \mu'_t$,
(*d*) $\mu(\text{S=N}) = -6.5 \pm 0.6$D, $M = 1.0 \pm 0.7$D, for $\mu = \mu''_t$.

Clearly the only acceptable solution is that corresponding to hypothesis (*a*), and this implies that the compound does exist, as a benzene solute, in the *syn* conformation.

Taking μ^*(Ph–CHO) = μ(*t*-Bu–CHO), and $\mu = \mu'_a$, leads to $\mu(\text{S=N}) = 3.2 \pm 0.2$D, $M = 1.9 \pm 0.2$D.

There also exists the possibility that, due to the peculiar shape of Me_2S=N group, the unique sulphur lone pair orbital is not hybridized. In the event that this limiting situation holds, each Me–S group should possesss a dipole moment equal to $1.13 - [\mu_h(\text{S}, 100°)/(2\cos 50°)] = -0.88$D,[30] where μ_h designates the hybridization moment of combined sulphur,[26] and derived values for μ(S=N) and M are 3.2 ± 0.2D and 4.5 ± 0.2D, respectively. Thus, in this case cancellation of μ_h(S) affects little the derived μ(S=N) value.

N-*o*-cyanobenzoyliminodimethylsulphur(IV) can exist in a number of conformations. Its high dipole moment 6.29D[29] favours a model in which the CN group is more close to the CO group, since

$$\mu(cis) = 7.2 \pm 0.2\text{D}, \quad \mu(trans) = 0.6 \pm 0.2\text{D},$$

as calculated using μ(Ph–C≡N) = 4.05D.[12] In order to make the measured dipole moment compatible to that calculated, a twist (O, CN)-*cis* model by a 59 ± 5° phenyl-rotational angle is in order.

The $Me_3\overset{+}{N}\text{–}\overset{-}{N}$ *and* Me_2S=N *dipole moments*

(1) As deduced from the dipole moment of N-trimethylammoniobenzamidate, $\mu(Me_3\overset{+}{N}\text{–}\overset{-}{N})$ is 7.5 ± 0.1D, and it contains an axis component equal to the trigonal-nitrogen hybridization moment.[27] Since $\mu_h(\text{N}sp^2) - \mu_h(\text{N}sp^3) = 0.14$D,[26] one has

$$\mu(Me_3\overset{+}{N}\text{–}\overset{-}{N}) = \mu(Me_3N) + 0.14 + \mu(\overset{+}{N}\text{–}\overset{-}{N}) \\ = 1.0 + \mu(\overset{+}{N}\text{–}\overset{-}{N})$$

whence $\mu(\overset{+}{N}\text{–}\overset{-}{N}) = 6.5 \pm 0.1$D, which compares fairly well with the theoretical value (4.8) × 1.47 = 7.06D.

As $\mu(\overset{+}{N}\text{–}\overset{-}{C})$ is estimated to be $6.5 - \mu(\text{C–N}) = 6.1$D, analysis of the high dipole moment found for N-pyridiniumcyclopentadienylide (13.5D[12]) is consistent with a mesomeric moment (due to negative-carbon lone pair delocalization towards the cyclopentadienylide ring) equal to 7.0D,

$$M = \mu - [\mu(\overset{+}{N}\text{–}\overset{-}{N}) + \mu(\text{pyridine}) - \mu_h(\text{N } sp^2)] \\ = 13.5 - [6.1 + 2.20 - 1.78].$$

On account of the possible (ylidic↔ylene) character of their $S^{IV}C$, $P^{V}C$ and $As^{V}C$ bonds, sulphonium-phosphonium- and arsonium-cyclopentadienylides exhibit much lower mesomeric moments, of 1.5–2.0D.[5,29]

Despite trimethylamine oxide contains the (N–O) bond moment, which is *ca* 1.0D,[31] its dipole moment (4.87 ± 0.15D or 5.02D[12]) is inferior to that of $(Me_3\overset{+}{N}\text{–}\overset{-}{N})$, 7.5 ± 0.1D.† This can be partly understood by assuming that μ_h(O) is less than $\mu_h(\text{N } sp^2)$, due to no hybridization, or less (*s*, *p*) mixing, of the lone pair orbitals of the terminal O atom.

