

THE CONFORMATION OF α -NITRO SULFONES. CONCERNING THE GAUCHE EFFECT*

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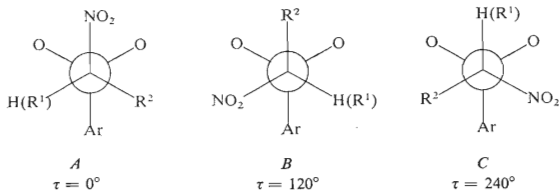
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From dipole moments of seven aromatic α -nitro sulfones *I–VII*, measured in benzene solution, the conformation with the nitro group antiperiplanar to one oxygen atom was deduced. With unsymmetrical derivatives, the two possible forms, *B* and *C*, seem to be populated in approximately equal amounts; hence the "folded" conformation (*C*) is not particularly favoured. The ¹H-NMR spectra are consistent with the occurrence of the form *C* but a conformational change with temperature has not been proven. The conformation is discussed in terms of the gauche rule and attention is called to the overall symmetry as the possible controlling factor.

A new efficient synthesis of α -nitro sulfones¹ has been exploited mainly to studies of their reactivity^{2,3}, the physical properties being investigated only in a restricted extent¹. The present paper is concerned with the solution conformation of these compounds which is of interest from two points of view. Firstly, the conformation around the C—S bond (*A*, *B*, or *C*) will be controlled mainly by the presence of the two strongly polar groups, SO₂ and NO₂, and may be discussed in terms of the often quoted gauche rule⁴. Secondly, in one of the possible forms (*C*) the two groups Ar and R² will be brought into proximity, giving rise to folded conformations which were encountered with other sulfonyl derivatives^{5,6}.



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As far as the gauche effect is concerned, the general rule⁴ predicts the conformation with maximum number of synclinal (gauche) positions of polar bonds and/or of lone electron pairs to be preferred. Accordingly, the forms *B* and *C* are equivalent and even *C* is of comparable stability. However, this rule is — in spite of some ingenious theoretical treatments⁷⁻⁹ — still essentially empirical in character and does not cover more complex cases when polar bonds of diverse orientation, or polar bonds together with electron pairs are present^{4,10,11}. Since α -nitro sulfones contain different types of polar bonds but no lone pairs immediately involved, a conformational study could shed new light on this problem, particularly in comparison with other sulfonyl derivatives.

The folded conformations may either result from attracting forces between the two sterically adjoining groups, or, alternatively, from the interactions in the middle of the molecule, forcing these peripheral groups into near positions. A detailed analysis revealed that the latter factor is decisive in the particular example of substituted phenyl benzyl sulfones⁵ although attracting forces may exist. The folded conformation could be in the latter case also governed by the gauche rule with the π -electrons of the benzene nucleus taking the role of the lone electrons. In the case of α -nitro sulfones the preference of the folded conformation would mean that the form *C* is favoured against *B*; on the opposite, if the polar bonds only controlled the conformation, both forms would be equally populated.

Our experimental approach was based mainly on dipole moment measurements in solution. Due to the presence of strongly polar groups this method can safely decide between the form *A* on the one side and *B* or *C* on the other side. Our set of compounds (Table I) consisted entirely of aromatic derivatives. Important is the pair *IV*–*V* in which the substituent in the *para* position enabled us to apply the graphical method of evaluation¹² under the presumption that the substituted and unsubstituted compounds have the same conformation. The compound *V* is thus the only one which allows to discriminate between the forms *B* and *C*.

EXPERIMENTAL AND RESULTS

Materials. The α -nitro sulfones *I*–*VII* (Table I) were described previously¹. Methyl phenyl sulfone (m.p. 88°C) and methyl benzyl sulfone (m.p. 127°C) were from the laboratory stock.

Physical measurements. Dielectric constants and densities of benzene solutions were measured at 25°C, usually at five concentrations within the range of 0.005–0.05M. A heterodyne apparatus with the frequency of 1.2 MHz was used. The dipole moments were evaluated according to Halverstadt and Kumler¹³. The molar refractions R_D were calculated from Vogel's increments¹⁴, valid at 20°C, and from the increments of 8.67 cm³ for the SO₂ group (based on the data¹⁵ for the helium line) and 0.2 cm³ for the conjugation¹⁶ SO₂–C₆H₅. The atomic polarization was accounted for by corrections of 5 or 15%, respectively, of the R_D value, considered to represent possible limiting values. The results are listed in Table I.

The ¹H-NMR spectra were measured on a Varian XL-100 (100 MHz) instrument at a concentration of c. 0.1M. For low temperature measurements (–80 to +35°C) perdeuterioacetone was

used as solvent and tetramethylsilane as internal standard; at high temperatures (35–100°C) they were replaced by perdeuteriodimethyl sulfoxide and hexamethyldisiloxane, respectively. The chemical shifts are given in Table II.

