

STUDY OF DIPOLE MOMENTS OF PHENYLSULPHONYL ISOTHIOCYANATES

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The dipole moments of 4-substituted phenylsulphonyl isothiocyanates have been measured in benzene at 20°C. The steric arrangement of SO₂NCS group is discussed on the basis of comparison of the dipole moment values measured with those calculated by vectorial addition of bond moments for the conformers formed by rotation around the S-N bond.

So far no data are available in the literature about the dipole moments of sulphonyl isothiocyanates. As far as analogous derivatives are concerned, dipole moments of isothiocyanates, isocyanates, isoselenocyanates, and acylisothiocyanates were published¹⁻⁵.

In the case of phenylsulphonyl isothiocyanates we were mainly interested in the polar character of SO₂NCS group and its effect on the aromatic ring. Our earlier work⁶ dealt with the problem of structure and polar character of SO₂NCS group on the basis of IR, UV, and NMR spectral studies. As the results of these spectral measurements were not exhaustive, we directed our subsequent studies on electronic effects of SO₂NCS group using the dipole moments.

In order to elucidate the steric arrangement of SO₂NCS group we started from the present knowledge⁷⁻⁹ about structure of —SO₂—X groups from the standpoint of the gauche effect¹⁰. We examined the conformers of phenylsulphonyl isothiocyanates formed by the rotation around the S—N(trigonal) bond. The dipole moments were measured in benzene according to Halverstadt and Kumler¹¹ and were evaluated by the graphical method¹².

EXPERIMENTAL

Reagents

Phenylsulphonyl isothiocyanate, b.p. 73–80°C/1 Pa, 4-chlorophenylsulphonyl isothiocyanate, b.p. 96–100°C/1 Pa, and 4-methylphenylsulphonyl isothiocyanate, b.p. 116–120°C/1 Pa were prepared by the known¹³ thermolysis of N-phenylsulphonyl dithiocarbamates. No other 4-substituted phenylsulphonyl isothiocyanates suitable for investigation of dipole moments have been synthesized so far.

Dipole Moments

The relative permittivities (ϵ) were measured with a Dipolmeter DM 01 (Wissenschaftliche-technische Werkstätten) with the accuracy of 0.0001, using a thermostatted dielectric cell DFL 2 of 4 ml volume, and pure distilled benzene (for UV spectral measurements) as the solvent. The measurements were carried out at four concentration values from $1.5 \cdot 10^2$ to $8 \cdot 10^2 \text{ mol l}^{-1}$ at $20 \pm 0.005^\circ\text{C}$ at the frequency of 2.0 MHz.

The resulting dipole moments were calculated according to Halverstadt and Kumler¹¹ with a correction for atomic polarization (5–15%). The molar refraction, R_D , was calculated from the published¹⁴ increments. The results are given in Table I.

The following standard values of bond and group moments (in Cm) were used in the theoretical calculations: H-C_{Ar} 0, $\text{C}_{\text{Ar}}\text{-Cl}$ 5.33, $\text{C}_{\text{Ar}}\text{-CH}_3$ 1.23, C-S 3.0, SO_2 10.67, the correction for the conjugation of ArSO_2 3.33 (ref.⁹), NCS 9.7, θ 20° (ref.¹). Bond angles: $\text{C}_{\text{Ar}}\text{-S-O}$ 109° , O-S-O 119° , $\text{C}_{\text{Ar}}\text{-S-N}$ 105° (refs^{7,15}). The dipole moments were calculated graphically by the vectorial addition of the bond moments.

DISCUSSION

Table I presents the results of measurements as well as the values of the dipole moments measured for the compounds investigated. The dipole moments measured for 4-substituted phenylsulphonyl isothiocyanates were compared with those of NCS , NCSe , NCO , and CONCS groups^{1,5,16}, and the following order of increasing μ was found: $\text{NCO} < \text{NCS} < \text{NCSe} < \text{CONCS} < \text{SO}_2\text{NCS}$.