(2) Due to the approximate character of the treatment, and some uncertainty in the **M** direction, the (S=N) bond moment given above (3.6 ± 0.2D) is not very precise.

---

†The (N–O) bond moment has been deduced from the experimental dipole moment of isoxazolidine. It does not contain a term due to the hybridization moments of the bonded atoms, as $\mu_h(\text{O } sp^3) \sim \mu_h(\text{N } sp^3)$, 1.6 and 1.7D.[26]

Eliel *et al.*[29] have derived the following figures of $\mu(S{=}N)$, 3.59, 3.75, 4.01, 4.40 and 4.63D, from $\mu(Me_2S{=}NC_6H_4X) = 5.53, 5.88, 6.11, 8.94$ and 10.1D for $X = p$-F, p-Cl, p-Br, p-CN or p-NO$_2$, by taking $\mu(N{-}C_6H_4{-}X)$ as deduced from $\mu(p\text{-}XC_6H_4NH_2)$. This assumption is not adequate as the trigonally-hybridized nitrogen lone pair cannot conjugate with the phenyl ring which in these molecules, especially in the p-nitro derivative studied by X-ray diffraction,[29] is coplanar with the $(C_{ar}NS)$ plane. Consequently, a better assumption concerning the $(N{-}C_6H_4{-}X)$ moments is to suppose

$$\begin{aligned}\mu(N{-}C_6H_4{-}X) &= \mu(Ph{-}X)\\ &\quad -[\mu(\text{mesityl}{-}N) + \mu_h(N\ sp^2)\\ &\quad -\mu_h(N\ sp^3)]\\ &= \mu(Ph{-}X) - (1.24 + 0.14),\end{aligned}$$

where $\mu(\text{mesityl}{-}N)$ is derived from non-conjugated N,N-dimethylmesidine.[32] By so doing, and taking $\mu(Ph{-}X) = 1.48, 1.59, 1.56, 4.05,$[12] and 3.98D, dipole moment analysis of $Me_2S = NC_6H_4X$ derivatives leads to $\mu(S{=}N) = 3.8$ or 4.8, 5.1 or 6.2, 5.2 or 6.4, 6.4 or 8.0, and 7.7 or 9.2D, according to whether $\mu(Me{-}S)$ is taken as +1.13 or −0.88D (p. 559). The differences between these values and $\mu(S{=}N) = 3.6 \pm 0.2D$ as derived from $\mu(Me_2S{=}NCOPh)$, may be due to the $(S{=}N{-}Ar)$ mesomeric moment being ignored. That the apparent $\mu(S{=}N)$ figures are much greater when deduced from derivatives having strong electron-attracting substituents (p-CN and p-NO$_2$) supports the presence of $(S{=}N{-}Ph)$ mesomeric moments and the existence of $(S{=}N \ldots C{\equiv}N)$ and $(S{=}N \ldots NO_2)$ interaction moments. Benzylidene-p-nitraniline ($\mu = 5.71D$[33]) exhibits a $(C{=}N \ldots NO_2)$ interaction moment of 1.0D.

The relatively high value of $\mu(S{=}N)$, as compared to $\mu(C{=}N) = 1.4D$,[27] is probably chiefly due to the weakness of $(2p\pi - 3d\pi)$ bonding. Simple Hückel calculations show that decrease in π-bond energy results in an increase of the π-bond moment. Taking $\alpha(A) = 0$, $\alpha(B) = 1$ and $\beta(A{=}B) = 2$ or 1, all in β units, leads to $\mu_\pi = 0.24 \times (4.8) \times R$ and $0.46 \times (4.8) \times R$ Debye units, respectively.

As $\mu(S{-}N)$ probably is slightly greater than $\mu(C{-}N) = 0.4D$, 0.5D say, $\mu_\pi(S{=}N)$ would be *ca* 3D, suggesting the $(S{=}N)$ π-bonding to be highly ionic in character, ~40%. This is in reasonable accord with the value (55%) found by X-ray photoelectron spectroscopy.[34]

Analysis of the known[35] dipole moments of ethylene-sulphurdiimide and trimethylene-sulphurdiimide (1.24 and 2.24D) can afford a value for $\mu(N{=}S{=}N)$ (Fig. 3).

