

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

H. Lumbroso,

Laboratoire de Chimie Générale, Université Pierre et Marie Curie, Paris, France

E. Montoneri,

Dipartimento di Chimica Industriale ed Ingenieria Chimica, Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milano, Italy

and G. C. Pappalardo

Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania, Viale A. Doria 8, 95125 Catania, Italy

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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 benzene-sulphonyl chlorides [1–6], naphthalene- and anthracene-sulphonyl 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

* 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.

Reprint requests to H. Lumbroso, Laboratoire de Chimie Générale, Université Pierre et Marie Curie, 4, Place Jussieu, 75230 Paris-Cedex 05, France.

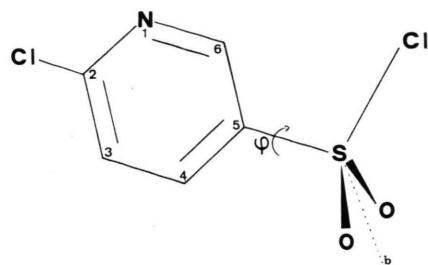


Fig. 1. Conformation *A* ($\phi = 0^\circ$) of 2-chloropyridine-5-sulphonyl chloride. The actual structure of the compound, which fits its electric dipole moment in benzene, results from the *A*-model by a 40° rotation of the SO_2Cl group around the C(5)-S bond axis.

of the solute ($P_{2\infty} = 124.6 \text{ cm}^3$), 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, $E^P + A^P$, was assumed to equal the molecular refraction ($R_D = 43.9 \text{ cm}^3$) 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 $P_{2\infty} = 124.6 \text{ cm}^3$ and $R_D = 44.0 \text{ cm}^3$, the electric dipole moment of 2-C-5-S-C is calculated to be $\mu = (2.00 \pm 0.02) \text{ D}$ (1 Debye = $3.3356 \times 10^{-30} \text{ C m}$). 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 $\phi = 0^\circ$, 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: $E(A) = -129.53941 \text{ a.u.}$, $\mu(\text{\AA}) = 0.36 \text{ D}$; $E(B) = -129.53204 \text{ a.u.}$, $\mu(B) = 3.45 \text{ D}$, and $E(C) = -129.53500 \text{ a.u.}$, $\mu(C) = 4.58 \text{ D}$.

Discussion

The conformation of 2-C-5-S-C implies a sulphonylchloride-group rotational angle ϕ about the C(5)-SO₂Cl bond axis. The function $\mu(\phi)$ 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 ($\mu = 3.23 \text{ D}$ [4]),

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in terms of μ (PhSO₂Cl) and μ (PhCl) = 1.59 D [16], shows that μ (PhSO₂Cl) is a vector situated in the CIS 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], μ (PhCl), and either of a 0.09 D Δm vector directed along the Cl-Car bond axis or (better) a 0.17 D M_2 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 those so calculated indicates either $\phi = 42^\circ$ 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 $\mu^2(\phi) = \alpha - \beta \cos \phi$. 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 $\phi = 75 \pm 3^\circ$ [6] or with $\phi = 90^\circ$ [8], and methyl phenyl sulphone in the crystalline state a model with $\phi = 75^\circ$ [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 ($\phi = 90^\circ$) [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 ($\phi = 0^\circ$) 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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