THE GAUCHE EFFECT ON CONFORMATION. α-SUBSTITUTED SULFONES AND N-SUBSTITUTED SULFONAMIDES

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The dipole moments of α-halogenosulfones *IIa—f* in benzene solution revealed the conformation *C*, those of N-methyl-N-nitrosulfonamides *IIIa—c* the conformation *F*. In either case the conformational preference is governed by the gauche rule which may be worded in a modified version that symmetrical positions of polar bonds and/or of lone electron pairs are disfavoured. A lone electron pair appears to be more significant than a polar bond.

The conformation around a single bond is controlled mainly by non-bonded interactions (steric factors). If, however, polar bonds are involved, they tend to take a synclinal position rather than an antiperiplanar one[1]. For instance the *sc*-conformation of 1,2-dihalogenoethanes is populated to an appreciable extent, in spite of the steric and/or electrostatic repulsion of the two halogen atoms. A similar effect is exerted by lone electron pairs; *e.g.* in dialkyl disulfides or diselenides[1] the polarity of C-S or C-Se bonds is very low, so the lone pairs are decisive. The experimental phenomenon was called the gauche effect[1] and several theoretical explanations were advanced[2-7]. However, the conformation of more complex molecules is even difficult to predict, in particular when several polar bonds together with lone electron pairs are present[1,6,7].

Sulfonyl derivatives characterized by the grouping —SO_2—X— are particularly suitable for studying the gauche effect. They contain strongly polar S—O bonds in one moiety and variable polar bonds, with or without lone electron pairs in the other, so that their effects can be separated. Various derivatives were studied by electron diffraction and microwave spectroscopy in the gas phase[8], by X-ray in the crystal[9-11] (see also the references in [8]), and by means of dipole moments in solution[6,12-17]. A particularly instructive example was that of α-nitrosulfones[6] *I* which have only one polar bond in the second moiety and no lone electron pair; the favoured conformation is *A*. This example led us to express the gauche effect rule in a modified formulation[6], stressing the overall molecule symmetry, or the local symmetry on the respective bond, against the mere number of gauche interactions. Owing to its significance for the theory, we considered worthwile to extend the experimental investigation still to some similar compounds. In this communication we report the results obtained on α-halogenosulfones *II* and N-methyl-N-nitrobenzenesulfonamides *III*. The former group represents the simplest model compounds, eliminating possible specific effects of the nitro group; in nitrosulfonamides *III* the problem is complicated by the presence of a lone electron pair on nitrogen and the question arises whether this pair or the polar bond is more effective in controlling conformational preferences.

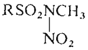
Our experimental approach was based as previously[6] on dipole moments in solution, taking advantage of polar substituents on the aromatic ring and of the graphical representation[18]. These aspects dictated the choice of compounds *IIa*–*f* and *IIIa*–*c* (Table I).

$R^1SO_2CHR^2NO_2$

I

RSO_2CH_2X

II


$RSO_2\underset{\substack{|\\ NO_2}}{N}CH_3$

III

EXPERIMENTAL

Materials. The α-halogenosulfones *IIa*–*f* were prepared by standard procedures starting from the pertinent sulfinic acids[19,20] (compounds *IIa*–*c*), magnesium derivatives of sulfones[21] (*IId*, *f*), or α-diazosulfones[22] (*IIe*). They were characterized by IR and ^1H-NMR spectra; the melting points (Table I) agreed fairly with the literature. N-Methyl-N-nitrobenzenesulfonamides *IIIa*, *b* were prepared according to the literature[23,24].

N-*Methyl*-N-*nitro*-4-*chlorobenzenesulfonamide* (IIIc) was prepared according to the method described[24] for *IIIb*, m.p. 78–79°C; for $C_7H_7ClN_2O_4S$ (250·7) calculated: 33·53% C, 2·81% H, 11·18% N; found: 33·80% C, 2·90% H, 11·23% N.

Physical measurements. The same procedure was used as previously[6]. When calculating the molar refractions from increments[25] (valid at 20°C) the value of 8·67 cm^3 was adopted for the SO_2 group as previously[6], as well as an exaltation[6] of 0·2 cm^3 for the conjugation C_6H_5—SO_2. For the NO_2 group on nitrogen the value from aliphatic nitro compounds[25] was adopted. As the dipole moments are large, the kind of calculation of R_D is unimportant. The results are listed in Table I.

Calculations. The dipole moments envisaged for the conformations *B*–*F* and for transitory conformations with the variable dihedral angle τ were calculated from standard bond and group moments[26] (in 10^{-30} Cm): H—C_{al} 1, H—C_{ar} 0, C—N 1·5, C_{al}—Cl 5·67, C_{al}—Br 5·67, C_{ar}—Cl 5·33, C—S 3·0, SO_2 group moment 10·67 (a vector intersecting the O—S—O angle), a mesomeric correction expressing the conjugation Ar—SO_2 3·33. The S—N bond moment, not available in standard tables[26], was estimated from the experimental dipole moment of N,N-dimethylbenzenesulfonamide[27]. The value of 3·0 (the negative end towards sulfur) does not correspond to the electronegativity of the two elements and has no general validity, it express rather the electron distribution in sulfonamides in relation to our system of bond moments. The moment of the nitro group bonded to nitrogen was derived from the dipole moment of dimethylnitramide in tetrachloromethane[28]; the value of 12·5 includes a contribution of the electron pair on nitrogen, similarly as other bond moments in this system[29].