The dipole moments of ethylene-sulphurdiimide **8** and of trimethylene-sulphurdiimide **9** can be expressed as

$$\begin{aligned}\mu(8) = {}&[\mu'(CH_2{-}N) + \mu_h(N\ sp^2) - \mu_h(N\ sp^3)] \cdot (\mathbf{u}_1 + \mathbf{u}_2)\\ &+ m(CH_2{-}N{=}S) \cdot (\mathbf{v}_1 + \mathbf{v}_2) + \mathbf{X}_8,\end{aligned}$$

$$\begin{aligned}\mu(9) = {}&[\mu''(CH_2{-}N) + \mu_h(N\ sp^2) - \mu_h(N\ sp^3)] \cdot (\mathbf{u}_1 + \mathbf{u}_2)\\ &+ m(CH_2{-}N{=}S) \cdot (\mathbf{v}_1 + \mathbf{v}_2) + \mathbf{X}_9.\end{aligned}$$

where $\mu'(CH_2{-}N) = \mu(N\text{-pyrrolidino})/2\cos 55° = 1.18D$ (from N-methylpyrrolidine,[36] 1.10D), $\mu''(CH_2{-}N) = \mu(N\text{-piperidino})/(2\cos 55°) = 0.80D$ (from N-methylpiperidine,[36] 0.82D), $\mu_h(N\ sp^2) - \mu_h(N\ sp^3) = 0.14D$, m is the hyperconjugation moment of $(CH_2{-}N{=}S)$ taken as $\mu(\text{propene}) = 0.35D$, and X_8 or X_9 the $(N{=}S{=}N)$ group moment in the molecules.

Analysis of $\mu(8)$ leads to $X_8 \sim 2.0D$. Assuming that **9** exists in a chair conformation, one derives $X_9 \sim 0.8D$, from $\mu(9)$.† By adding the moment of 2-chlorocyclohexane (2.2D) to that of $\mu(9)$ gives $\mu(9') \sim 0.7D$, which compares well with the experimental[35] value (0.75D).

These two X figures are much lower than expected on the basis of $\mu(S{=}N) = 3.6D$. This experimental fact can be explained by the following:

(i) The dipole moments of geminal CX_2 groups are markedly lower than calculated from $\mu(C{-}X)$, for instance[12] $\mu(H_2CCl_2) = 1.5D$, $\mu(CH_3{-}Cl) = 1.9D$; $\mu(SO) = 1.6D$ in SO$_2$, whilst $\mu(SO)$ from $\mu(Me_2SO) = 3.9D$ is 2.9D.

(ii) The sulphur hybridation moment in sulphur-diimides is much greater than that in $Me_2S{=}NCOPh$ (and $Me_2S{=}NAr$), and it is equal to $\mu_h(S\ sp^2) = 2.7D$.[27]

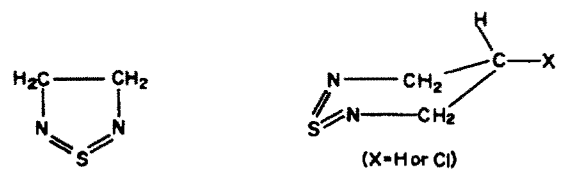
EXPERIMENTAL

Materials. Cryoscopic R.P. Benzene (from "Prolabo", Paris) was recrystallized and dried over metallic Na: at 25°, $d_4 = 0.8737$, $n_D = 1.4982$, $\epsilon = 2.2741$ (assumed). p-Dioxan, from "Eastman Kodak" (Rochester, N.Y., U.S.A.) was refluxed 12 hr with metallic Na, recrystallised twice, and dried with metallic Na: at 25°, $d_4 = 1.0284$, $n_D = 1.4982$, $\epsilon = 2.210$ referred to ϵ (benzene) = 2.2741. Pure nitrobenzene, from "Prolabo", stirred with Br$_2$, washed with NaOH and with water until neutral reaction, and dried with CaCl$_2$, was further distilled (b.p. = 87°/15 torr): at 20°, $d_4 = 1.2035$, $n_D = 1.5528$, in accord with best data from literature.[37]

