Gas Electron Diffraction Study of the Molecular Structure of Di-2-pyridyl Sulphide

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The gas-phase electron diffraction study of di-2-pyridyl sulphide has yielded $r_g(\mathrm{S-C})$ 1.786 ± 0.004 Å and $\sphericalangle$ C—S—C 104.4 ± 1.7°. The dimensions of the pyridyl groups were found to be consistent with those of free pyridine molecules. Models with various conformational properties could be used to approximate the experimental data.

The present electron diffraction investigation was primarily aimed at determining the sulphur bond configuration in di-2-pyridyl sulphide. This work is an extension of previous, mainly spectroscopic, studies on the conformational properties of this compound [1, 2] and its sulphone analog [2, 3] on one hand, and the electron diffraction investigation of diphenyl sulphide [4], sulphoxide, and sulphone [5] on the other hand. Unfortunately only a limited amount of information as regards the conformational properties of these compounds can be expected from electron diffraction [4, 5]. The geometry (r_s) of the pyridine molecule is known from microwave spectroscopic studies [6].

Experimental conditions and the general procedure of structure analysis were the same as in [4]. Electron diffraction patterns were taken at nozzle temperatures of 134—143 °C. Reduced molecular intensities (Fig. 1) were used in ranges $2.00 \leqq s \leqq 13.75$ and $8.00 \leqq s \leqq 34.00$ Å^{-1} with a data step of $\Delta s = 0.25$ Å^{-1}.

The experimental molecular intensities (Fig. 1) and radial distribution (Fig. 2) closely resemble those of diphenyl sulphide [4]. The C–C and C–N bond lengths and C ... C and C ... N non-bond distances cannot be well resolved partly because of the similarity of the electron scattering power of carbon and nitrogen. The relative positions of the nitrogen atoms proved to be unimportant indeed, thus we considered later only one of their possible orientations in a model with given ring planes.

Because of the complexity of the structure, several further constraints have been applied throughout this analysis: (i) the geometry of the 2-pyridyl group was assumed to differ from that of pyridine itself by a scale factor (β) only; (ii) the deformation of the ring geometry upon substitution was thus ignored but mean C–C and C–N bond lengths were considered; (iii) the S–C bond was assumed to bisect the adjacent N–C–C angle.

In addition to β, the following independent geometrical parameters were chosen: the S–C bond length, the C–S–C angle, and the dihedral angles (φ_1, φ_2) of the C–S–C plane with the ring planes (for their sign convention see Figure 2). Vibrational amplitudes l were treated similarly as in [4]. No shrinkage effects have been considered.

Several initial parameter sets of a great variety of conformers were refined, with the dihedral angles either fixed, or refined independently, or restricted to $\varphi_1 = \varphi_2$ (symmetry C_2) or $\varphi_1 = -\varphi_2$ (symmetry

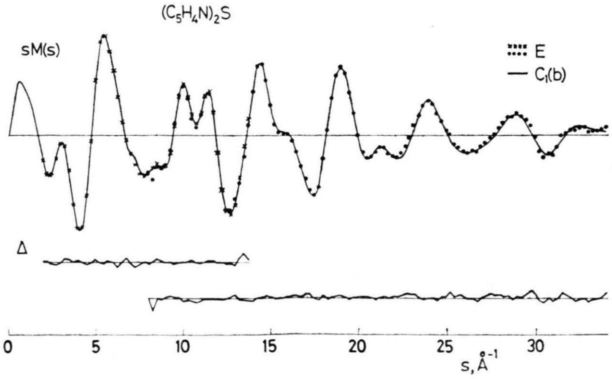

Fig. 1. Experimental, E, and theoretical, $C_1(b)$, molecular intensities and the difference curves Δ.

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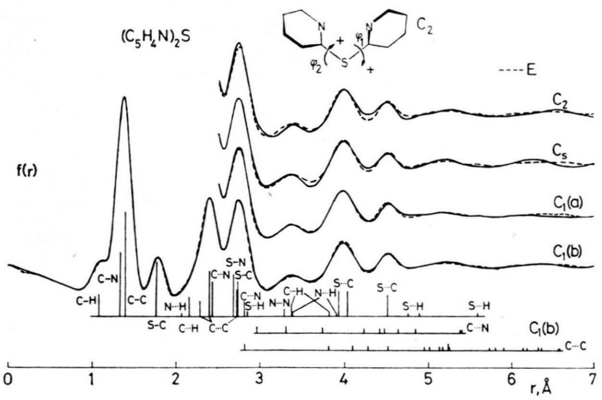

Fig. 2. Experimental, *E*, radial distribution and theoretical ones for models with the following (φ_1, φ_2), ∢ C—S—C, and *R*-factor, respectively: C_2 (16, 16), 107.3°, and 0.084; C_s (54, −54), 103.7°, and 0.079; C_1 (a) (0, 69), 104.9°, and 0.072; C_1(b) (23, 67), 104.4°, and 0.067. Contributions of model C_1(b) are marked (inter-ring C ... N and C ... C distances separately).

