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)–SCl group is rotated by 40° from the 2-chloro-1-pyridyl group (see Figure 1). Such a model, with the S–Cl chlorine atom close to the 1-azanitrogen atom, may be explained by interplay of two conflicting factors, namely sulphonylchloride-arene conjugation and lesser repulsion between one of the oxygen atoms and the aza-nitrogen atom.

Introduction

Physico-chemical studies have been devoted to benzenesulphonyl 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-iodo- 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

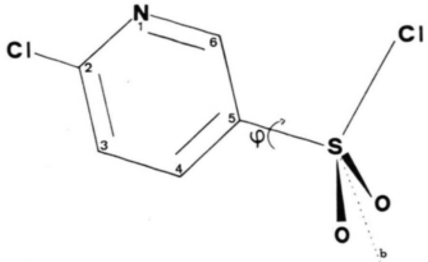

Fig. 1. Conformation *A* ($\varphi = 0°$) of 2-chloropyridine-5-sulphonyl chloride. The actual structure of the compound, which fits its electric dipole moment in benzene, results from the *A*-model by a 40° rotation of the SO_2Cl group around the C(5)–S bond axis.

of the solute ($P_{2\infty} = 124.6$ cm^3), extrapolated to infinite dilution, was calculated from the experimental ratios [10],

$$\alpha = \sum (\varepsilon - \varepsilon_1)/\sum w = 2.25$$

and

$$\beta = \sum (v - v_1)/\sum w = -0.470 \text{ cm}^3\,\text{g}^{-1},$$

where w is the weight fraction of the solute, ε and v are the dielectric permittivity and specific volume of the solutions, and the subscript 1 refers to the pure solvent ($\varepsilon_1 = 2.2642$, $v_1 = 1.1511$). The α value was calculated by a least-squares analysis of the $\varepsilon(w)$ polynomial function, here linear. The distortion polarization of the solute, ${}_EP + {}_AP$, was assumed to equal the molecular refraction ($R_D = 43.9$ cm^3) calculated by additivity from the literature experimental refractions of liquid benzenesulphonyl chloride (41.03), chlorobenzene (31.14), pyridine (24.07) and benzene (26.18). From $P_{2\infty} = 124.6$ cm^3 and $R_D = 44.0$ cm^3, the electric dipole moment of 2-C-5-S-C is calculated to be $\mu = (2.00 \pm 0.02)$ D (1 Debye = 3.3356×10^{-30} *C m*). The techniques used for the measurement of dielectric permittivities and specific volumes are described elsewhere [10, 11].

Total energies and dipole moments were calculated for three conformations of the compound (*A*, *B* and *C* with $\varphi = 0°$, 90° and 180°, respectively, see Fig. 1), by means of the CNDO/2 technique [12]. 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 benzenesulphonyl chloride [6]. Results: $E(A) = -129.53941$ a u, $\mu(A) = 0.36$ D; $E(B) = -129.53204$ a u, $\mu(B) = 3.45$ D, and $E(C) = -129.53500$ a u, $\mu(C) = 4.58$ D.

Discussion

The conformation of 2-C-5-S-C implies a sulphonylchloride-group rotational angle φ about the C(5)–SO_2Cl bond axis. The function $\mu(\varphi)$ can be calculated from the dipole moments of benzenesulphonyl 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*-chlorobenzenesulphonyl chloride ($\mu = 3.23$ 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 μ ($PhSO_2Cl$) and μ (PhCl) = 1.59 D [16], shows that $\boldsymbol{\mu}$ ($PhSO_2Cl$) is a vector situated in the ClS*b* plane (*b* is the bisector of the angle OSO), close to the oxygen atoms because μ (S–Cl) is much smaller than μ (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 μ (pyridine) = 2.20 D [17], $\boldsymbol{\mu}$ (PhCl), and either of a 0.09 D $\Delta \boldsymbol{m}$ vector directed along the Cl–Car bond axis or (better) a 0.17 D $\boldsymbol{M}_2$ vector lying along the Cl ... N line (see [18]). Taking $\widehat{CNC} = 117°$ and $\widehat{NCCl} = 116°$ from the well-known structures of pyridine [13] and 2-chloropyridine [14], calculation leads to $\mu^2(\varphi) = 10.11 - 8.17 \cos\varphi$ or $10.62 - 8.52 \cos\varphi$, and $9.87 - 8.17 \cos\varphi$ if assuming $\Delta m = 0$ and $M_2 = 0$. Comparison of the experimental dipole moment of the compound (2.00 D) with those so calculated indicates either $\varphi = 42°$ or (better) 39°, and 44°. A similar φ angle (~ 40°) is obtained from the CNDO/2 calculated dipole moments for *A*, *B* and *C*-conformers (0.36, 3.45 and 4.58 D), if assuming $\mu^2(\varphi) = \alpha - \beta \cos\varphi$. From these results, a φ 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 φ 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 $\varphi = 75 \pm 3°$ [6] or with $\varphi = 90°$ [8], and methyl phenyl sulphone in the crystalline state a model with $\varphi = 75°$ [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 ($\varphi = 90°$) [22]. Electrostatic repulsion (in the orthogonal model) between one of the sulphonyl oxygen atoms and the aza-nitrogen atom tends to favour an *A*-model ($\varphi = 0°$) 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 sulphoxide (3.96 D [24]). For isopropyl 2-pyridyl sulphone there exists somme attraction between the alkyl group and aza-nitrogen atom.

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