Trimethylammoniobenzamidates **1–6**. These were prepared as follows: To an ice cold soln of N,N-dimethylhydrazine (2.49 g, 0.04M) in dichloromethane was added sequentially and with stirring dicyclohexylcarbondiimide (8.24 g, 0.04M) and the carboxylic acid (0.04M) portionwise.[38] After 12 hr the precipitated urea was filtered off and the filtrate was extracted with 4N HCl in order to free the hydrazide, as its hydrochloride, from residual urea. The hydrazide was then regenerated by addition of base and extraction into methylene chloride. Removal of solvent gave

---

† Part of the $(X_8{-}X_9)$ difference is due to assumptions in the additivity computations. The given X_8 figure should be diminished by $\mu'(CH_2{-}N) - \mu(Me{-}N) = 1.18 - 0.86 = 0.32D$. The discussion in reference[4] on the dipole moments of ethylene- and trimethylene-sulphurdiimides should be revised (see the present text).



8 Ethylene-sulphurdiimide

9 and **9'** Trimethylene-sulphurdiimides

Fig. 3. Sulphur-diimides examined by Kresze and Grill.[35]

crude hydrazide $ArCONHNMe_2$, which was recrystallized from EtOAc, m.p. and microanalytical data are given in Table 2 (the hydrazides are indicated by the suffix H).

The hydrazide was dissolved in chloroform and excess MeI was added; the soln was stirred overnight and the precipitated hydrazonium iodide, $ArCONH\overset{\oplus}{N}Me_3I^{\ominus}$, filtered off. This was used directly in the preparation of the benzamidate. The solid iodide was treated directly with an equimolar quantity of N NaOH aq and then extracted into chloroform (3 × 200 ml). The combined chloroform extracts were gravity filtered through a sintered glass funnel. After removal of solvent from the clear soln the benzamidate was obtained, this was then recrystallized from EtOAc. M.ps and microanalytical data are presented in Table 2.

Benzoyliminodimethylsulphur(IV) was prepared according to Swern.[39]

Physical measurements. The dipole moments were measured in benzene (or dioxan) at 27.0°, for the laboratory temp is normally 22–24°. The total polarization of the solute, extrapolated to infinite dilution, was calculated from the ratios[41]

$$\alpha_0 = \lim_{(w=0)} \frac{\epsilon - \epsilon_1}{w} \quad \text{and} \quad \beta = \frac{\Sigma(v - v_1)}{\Sigma w},$$

where w is the weight fraction of the solute, ϵ and v are, respectively, the dielectric constant and specific volume of the solutions; subscript one refers to the pure solvent as used, i.e. prepared in the *same* way as the solutions. The α_0 value has been determined by least-squares analysis of the $\epsilon(w)$ polynomial function (linear or, in some cases, quadratic). A Sartorius microbalance was used to make the solutions. Specific volumes have been accurately determined with a Digital Microdensimeter DMA 02C (Anton Paar KG, Graz, Austria). The distortion polarization $_EP + _AP$ was assumed to equal the molecular refraction of the solute (R_D). Differences between the refraction indices of solutions and the solvent were measured using a thermostated "VEB Carl Zeiss" interferometer (from Jena, D. D. R.). The technique for the measurement of dielectric constants has been described elsewhere.[42,43]

For each solute examined, w_{max} (reported with only three decimal points), α_0, β, $P_{2\infty}$, R_D and μ (in Debye units) are given in Table 3.

REFERENCES

[1] J. Timpe, *Z. Chem.* 12, 250 (1972).

[2] W. J. McKillip, E. A. Sedor, B. M. Culbertson and S. Wawzonek, *Chem. Revs.* 73, 255 (1973).

[3] R. Hoffmann, D. B. Boyd and S. Z. Goldberg, *J. Am. Chem. Soc.* 92, 3929 (1970).

[4] H. Lumbroso, C. Pigenet, A. Arcoria and G. Scarlata, *Bull. Soc. Chim. Fr.* 3838 (1971); H. Lumbroso, D. M. Bertin and P. Froyen, *Ibid.* 819 (1974).

[5] H. Lumbroso, D. Lloyd and G. S. Harris, *C.R. Acad. Sci. Paris* (C) 278, 219 (1974).