The bond angles used were chosen in agreenent with the crystallographic data[8-10]: C—S—C 105°, C_{ar}—S—O 109°, O—S—O 119° (this angle itself is irrelevant for the dipole moment values), S—C—H_{al} 110°, C—S—N 105°, S—N—N 115°, S—N—C 115°, C—N—N 115°. The results of the calculation are given in Table I, last column, and in Figs 1 and 2.

RESULTS AND DISCUSSION

The two classes of compounds under investigation have a common advantage, *viz.* the presence of strongly polar groups; this makes the results from dipole moments rather definite. However, in the case of N-nitrosulfonamides *III* this advantage is

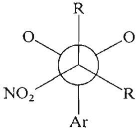
TABLE I

Polarization Data of α-Halogenosulfones *II* and N-Methyl-N-nitrosulfonamides *III* (benzene, 25°C)

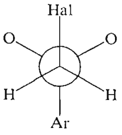
	Compound	M.p. °C	α^a β^a	P_2^0, cm^3 R_D^{20b}, cm^3	$\mu(5)^c$ $\mu(15)^c$	$\mu_{calc}{}^d$ 10^{-30} Cm
IIa	$C_2H_5SO_2CH_2Cl$	30—31	11·4 —0.458	334·5 29·5	12·9 12·8	12·8
IIb	$C_6H_5SO_2CH_2Cl$	50—51	10·2 —0·440	405 44·7	14·0 13·9	14·4
IIc	4-$CH_3C_6H_4SO_2CH_2Cl$	79—81	11·4 —0·441	483 49·4	15·5 15·4	15·1
IId	$C_6H_5SO_2CH_2Br$	50—51	8·98 —0·610	471·6 47·6	15·1 15·0	14·4
IIe	4-$CH_3C_6H_4SO_2CH_2Br$	86—88	10·5 —0·601	531·6 52·3	16·1 16·0	15·1
IIf	4-$ClC_6H_4SO_2CH_2Br$	124—126	5.20 —0·624	305·1 52·5	11·6 11·5	11·4
IIIa	$C_6H_5SO_2N(CH_3)NO_2$	42—43	7·84 —0·466	362·1 49·4	13·0 12·9	13·1
IIIb	4-$CH_3C_6H_4SO_2N(CH_3)NO_2$	57	9·42 −0·420	457·1 54·0	14·8 14·6	13·5
IIIc	4-$ClC_6H_4SO_2N(CH_3)NO_2$	78—79	3·94 —0·496	234·0 54·2	9·8 9·6	11·9

[a] Slopes of the plots ε_{12} *vs* w_2 and d_{12}^{-1} *vs* w_2, respectively; [b] calculated from increments, see Experimental; [c] correction for the atomic polarization 5%, or 15% of the R_D value, respectively; [d] calculated from bond moments for the conformations *C* ($\tau = 120°$) and *F* ($\tau = 240°$), respectively.

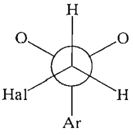
partly cancelled by some uncertain values of bond moments. Hence let us discuss the halogenosulfones *II* first. Note that the dipole moment data in Table I are internally consistent. In particular the small difference between the corresponding bromo and chloro derivatives (*IId*, *e* and *IIb*, *c*, respectively) is nearly constant, similarly also the effect of the 4-methyl substituent in *IIc* and *IIe*. Even the aliphatic derivative *IIa* does not deviate since the difference against *IIb* reflects the mesomeric correction. Hence the conclusion seems allowed even without any calculation that all the derivatives possess the same conformation.



A



$\tau = 0°$
B



$\tau = 120°$
C

In order to decide between the conformations *B* and *C*, a comparison of compounds *IId*, *e*, *f* is most conclusive, using the well-tried graphical representation[18]. Fig. 1 reveals that the preference for *C* is beyond any doubt as far as only two possibilities are considered; for the form *B* the expected dipole moments would be as high as $22-23\ 10^{-30}$ Cm in the case of *IId* and *IIe*. A closer inspection of Fig. 1 suggests that the

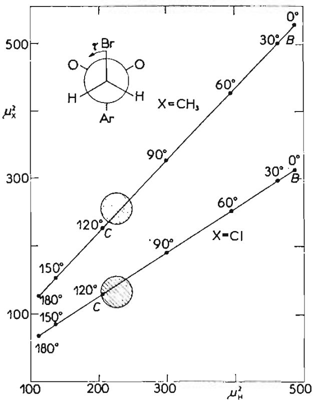
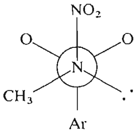


FIG. 1

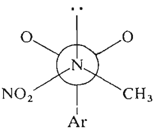
Comparison of Squared Dipole Moments of α-Bromosulfones *IId*–*f*

The unsubstituted compound *IId* on the *x*-axis, the methyl and chloro derivatives *IIe*, *f* on the *y* axis; full points calculated for conformations between *B* and *C* with variable dihedral angle τ; hatched points experimental.