Calculations. The dipole moments expected for the conformations *A–C* of compounds *I–VII*, or for other conformations with the varying dihedral angle τ , were calculated according to the simple bond moment scheme. Standard values of bond and group moments¹⁷ were used: H—C_{ar} 0.3 D, H—C_{ar} 0 D, C_{ar}—Cl 1.60 D, C—O 0.74 D, C—S 0.9 D, C_{ai}—NO₂ 3.0 D, SO₂ group moment 3.2 D (as a vector intersecting the O—S—O angle), mesomeric moments expressing the conjugation Ar—SO₂ and Ar—O 1.0 and 0.6 D, respectively. The bond angles used were C—S—C 105°, C_{ar}—S—O 109°, O—S—O 119°, S—C—N 108°, C_{ar}—O—C_{ai} 120°. With the compound *VI* two equally populated planar conformations of the methoxy group were accounted for. In the case of compound *VII* the free rotation approximation with respect to the CH₂—S bond was used which, however, affects the dipole moment only slightly.

TABLE I
Polarization Data of α -Nitro Sulfones R³SO₂CR¹R²NO₂ (benzene, 25°C)

No	R ¹	R ² R ³	α^a β^a	P_{2D}^0, cm^3 R_D^{0b}, cm^3	$\mu(5)^c, \text{D}$ $\mu(15)^c, \text{D}$	$\mu_{\text{calc}}^d,$ D
<i>I</i>	H	H 4-CH ₃ C ₆ H ₄	8.74 -0.420	399.8 50.2	4.12 4.09	4.38
<i>II</i>	CH ₃	CH ₃ 4-CH ₃ C ₆ H ₄	9.04 -0.336	471.7 59.5	4.62 4.60	4.38
<i>III</i>	H	C ₂ H ₅ 4-CH ₃ C ₆ H ₄	9.72 -0.354	501.4 59.5	4.47 4.44	4.38
<i>IV</i>	H	C ₆ H ₅ 4-CH ₃ C ₆ H ₄	10.72 -0.393	651.7 74.6	5.29 5.25	4.33 ^e 5.05 ^f
<i>V</i>	H	4-ClC ₆ H ₄ 4-CH ₃ C ₆ H ₄	8.47 -0.426	588.0 79.5	4.96 4.93	4.35 ^e 4.89 ^f
<i>VI</i>	H	4-CH ₃ OC ₆ H ₄ 4-CH ₃ C ₆ H ₄	9.54 -0.406	646.5 81.5	5.24 5.20	4.49 ^{e,g} 5.20 ^{f,g}
<i>VII</i>	H	C ₆ H ₅ C ₆ H ₅ CH ₂	6.04 -0.422	393.2 74.2	3.92 3.87	3.78 ^{e,h}

^a Slopes of the Halverstadt-Kumler¹³ plots, ϵ_{12} vs w_2 and d_{12}^{-1} vs w_2 , respectively; ^b calculated from increments valid for 20°C, see Experimental; ^c correction for the atomic polarization 5%, or 15% of the R_D value, respectively; ^d calculated for the dihedral angle $\tau = 120^\circ$ unless otherwise noted; ^e for a 1 : 1 mixture of conformations with the dihedral angles $\tau = 120^\circ$ and 240° ; ^f for a 1 : 1 mixture of conformations with the dihedral angles $\tau = 105^\circ$ and 255° ; ^g the two planar conformations of the methoxyl group were taken as equally populated; ^h with the assumed free rotation of the C₆H₅CH₂ group around the C-S bond.

The calculated dipole moments are listed in Table I only for the actual conformations; the remaining values are represented graphically in Figs 1 and 2.

DISCUSSION

The compounds *I* and *II* represent the simplest problem since the two *sc* conformations, *B* and *C*, are identical and it is only to decide between them and the *ap* conformation *A*. In the case of compound *III* the forms *B* and *C* differ but cannot be distinguished on the basis of dipole moment data.

The comparison of calculated and experimental moments is shown in Fig. 1. Within the framework of the simple bond moment scheme the theoretical values for *I–III* are equal and depend on the dihedral angle τ following a sinusoidal curve. The experimental values for these compounds are distinctly different, nevertheless they yield accordant results as far as the conformation is concerned: the dihedral angle τ is determined to $120 \pm 5^\circ$. For the compound *III* the result is ambiguous, either $\tau = 120^\circ$ or $\tau = 240^\circ$.

