An Experimental and Theoretical Dipole Moment Study of 2-Chloropyridine-5-sulphonyl Chloride

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Analysis of the dipole moment of 2-chloropyridine-5-sulphonyl chloride in benzene at 30 °C (2.00 D) supports a model in which the C(5)—SCI group is rotated by 40° around the C(5)—S bond axis. The function <p(φ) = 129.53941 a.u., <p(φ = 90°) = 129.53941 a.u. and <p(φ = 180°) = 129.53941 a.u. was assumed to equal the molecular refraction (Rm = 43.9 cm3) calculated by additivity from the literature experimental refractions of liquid benzencesulphonyl chloride (41.03), chlorobenzene (31.14), pyridine (24.07) and benzene (26.18). From P2x = 124.6 cm3 and Rm = 44.0 cm3, the electric dipole moment of 2-C-5-S-C is calculated to be μ = (2.00 ± 0.02) D (1 Debye = 3.3356 x 10−30 C m). The techniques used for the measurement of dielectric permitivities and specific volumes are described elsewhere. Total energies and dipole moments were calculated for three conformations of the compound. A preferred conformation of 2-C-5-S-C in benzene is suggested.

Introduction

Physico-chemical studies have been devoted to benzencesulphonyl chlorides [1–6], naphthalene- and anthracenesulphonyl chlorides [5], 2-furansulphonyl chloride [7], 2-thiophenesulphonyl chloride [7, 8] and its 5-methyl-, 5-chloro-, 5-bromo-, 5-ido- and 5-nitro-substituted derivatives [7], none dealing with pyridinesulphonyl chlorides.

In the present Note we report on a measurement of the dipole moment of 2-chloropyridine-5-sulphonyl chloride (2-C-5-S-C) in benzene at 30 °C, and on CNDO/2 calculated energies and dipole moments for three selected conformers of the compound. A preferred conformation of 2-C-5-S-C in benzene is suggested.

Experimental

2-C-5-S-C was prepared as indicated in Ref. [9]: m.p. 51 °C (lit. 50–51 °C corr. [9]), b.p. 132°/8 torr.

The dipole moment of the compound was measured with the Debye refractivity method. The total polarization of the solute (P2x = 124.6 cm3), extrapolated to infinite dilution, was calculated from the experimental ratios [10],

\[
\alpha = \frac{\sum (\epsilon - \epsilon_i) / \sum w} = 2.25
\]

and

\[
\beta = \frac{\sum (\epsilon - \epsilon_1) / \sum w} = -0.470 \text{ cm}^3 \text{ g}^{-1},
\]

where w is the weight fraction of the solute, \(\epsilon\) and \(\epsilon_i\) are the dielectric permittivity and specific volume of the solutions, and the subscript 1 refers to the pure solvent (\(\epsilon_1 = 2.2642\), \(\epsilon_1 = 1.1511\)). The α value was calculated by a least-squares analysis of the \(\epsilon(\omega)\) polynomial function, here linear. The distortion polarization of the solute, \(\mu P + \mu P\), was assumed equal to the molecular refraction (Rm = 43.9 cm3) calculated by additivity from the literature experimental refractions of liquid benzencesulphonyl chloride (41.03), chlorobenzene (31.14), pyridine (24.07) and benzene (26.18).

From P2x = 124.6 cm3 and Rm = 44.0 cm3, the electric dipole moment of 2-C-5-S-C is calculated to be μ = (2.00 ± 0.02) D (1 Debye = 3.3356 x 10−30 C m). The techniques used for the measurement of dielectric permitivities and specific volumes are described elsewhere.

Total energies and dipole moments were calculated for three conformations of the compound (A, B and C with \(\phi = 0°\), 90° and 180°, respectively, see Fig. 1), by means of the CNDO/2 technique. The computations were performed with a CDC 7600 computer system using Pople’s standard programme. The relevant dimensions were taken from the structures of pyridine [13], 2-chloropyridine [14], and benzencesulphonyl chloride [6]. Results: E(A) = −129.53941 a.u., μ(A) = 0.36 D; E(B) = −129.53204 a.u., μ(B) = 3.45 D, and E(C) = −129.53500 a.u., μ(C) = 4.58 D.