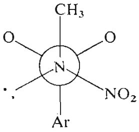
dihedral angle τ could be somewhat below 120°, say approximately 115°. The difference may originate from the inaccuracy of the bond moment scheme but a shift in the same direction was observed even with α-nitrosulfones[6]. In the crystal of *p*-toluenesulfonylmethyl perchlorate[11] this angle is 116° (formula *C* with $OClO_3$ in the place of Hal). In Table I, last column we give the theoretical dipole moments for all the compounds *IIa*–*f* as calculated with $\tau = 120°$. The difference against experimental values approaches only in one case (*IIe*) the value of $1 . 10^{-3}$ Cm, usually it is much lower. Note particularly the good agreement for the compound *IIa*. It indicates that our results are valid even for aliphatic derivatives although our method of data processing hinges mainly on aromatic derivatives bearing *para* substituents.



$\tau = 0°$
D



$\tau = 120°$
E



$\tau = 240°$
F

In the case of N-methyl-N-nitrobenzene sulfonamides *III* the conformations *D*–*F* come into consideration, in which the two polar bonds and the lone electron pair successively appear in the gauche positions. An experimental decision requires first

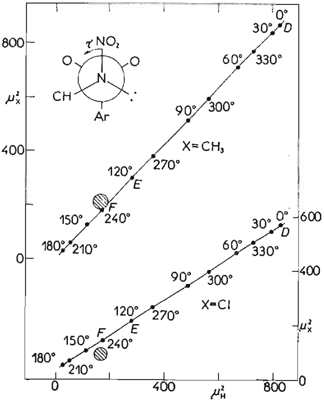


FIG. 2

Comparison of Squared Dipole Moments of N-Methyl-N-nitrobenzenesulfonamides *IIIa*—*c*

The unsubstituted compound *IIIa* on the *x* axis, the methyl and chloro derivatives *IIIb*, *c* on the *y* axis; full points calculated for conformations between *D*, *E*, and *F* with variable dihedral angle τ; hatched points experimental.

to determine the bond moment N—S and group moment N—NO_2 as described in the Experimental. Since these values are based each on a single compound, they introduce some uncertainty into the results. The fit displayed in Fig. 2 is in fact much better than could be anticipated. The conformation *F* is clearly favoured over *E* while *D* is ruled out. Of the calculated dipole moments in Table I, last column, only that of *IIIc* differs significantly from the experimental value. The great partial moments of the two rotating parts are brought to advantage still more than in Fig. 1; for instance the calculated dipole moment of *IIIb* in the conformation *D* would be as high as $29 \cdot 10^{-30}$ Cm.

If the preference of the rotamer *F* is governed by the gauche rule, it means that the lone electron pair is more effective in controlling conformation than the weakly polar N—C bond; it is obvious that the bond to a strongly polar NO_2 group is also more effective. In the case of sulfonanilides the preferred conformation has the hydrogen atom between the two oxygens[17], hence an aryl group is more effective than hydrogen. Further experiments would be necessary to estimate the relative efficiency of an electron pair compared with a strongly polar bond. If the conformation of a complex compound is to be predicted, it is, however, of little use to count the number of gauche interactions between polar bonds and between electron pairs[1]; the overall symmetry plays a more important part. Previously we have proposed the simple rule[6], which has a surprisingly broad validity, that symmetrical conformations involving polar bonds and lone electron pairs are disfavoured. The significance of core symmetry was accounted for in terms of a Jahn–Teller second-order effect[3]. In particular the conformations of sulfonyl compounds are illustrative since they cannot be rationalized by any other similarly simple rule, as shown already previously[6]. The two cases described in this paper have furnished a new piece of evidence. Of all the sulfonyl compounds listed in a recent review[8], only two prefer symmetrical conformations, *viz.* dimethylamidosulfonyl chloride and tetramethylsulfamide. We do not see any explanation for this exception since the behaviour of sulfonanilides is normal[17]. The sulfonyl compounds yield also examples that the symmetry control usually predominates in competition with electrostatic forces. While in halogenosulfones *II* the symmetrical conformations are simultaneously destabilized by dipole repulsion, the opposite is true in alkyl sulfonates[12], alkyl thiosulfonates[15], and 1,2-disulfones[30]. Though symmetrical conformations are never favoured. The latter compounds as well as *II* show also that even non-bonded interactions (steric effects) are not decisive in strongly polar molecules. They can, however, become important if the polar character is less pronounced.

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