Compound *VII* presents two additional problems: the unknown conformation around the $\text{CH}_2\text{—S}$ bond, for which free rotation was assumed, and the different polarity of the R^1 and R^2 groups. Hence the calculated moments for the conformations *B* and *C*, or, more generally, for the dihedral angles τ and $360 - \tau$, are not equal. However, their difference is rather small and amounts 0.41 D for $\tau = 120^\circ$ or 240° , respectively. In Fig. 1 only the average values for the angles τ and $360 - \tau$ are plotted and the result is again ambiguous: either the form *B* or *C* is admissible.

TABLE II
The $^1\text{H-NMR}$ Chemical Shifts of α -Nitro Sulfones and Model Compounds

Compound	Chemical shifts ^a δ (temperature shifts ^b)			
	CH_3	CH_2	CH	aromatic
$\text{C}_6\text{H}_5\text{SO}_2\text{CH}_3$	3.11 (–0.19)	—	—	7.8 (–0.10)
$\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{CH}_3$	2.82 (–0.17)	4.38 (–0.20)	—	7.4 (–0.10)
<i>VII</i>	—	4.78 (–0.31) ^c	7.17 (–0.47) ^c	7.4 (–0.1) ^c
<i>I</i>	2.51 (–0.02) ^c	6.21 (–0.36) ^c	—	7.52; 7.88 (–0.06) ^c
<i>VI</i>	2.44 (+0.01)	—	7.12 (–0.48)	7.40; 7.66 (–0.06)
	3.82 ^d (–0.01)			6.96; 7.56 (–0.08)

^a In perdeuterioacetone at 35°C ; ^b difference of the δ values shifts at $+35$ and -70°C , obtained from measurements at 5–8 different temperatures; ^c similar temperature dependence was found within the interval $+30$ to 100°C in perdeuteriodimethyl sulfoxide; ^d OCH_3 group.

In order to decide between the latter two possibilities we must exploit the substitution in the *para* position of an aromatic derivative. In Fig. 2 the experimental and calculated dipole moments of the compounds *IV* and *V* are compared using a two-dimensional graph¹². No single calculated point matches the experimental results but several solutions are admissible assuming a mixture of two forms since various mixtures are represented in the graph by a tie-line of the respective points. The simple assumption of a 1 : 1 mixture of *B* and *C* agrees with experiment moderately well; if the dihedral angles are modified, say to 105° and 255°, respectively, the agreement is improved. However, there are even other possibilities and the accuracy of the whole procedure does not warrant such amendments much credit. A definite finding supported by all the dipole moment data is the pronounced preference of *sc* conformations (*B*, *C*) over *ap* (*A*); the latter has been never detected. If two *sc* forms are possible, the experimental data can be reconciled with their approximately equal population. The calculated values of dipole moments for the envisaged conformations or their respective mixtures are listed in Table I, last column. They differ from the experimental values by 0.3 D at most.

The above findings are compatible with the ¹H-NMR spectra of selected derivatives (Table II) which, however, are of little diagnostic value taken by themselves. The temperature shifts of C—H signals of *VI* and *VII*, as well as of the CH₂ signals of *I* and *VII* are marked and could be interpreted by a conformational change. They cannot be, however, attributed to the equilibrium *B* ⇌ *C* since they are observed even for the compound *I* whose forms *B* and *C* do not differ. Furthermore a change

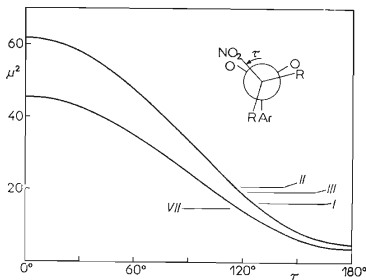


FIG. 1

Dependence of Squared Dipole Moments for Various Conformations of α -Nitro Sulfones *I*, *II*, *III*, and *VII* on the Dihedral Angle τ

Experimental values are shown by abscissae. The calculated values for *VII* are averages of the conformations with the angles τ and $360 - \tau$, respectively.

of the equilibrium $B(C) \rightleftharpoons A$ could be involved but is not proven since an alternative explanation is possible assuming rotation of the phenyl ring (with compounds *VI* and *VII* of two phenyl rings); this is not manifested in the dipole moment values but can affect the NMR signals appreciably. Interestingly, the temperature shifts of the same direction and of similar magnitude were observed for simple model compounds methyl phenyl sulfone and methyl benzyl sulfone. The rotation around the C—S bond cannot thus be detected due to these additional degrees of freedom. Note that the direction of the shift for methyl phenyl sulfone does not confirm its assumed¹⁸ stable conformation *D*, which would change in the direction toward *E* at higher temperatures.* The only relevant finding from the ¹H-NMR spectra are thus the chemical shifts of aromatic protons in *VI* which point out the interaction of the two rings in the form *C*.