[6] L. Michael, Ph.D. Thesis, Cincinnati, Ohio, U.S.A. (1969).

[7] A. F. Cameron, N. J. Hair, D. G. Morris and D. M. Hawley, *Chem. Comm.* 725 (1971).

Table 2. M.p. and microanalytical data

Compound†	Substituent	m.p.	Found C	Found H	Found N	Calc. C	Calc. H	Calc. N
2	*p*-F	174–5	61.4	6.7	14.3	61.2	6.7	14.3
5	*p*-Cl	103–4	56.6	6.3	13.3	56.5	6.2	13.2
6	*p*-NO_2	221–2	54.1	5.9	19.1	53.8	5.9	18.8
4	*m*-Cl	114–6	56.7	6.5	13.2	56.5	6.2	13.2
3	*o*-Cl	128–130	56.6_5	6.2	13.2	56.5	6.16	13.2
2H	*p*-F	101–2	59.0	6.3	13.4	59.3	6.1	13.4
5H	*p*-Cl	132–3	54.4	5.6_5	13.9	54.4	5.6	14.1
6H	*p*-NO_2	149–50	51.4	5.4	20.5	51.7	5.3	20.1
4H	*m*-Cl	100–2	54.7	5.6	13.8_5	54.4	5.6	14.1
3H	*o*-Cl	107–8	54.6	5.7	13.9	54.4	5.6	14.1

†1 had m.p. 168–70° (lit.[40] 169–70°); 1H had m.p. 106–8° (lit.[39] 105–7°).

Table 3. Physical data from benzene (or dioxan) dipole moments determinations

Compound	w_{max}	α_0	$-\beta$	$P_{2\infty}$	R_D	μ†
$C_6H_5CO\overset{-}{N}{-}\overset{+}{N}Me_3$	0.009	17.0	0.287	617.5	53.1‡	5.27
p-$FC_6H_4CO\overset{-}{N}{-}\overset{+}{N}Me_3$	0.010	23.8	0.340	896.0	52.9	6.58
o-$ClC_6H_4CO\overset{-}{N}{-}\overset{+}{N}Me_3$	0.021	14.6	0.351	636.4	57.4‡	5.34
m-$ClC_6H_4CO\overset{-}{N}{-}\overset{+}{N}Me_3$	0.012	18.6_5	0.342	799.5	57.7‡	6.04
p-$ClC_6H_4CO\overset{-}{N}{-}\overset{+}{N}Me_3$	0.009	22.4	0.354	949.3	58.1	6.62
p-$NO_2C_6H_4CO\overset{-}{N}{-}\overset{+}{N}Me_3$	0.007	47.7	0.183	1806.5	59.6	9.28§
$Me_2S{=}NCOC_6H_5$	0.009	12.3_5	0.335	466.3	52.9‡	4.51
Nitrobenzene	0.065	13.91	0.316	353.4	32.7	3.98‖
Nitrobenzene	0.056	16.55	0.141	364.8	32.7	4.04§,‖

†In benzene, if not otherwise specified.

‡As determined in solution; others calculated from the pertinent experimental refraction using the equation $R_D = R_0 + R(Ph{-}X) - R(\text{benzene})$, where $R_0 = 53.1\ cm^3$.

§In dioxan.

‖Literature values: see Ref. 12, $\mu = 3.96$, 4.00D.[44]

[8] A. F. Cameron, N. J. Hair and D. G. Morris, *J. Chem. Soc.* Perkin Trans. *2*, 1071 (1972).

[9] A. F. Cameron, F. D. Duncanson and D. G. Morris, *Acta Crystallogr.* **32B**, 1998 (1976).

[10] L. Pauling, *The Nature of the Chemical Bond*, 2nd Edn. Cornell University Press, Ithaca, New York (1948).

[11] C. Pigenet and H. Lumbroso, *Bull. Soc. Chim. Fr.* 3743 (1972).

[12] A. L. McClellan, *Tables of Experimental Dipole Moments*, Vol. 1, Freeman, San Francisco (1963); Vol. 2, Rahara Enterprises, El Cerrito, Calif. U.S.A. (1974).