C_s). The dihedral angles tested include all different combinations of 0°, 30°, −30°, 60°, −60°, and 90°, additionally $\varphi_1 = 10°$, 45°, and 80° for the C_2 and C_s models, and some further combinations for the asymmetric models, and finally, some of the modifications of these obtained by adding 180° to φ_1 or φ_2 or both.

The parameters r(S—C), l(S—C), and the factor β could be established unambiguously, while there was strong correlation between the angle parameters and the amplitudes of longer distances. In some cases extreme C–S–C angles were obtained, but these models could be ruled out by reason of discrepancies between experimental and calculated distributions.

For the symmetric models, those with C_s symmetry gave somewhat better agreement with the experimental data than those with C_2 symmetry. Conformations with fixed $\varphi_1 = 0$ were scanned in the range $0 \leqq \varphi_2 \leqq 90°$ and could be fitted even better. The best models of the three sets are characterized in Figure 2. The all-planar forms were clearly not the best models [7]. The less constrained asymmetric models could of course be fitted more perfectly. Refinements have shown that least-squares minima are accompanied by broad areas of the variables (φ_1, φ_2) with nearly the same good fit to the experimental data. Such local minima, also for the restricted conformations, are illustrated in Figure 3. The best agreement with the electron diffraction data was achieved for model C_1(b) (23, 67) (Figures 1, 2, 3). These numerical values of the dihedral angles are certainly not invariant to assumed l values and other conditions of the refinement. This model can be considered only as a typical representation of the electron diffraction findings on the conformational behaviour of di-2-pyridyl sulphide, but by far not to be a unique solution. Furthermore, mixtures of various forms have not been considered, although they would further improve the agreement. Because of the relatively small contribution of the rotation-dependent interactions to the electron scattering of this molecule, it would be difficult to assess, if possible at all, whether such an improvement reflects the real physical situation or not. This experimental investigation is probably also hindered by the large-amplitude motion of the pyridyl rings around their respective S–C bonds.

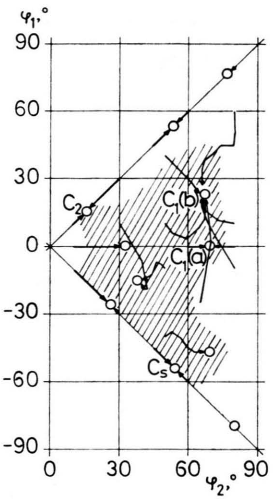

Fig. 3. Local minima of the *R*-factor and refinement paths leading to them, partly with restrictions $\varphi_1 = \varphi_2$ or $\varphi_1 = -\varphi_2$ or $\varphi_1 = 0$. Models C_2, C_s, C_1(a), and C_1(b) of Fig. 2 are marked. Hatching indicates shallow areas around minima. Note that (i) the lines $\varphi_1 = \varphi_2$ and $\varphi_1 = -\varphi_2$ are symmetry axes of the map and (ii) besides φ_1 and φ_2 other parameters were also allowed to vary.

The conclusions of this structure analysis can be summarized as follows.

(1) The overall model applied well represents the structure of di-2-pyridyl sulphide in spite of the severe geometric constraints.

(2) The S–C bond distance and C–S–C bond angle are well determined:

$$r_g(\text{S–C}) \quad 1.786 \pm 0.004 \text{ Å}$$
$$\sphericalangle \text{ C–S–C} \quad 104.4 \quad \pm 1.7° .$$

The error estimates given include standard deviations from the least-squares procedure, systematic scale errors, and the effect of correlation between data points, as described in [8]. This error estimate of the C–S–C angle has been doubled then in view of the correlation of this angle with other parameters.

(3) The bond lengths of the ring are consistent with those in the free pyridine molecule [6]. The value of β was determined to be 1.0035 ± 0.0021 and the increase in the bond lengths is at least partly a consequence of the present analysis yielding r_g values versus the microwave spectroscopic r_s data [6]. As mean values for the C–C and C–N bonds are determined (1.400 Å, and 1.344 Å, resp.), the ignored ring deformation upon substitution is thought to have no considerable effect on our results [9].

(4) As regards the conformational properties, the present analysis is consistent with the notion of the rings performing large-amplitude torsional motion or a rapid interconversion of various forms [1, 10–12] and with the broad potential energy minima revealed by quantum chemical calculations [1].

The sulphur bond angle in di-2-pyridyl sulphide is similar to that in diphenyl sulphide ($103.7 \pm 1.3°$ [4]), while r_g(S–C) was determined to be shorter in the latter molecule (1.773 ± 0.005 Å [4]). In dimethyl sulphide ∢C–S–C is smaller, the S–C bond is longer ($99.2 \pm 0.6°$ and r_g 1.811 ± 0.004 Å [13]) than in di-2-pyridyl sulphide.

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