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Electron Diffraction Studies of 2,2′-Dithienyl Vapour

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Electron diffraction studies based upon the sector method have been carried out on 2,2′-dithienyl. The obtained structure parameters of the thienyl ring are in good agreement with values obtained by micro-wave investigations for thiophene. The molecule as a whole does not seem to be planar. The angle of twist is found to be 34°.

In a series of earlier papers structure investigations have been carried out on molecules composed of ring systems linked together with single bonds [1-6]. As a member of this series of molecules 2,2′-dithienyl has been included, and an electron diffraction study based upon the sector method has been undertaken.

The sample used in the present investigation was prepared by Siv. Ing. Oddrun Holmboe at the Institute of Organic Chemistry at the Technical University of Norway. The electron diffraction diagrams were taken with the Oslo apparatus at a temperature of 130°C. The photometer curves were read off at an interval of 0.25 s units. Reproducible intensity data were obtained in the s interval ranging from 1.25 Å^{-1} to approximately 45 Å^{-1}. The photometer curves were subjected to the necessary corrections as for the photographic plates, sector corrections, *etc.*[7] To obtain intensity values suited for Fourier transformations the background due to atomic and incoherent scattering has to be subtracted. The theoretical background fitted the experimental intensity curve very well except for a small deviation in the s region beyond $s = 20$ Å^{-1}, where a minor correction had to be made. Difference curves between experimental intensity curves and the background were calculated and multiplied by an artificial damping factor $\exp(-ks^2)$. Radial distribution curves were calculated using k values of 0.0009 and 0.0036. A preliminary model from these curves was used for calculating a theoretical radial distribution curve and the corresponding intensity curve. Experiences thus obtained were used for further corrections of the background. A final intensity curve ready for Fourier transformation is given in Fig. 1. The curve has been multiplied by $\exp(-0.0036\, s^2)$. The upper curve of Fig. 2 is the corresponding Fourier transformation after the subtraction of the envelope [7]. This curve was well suited for the study of the interplanar twist in the molecule.

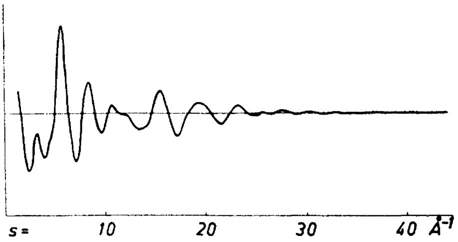

Fig. 1. Experimental intensity curve for Fourier transformation. ($k = 0.0036$).

A new model was obtained from this improved radial distribution curve. From the position of the peaks corresponding to the distances S—S and C_2—S_{10} (see Fig. 3) it could immediately be concluded that a planar model was improbable. An interplanar angle of approximately 30° had to be assumed.

The new model was used as the starting model for a least square procedure. The structure parameters, listed in the second column of Table 1, are the result of two successive approximations combined with further studies of the radial distribution curve. These values were obtained entirely from our experiment, and it is very satisfactory to compare them with those obtained by Bak *et al.* for thiophene by the micro-wave method [8]. For comparison Bak's two alternative sets of parameters are given in the third and fourth columns of Table 1. It should be pointed out that our values were calculated under the assumption of planar thienyl rings and mirror symmetry in the rings. We have also assumed that the bridge bond between the two rings is in the plane of each of them.

In order to obtain further improvements in the determination of the angle of twist, Bak's parameters for thiophene were used in the thienyl rings. If Bak's model I were used, it would be possible to determine the three additional parameters necessary for elucidating the structure of the 2,2'-dithienyl molecule, namely C_1—C_6, $\angle C_1$—C_6—S_{10}, and the angle of twist φ. The least square

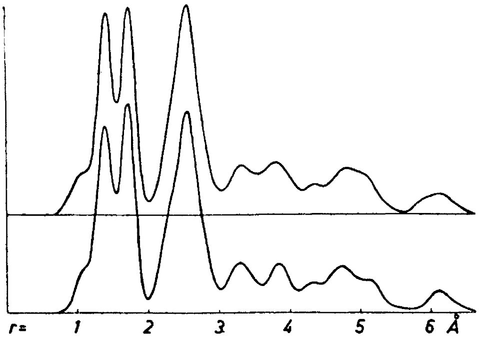

Fig. 2. Upper curve experimental and lower curve theoretical radial distribution curve. ($k = 0.0036$.)

Table 1. Structure parameters of 2.2'-dithienyl obtained from electron diffraction studies (present work) and structure parameters of thiophene obtained from micro-wave studies (Bak *et al.*[8]).

	E. D. data for 2.2'-dithienyl	M. W. data for thiophene (Bak *et al.*[8])			
		I	II		
C_4-H_4	1.08 Å	1.085 Å	1.079 Å		
C_2-H_2		1.073 Å	1.079 Å		
C_1-S_5	1.717 Å	1.718 Å	1.723 Å		
C_1-C_2	1.357 Å	1.352 Å	1.360 Å		
C_2-C_3	1.433 Å	1.455 Å	1.430 Å		
$C_1-S_5-C_4$	92.02°	91.30°	91.67°		
C_1-C_6	1.480 Å			1.501 Å	1.476 Å
$C_1-C_6-S_{10}$	120.1°			119.4°	120.0°
	33.8°			34.2°	34.3°

procedure gave as a result for the three additional parameters the values listed in the fifth column of Table 1. In the sixth column the corresponding values obtained from Bak's model II are listed.

The obtained angle of twist of approximately 34° can no doubt be explained by steric difficulties. In the case of a planar molecule the distance between an S atom and the nearest H atom is approximately 2.92 Å. At an angle of 34° the distance increases to 3.09 Å which value should be compared with the van der Waals distance between sulphur and hydrogen of approximately 3.10 Å.

Unfortunately the angle of twist, φ, is not at all determined with an accuracy corresponding to the three values of Table 1. An error estimate based upon least square calculation will lead to a too optimistic result. A more realistic estimate of errors can be carried out by a discussion of the radial distribution curve, including the effects of anharmonic oscillation about the equilibrium angle. In spite of all the sources of error and the small effect upon the decisive distances for the φ determination at small φ values, we feel that the rigid planar model can be excluded. It seems, however, difficult to exclude a more or less free rotation through a certain angle interval. From steric considerations it seems for instance probable that the molecule has a practically free rotation from a φ value corresponding to a contact between H_2 and S_{10} (φ approximately 34°) up to a φ value corresponding to contact in a *cis* like molecule (φ approximately 85°). It is not unlikely that there exist two minima on the energy curve at approximately 34° and 85° with a flat maximum in between. As a matter of fact a better agreement between experimental and theoretical

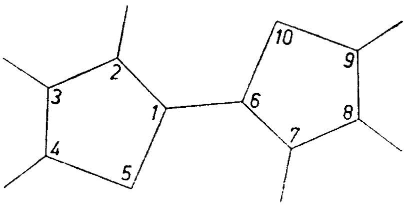

Fig. 3. Numbering of the atoms in the 2,2'-dithienyl molecule.

distribution curves can be obtained if the constancy of φ is abandoned. If, in addition to the molecules with a φ value equal to 34°, there are included a number of other molecules with φ values larger than this value, according to a certain distribution, a nearly complete correspondence can be obtained. Theoretically one might along this line obtain information about the molecular population at various φ values. This is, however, omitted in the present work, as such calculations do not seem to be justified by the present experimental material.

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