[13] O. A. Osipov, V. I. Minkin and A. D. Garnovskii, *Spravochnik po Dipol'nym Momentam* (Handbook on Dipole Moments), Izd. Vysshaya Shkola, Moscow (1971).

[14] H. Lumbroso and C. G. Andrieu, *Bull. Soc. Chim. Fr.* (I), 1575 (1973).

[15] H. Lumbroso, J. Curé and C. G. Andrieu, *J. Mol. Struct.* (1978).

[16] T. H. Goodwin, M. Przybylska and J. M. Robertson, *Acta Crystallogr.* **3**, 279 (1950).

[17] C. W. Fryer, F. Conti and C. Franconi, *Ric. Sci. Rend. Sez.* A, **35**, 788 (1965).

[18] H. S. Gutowsky, J. Jonas and T. H. Siddall, III, *J. Am. Chem. Soc.* **89**, 4300 (1967).

[19] R. J. Abraham and T. M. Siverns, *Tetrahedron* **28**, 3015 (1972).

[20] T. Drakenberg, R. Jost and J. Sommer, *J. Chem. Soc.* Chem. Comm. 1011 (1974).

[21] R. P. Shibaeva and L. Atovmyan, *Zh. Strukt. Khim.* **9**, 90 (1968).

[22] A. M. Ronn and R. C. Woods, III, *J. Chem. Phys.* **45**, 3831 (1966).

[23] Cf. H. Lumbroso and C. Carpanelli, *Bull. Soc. Chim. Fr.* 3198 (1964).

[24] N. J. Leonard and L. E. Sutton, *J. Am. Chem. Soc.* **70**, 1564 (1948).

[25] R. A. Y. Jones, A. R. Katritzky and A. V. Ochkin, *J. Chem. Soc.* (B) 1795 (1971).

[26] J. H. Gibbs, *J. Phys. Chem.* **59**, 644 (1955).

[27] H. Lumbroso and G. Pifferi, *Bull. Soc. Chim. Fr.* 3401 (1969).

[28] L. Pierce and M. Hayashi, *J. Chem. Phys.* **35**, 479 (1961).

[29] E. L. Eliel, J. Koskimies, A. T. McPhail and D. Swern, *J. Org. Chem.* **41**, 2137 (1976).

[30] H. Lumbroso, C. Liégeois, D. Lloyd and R. W. Millar, *Tetrahedron* **33**, 2583 (1977).

[31] H. Lumbroso, D. M. Bertin and G. Cum, *C.R. Acad. Sci. Paris* (C) **269**, 5 (1969).

[32] K. B. Everard and L. E. Sutton, *J. Chem. Soc.* 2821 (1951).

[33] D. Pitea, D. Grasso and G. Favini, *Gazz. Chim. Ital.* **100**, 519 (1970).

[34] C. E. Mixan and J. B. Lambert, *J. Org. Chem.* **38**, 1350 (1973).

[35] G. Kresze and H. Grill, *IVth Symp. Organic Sulfur*, Venice, Italy (15-20 June 1970).

[36] D. Mazet, W. D. Weringa and H. Lumbroso, *C.R. Acad. Paris* (C), **270**, 1537 (1970).

[37] J. N. Timmermans, *Physical Constants of Organic Pure Compounds*. Elsevier, New York (1950).

[38] R. F. Smith, A. C. Bates, A. J. Battisti, P. G. Byrnes, C. T. Mroz, T. J. Smearing and F. X. Albrecht, *J. Org. Chem.* **33**, 851 (1968).

[39] A. K. Sharma, T. Ku, A. D. Dawson and D. Swern, *Ibid.* **40**, 2759 (1975).

[40] M. S. Gibson and A. W. Murray, *J. Chem. Soc.* 880 (1965).

[41] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.* **64**, 2988 (1942).

[42] H. Lumbroso, D. M. Bertin and P. Cagniant, *Bull. Soc. Chim. Fr.* 1720 (1970).

[43] H. Lumbroso, D. M. Bertin, F. Fringuelli and A. Taticchi, *J. Chem. Soc.* Perkin Trans. *2*, 775 (1977).

[44] V. Vsetecka and O. Exner, *Coll. Czech. Chem. Comm.* **39**, 1140 (1974).