

# 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)–SO<sub>2</sub>Cl 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-azanirogen 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

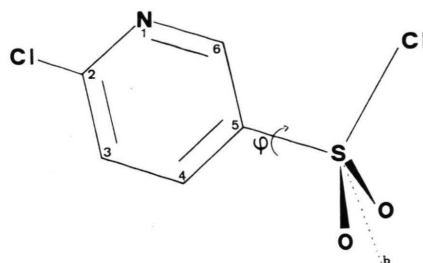


Fig. 1. Conformation *A* ( $\varphi = 0^\circ$ ) of 2-chloropyridine-5-sulphonyl chloride. The actual structure of the compound, which fits its electric dipole moment in benzene, results from the *A*-model by a 40° rotation of the SO<sub>2</sub>Cl group around the C(5)–S bond axis.

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,  $\varepsilon$  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  $\alpha$  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  $\varphi = 0^\circ$ ,  $90^\circ$  and  $180^\circ$ , 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:  $E(A) = -129.53941 \text{ a.u.}$ ,  $\mu(A) = 0.36 \text{ D}$ ;  $E(B) = -129.53204 \text{ a.u.}$ ,  $\mu(B) = 3.45 \text{ D}$ , 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  $\varphi$  about the C(5)–SO<sub>2</sub>Cl 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 ( $\mu = 3.23 \text{ D}$  [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<sub>2</sub>Cl) and  $\mu$  (PhCl) = 1.59 D [16], shows that  $\mu$  (PhSO<sub>2</sub>Cl) is a vector situated in the ClSb 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 either of a 0.09 D  $\Delta m$  vector directed along the Cl—C<sub>ar</sub> 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  $\mu^2(\varphi) = 10.11 - 8.17 \cos \varphi$  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  $\varphi = 42^\circ$  or (better)  $39^\circ$ , and  $44^\circ$ . A similar  $\varphi$  angle ( $\sim 40^\circ$ ) 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  $\varphi$  angle of about  $40^\circ$  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  $\varphi$  angle of  $58^\circ$  or  $51^\circ$  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  $\varphi = 75 \pm 3^\circ$  [6] or with  $\varphi = 90^\circ$  [8], and methyl phenyl sulphone in the crystalline state a model with  $\varphi = 75^\circ$  [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 ( $\varphi = 90^\circ$ ) [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 ( $\varphi = 0^\circ$ ) 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 some attraction between the alkyl group and aza-nitrogen atom.

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