When calculating the dipole moments of 4-substituted phenylsulphonyl isothiocyanates we tried to bring into harmony the ideas about tetrahedral structure of SO_2 group¹⁷ and the structure and conformation of NCS group. We were interested in the predominant conformation formed by the rotation around the S-N (trigonal) bond. With regard to the steric effect of functional groups and the relation of free electron pairs and polar bonds the most likely conformations are *A*, *B*, *C*.

TABLE I

The polarization values and the dipole moments of phenylsulphonyl isothiocyanates measured in benzene at 20°C

X	α	β_d	cm^3		10^{-30} C m		
			∞P_2	R_D	$\mu_{5\%}$	$\mu_{15\%}$	$\mu_{\text{calc.}}^a$
4- CH_3	31.86	0.514	521.11	54.29	15.71	15.62	15.67
H	30.72	0.955	488.35	49.64	15.23	15.14	14.43
4-Cl	12.50	0.826	236.61	44.83	10.04	9.92	9.09

^a The dipole moments calculated from the bond moments for the conformation *B* ($\tau = 90^\circ$).

The comparison of the dipole moments calculated for various conformations with the values measured was carried out on the basis of sinusoidal dependence of squares of calculated dipole moments on the dihedral angle τ (Fig. 1), and with application of the graphical method¹² (Fig. 2). From this comparison it follows that the more favourable is the clinal form of the *B* conformation of phenylsulphonyl isothiocyanates with the dihedral angle $\tau < 90^\circ$.

Furthermore we made an attempt at estimation of mesomeric interaction of the NCS group on the basis of the finding¹ that the mesomeric effect of NCX groups increases in the order: NCO < NCSe < NCS, which is connected with decreasing magnitude of positive charge at the carbon atom of the groups mentioned and with decreasing reactivity to nucleophilic addition reactions. In order to complete the above-mentioned series, we also investigated the rate of nucleophilic addition reaction of phenylsulphonyl isothiocyanate with 1-butanamine in cyclohexane ($k = 9\,699\text{ l. mol}^{-1}\text{ s}^{-1}$). The comparison of the rate constants of the compounds mentioned with that of benzoyl isothiocyanate¹⁸ ($k = 848\text{ l mol}^{-1}\text{ s}^{-1}$) showed that the reactivity of the heterocumulenes studied increases in the order: NCS < NCSe < NCO < < CONCS < SO₂NCS. This means that in comparison with the other heterocumulenes the NCS group of phenylsulphonyl isothiocyanates exhibits the smallest mesomeric interaction.

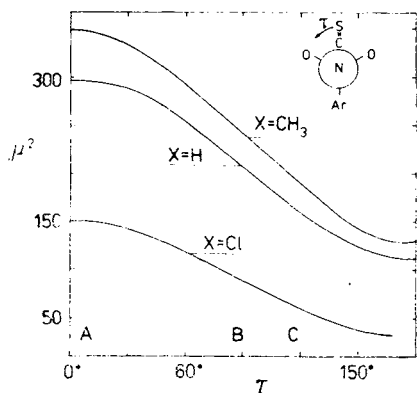


FIG. 1

The dependence of squares of dipole moments of phenylsulphonyl isothiocyanates on the dihedral angle τ

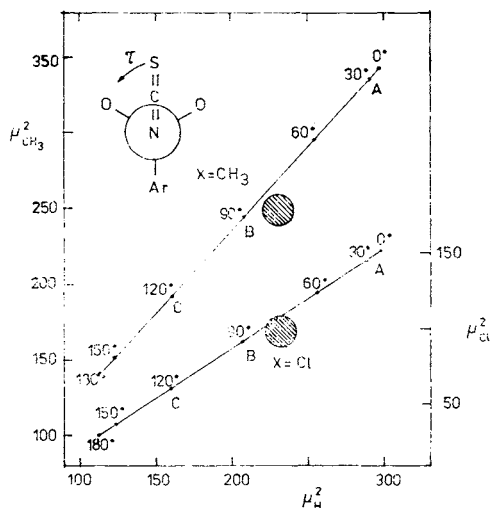


FIG. 2

Graphical comparison of squares of dipole moments of 4-substituted phenylsulphonyl isothiocyanates X = H (the *x* axis) and X = CH₃ or X = Cl (the *y* axis)

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