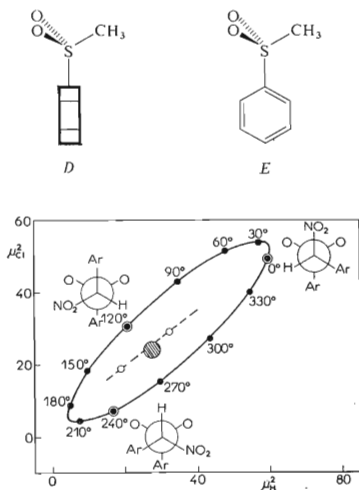


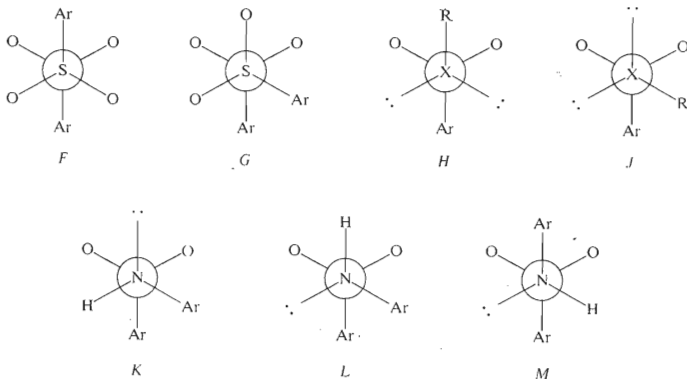
FIG. 2

Comparison of Squared Dipole Moments of α -Nitro Sulfones *IV* (x -axis) and *V* (y -axis)

Calculated values for various dihedral angles τ are represented by full points, for the 1 : 1 mixture by empty points; the hatched circle refers to the experimental dipole moments.

* Another explanation could be based on hydrogen bonding of the rather acidic CH or CH₂ groups to the solvent. Unexpected temperature induced shifts were observed for certain sulfones in dioxan solution (R. Remerie and J. B. F. N. Engberts, unpublished).

In conclusion, all the results agree with the idea that the interactions of polar substituents on the S—C bond determine the conformation of the whole molecule and no special effect favouring the folded conformation (*C*) has been detected. The conformation around the C—S bond itself seems at first glance to corroborate the gauche rule⁴, in particular if reference is made to 1,2-disulfones¹¹, alkyl sulfonates¹⁶ or thiosulfonates¹⁹, and *N*-substituted sulfonamides²⁰, all favouring the less symmetrical "gauche" forms *G*, *J*, *L* against the "trans" forms *F*, *H*, *K*, respectively. However, a closer inspection reveals that it is difficult to formulate a general rule to govern all these cases, and the following discussion is warranted.



Let us consider first the molecules without the participation of lone electron pairs. If we count mechanically all the gauche interactions between polar bonds⁴ (X/X interactions), no decision is possible between *A* and *B(C)*, or between *F* and *G*. If we differentiate polar bonds according to the direction of polarity¹¹, it follows that in the form *G* the gauche interaction of parallel bonds, in *B(C)* of antiparallel bonds must be decisive. Another theory stresses the *trans* position of polar bonds with donor substituents as the destabilizing factor⁸. This could explain the instability of *F* but hardly that of *A*. If the lone electron pairs come into play, the situation is still more complex since one cannot estimate whether an interaction bond-bond (X/X) or bond-pair (X/e) or pair-pair (e/e) is more effective⁴. It is true that the conformation of a particular molecule may be theoretically predicted using more or less sophisticated calculations⁷⁻¹⁰, but if a general rule with a certain predicting power is desired, a new conception is needed. In our opinion it is the overall symmetry of the pertinent conformation which has not been paid sufficient attention. On the example of fluoro-

methanol the symmetry of the *ap* form — involving the equivalency of the two electron pairs — was considered to be responsible for its higher energy⁷. This idea has not been elaborated for other molecules but is able to explain qualitatively all the mentioned cases. While in the form *H* the lower stability might be associated with the equivalency of lone electron pairs (or of oxygen atoms as well), in *A* and *F* it is clearly the equivalency, in *K* the virtual equivalency of the two oxygen atoms. In terms of symmetry even a particular rule¹⁰ is easily understandable, called the Edward-Lemieux effect or anomeric effect, according to which a polar bond placed between two electron pairs is disfavoured. Our reasoning would ultimately lead to the simple rule that less symmetrical forms are preferred for all molecules with polar bonds and lone electron pairs. This is of course already an oversimplification since for instance in less polar molecules the non-bonding interactions may overweight, preferring forms with remote substituents, *i.e.* generally more symmetrical. Nevertheless, the symmetry of electron pairs, or generally of molecular orbitals is certainly an important factor in determining conformation.

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