Discussion

The conformation of 2-C-5-S-C implies a sulphonylchloride-group rotational angle \(\phi\) about the C(5)–SO–Cl bond axis. The function μ(\(\phi\)) can be calculated from the dipole moments of benzencesulphonyl chloride (4.53 D [5]) and 2-chloropyridine (3.25 D [15]) in benzene by using the following vector additivity scheme. Dipole moment analysis of p-chlorobenzencesulphonyl chloride (μ = 3.23 D [4]),

* 3-Pyridinesulphonyl chloride (and derivatives) and 2-pyridinesulphonyl chloride, unlike 2-C-5-S-C, are not stable enough to be handled for a dipole moment determination.

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in terms of $\mu$ (PhSO$_2$Cl) and $\mu$ (PhCl) = 1.59 D [16], shows that $\mu$ (PhSO$_2$Cl) is a vector situated in the CIS$_b$ plane ($b$ is the bisector of the angle OSO), close to the oxygen atoms because $\mu$ (S–Cl) is much smaller than $\mu$ (S = O) (see later), acting at 27° to the Ph–S bond axis (cf. [7]). The dipole moment of 2-chloropyridine can be regarded as the vector sum of $\mu$ (pyridine) = 2.20 D [17], $\mu$ (PhCl), and of a 0.09 D $\Delta m$ vector directed along the Cl–Car bond axis or (better) a 0.17 D $\mu_m$ vector lying along the Cl–N line (see [18]). Taking CNC = 117° and NCCl = 116° from the well-known structures of pyridine [13] and 2-chloropyridine [14], calculation leads to $\mu^2(\phi) = 10.11 - 8.17 \cos \phi$ or 10.62 – 8.52 cos $\phi$, and 9.87 – 8.17 cos $\phi$ if assuming $\Delta m = 0$ and $M_2 = 0$. Comparison of the experimental dipole moment of the compound (2.00 D) with CNDO/2 calculated dipole moments for C- and C-conformers (0.36, 3.45, 4.58 D), if assuming $\mu^2(\phi) = z - \beta \cos \phi$. From these results, a $\phi$ angle of about 40° may be retained for the preferred conformation of 2-C-5-S-C in benzene. Interestingly, the benzene electric dipole moment of isopropyl 2-pyridyl sulphone (4.97 D [19]) is consistent with a similar model, with a $\phi$ angle of 58° or 51° as calculated using the benzene values for isopropyl 2-pyrazinyl sulphone or isopropyl phenyl sulphone (4.64 and 4.74 D [19]) and isopropyl 4-pyridyl sulphone (3.79 D [20]). These findings are of great interest because benzenesulphonyl chloride and 2-thiophenesulphonyl chloride in the gaseous phase exhibit a structure with $\phi = 75 \pm 3°$ [6] or with $\phi = 90°$ [8], and methyl phenyl sulphone in the crystalline state a model with $\phi = 75°$ [21].

The actual conformations of 2-C-5-S-C and isopropyl 2-pyridyl sulphone can be explained by interplay of two conflicting factors: Maximal sulphonyl-arene conjugation energy should occur for orthogonal models ($\phi = 90°$) [22]. Electrostatic repulsion (in the orthogonal model) between one of the sulphonyl oxygen atoms and the aza-nitrogen atom tends to favour an $\alpha$-model ($\phi = 0°$) since the S–Cl link is much less polar than the S = O one as indicated by the dipole moments of methane sulphonyl chloride (2.00 D [23]) and dimethyl sulfoxide (3.96 D [24]). For isopropyl 2-pyridyl sulphone there exists somme attraction between the alkyl group and aza-nitrogen atom.