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Electron Diffraction Studies on Fluoroderivatives of Biphenyl

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2,2′-Difluorobiphenyl, 2-fluorobiphenyl and 4,4′-difluorobiphenyl have been investigated. For comparison fluorobenzene was also studied. The bond distances found are: C—F 1.34 Å, aromatic C—C 1.40 Å and C—C in biphenyl bridge 1.52 Å. The angles between the phenyl rings are the following: in 2,2′-difluorobiphenyl 60° ± 5°, in 2-fluorobiphenyl 49° ± 5°, and in 4,4′-difluorobiphenyl 44° ± 5°.

Electron diffraction studies have led to the conclusion that biphenyl and biphenylderivatives are non-planar in the gaseous state [1-3]. The non-*ortho* substituted derivatives and biphenyl itself exhibit a deviation from planarity of approximately 45°. The *ortho* substituted derivatives show a somewhat greater deviation, the value of which depends upon the size of the substituent. The substituents studied so far are chlorine, bromine and iodine. In the present work fluorine derivatives have been investigated. The electron diffraction diagrams were taken with the new Oslo sector apparatus. The experimental intensity curves of the four compounds under investigation are given in Fig. 1.

2,2′-Difluorobiphenyl. The radial distribution curves $(\frac{\sigma(r)}{r})$ of 2,2′-difluorobiphenyl and fluorobenzene calculated by Fourier transformation of the corresponding intensity curves are reproduced in Fig. 2. A study of the $\frac{\sigma(r)}{r}$ curve and the intensity curve of fluorobenzene including calculation of theoretical curves led to the following parameters of this molecule: C—C: 1.40 Å, C—F: 1.34 Å. This is in fairly good agreement with values obtained by microwave studies [4] (C—C: 1.3916 Å and C—F: 1.348 Å). In the following a difference procedure, earlier described [2,3], has been applied:

The upper curve of Fig. 3 represents the difference of the two curves of Fig. 2. Before the subtraction was carried out the curves were normalised using the inner part ($1 < r < 3$) as the basis for the normalisation. By studying the upper curve of Fig. 3 the C—C bridge distance was found to be 1.52 Å. The lower curve of Fig. 3 is a theoretical $\frac{\sigma(r)}{r}$ difference curve containing contribu-

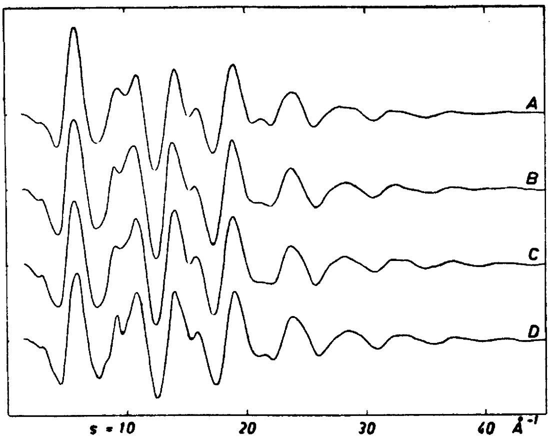

Fig. 1. Intensity curves. A: fluorobenzene, B: 2-fluorobiphenyl, C: 2,2'-difluorobiphenyl, D: 4,4'-difluorobiphenyl.

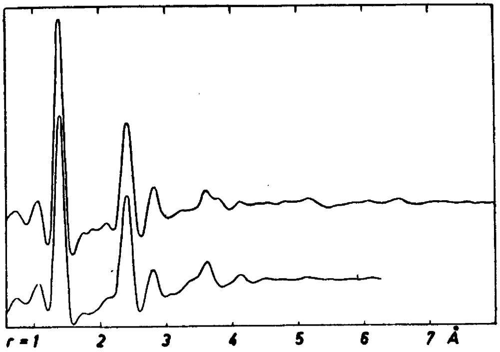

Fig. 2. $\frac{\sigma(r)}{r}$ *curves. Upper curve: 2,2'-difluorobiphenyl, lower curve: fluorobenzene.*

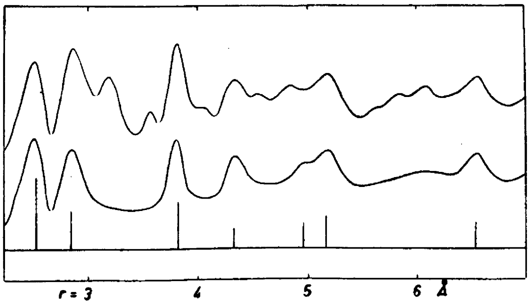

Fig. 3. Upper curve: difference between the two curves of Fig. 2. Lower curve: Theoretical $\frac{\sigma(r)}{r}$ *curve for all the unvariable distances between the two rings of 2,2'-difluorobiphenyl.*

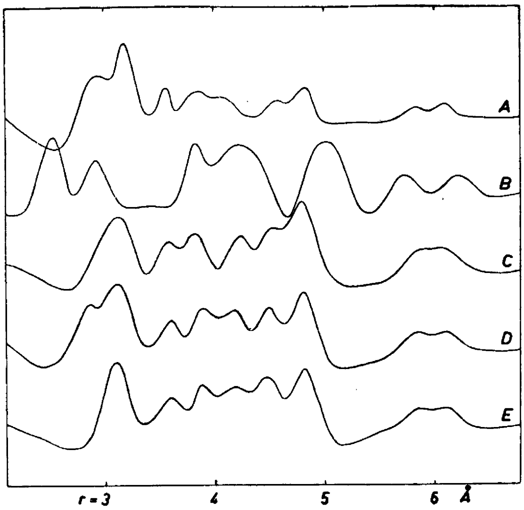

Fig. 4. Curve A: difference between the two curves of Fig. 3. B, C, D, and E: corresponding theoretical curves for various structures.

tions from all distances between the two rings of the 2,2′-difluorobiphenyl which are independent of the angle between the two rings. If we now take the difference between the two curves of Fig. 3 we get a $\frac{\sigma(r)}{r}$ difference curve with contribution only from distances that vary with internal rotation of the molecule about the central C—C bond. This curve, reproduced as curve A of Fig. 4, should be well fitted for the determination of the angle between the two ring planes. Curve B of Fig. 4 is the corresponding theoretical curve for a planar molecule, *trans* form (the *cis* form gives very much the same curve for the r region studied). Curves C, D, and E are calculated for models with the angle φ between the rings equal to 65°, 60°, and 120° respectively. (φ is equal

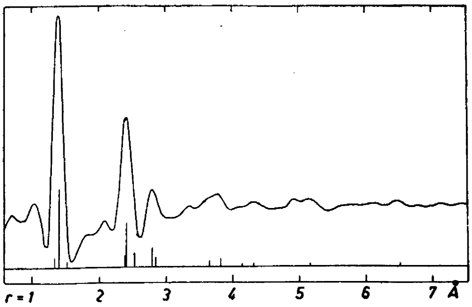

Fig. 5. $\frac{\sigma(r)}{r}$ *curve of 2-fluorobiphenyl.*

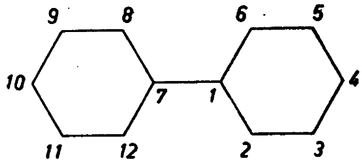

Fig. 6. The numbering of the carbon atoms in biphenyl derivatives applied in Tables 1 and 2.

to 0° for the *cis* position and 180° for the *trans* position). Curve D is no doubt the one of the theoretical curves which is in best accordance with curve A. Studies of the position of the maxima in the various curves of Fig. 4 lead us to the conclution that the φ value is 60° ± 5°.

The discrepancy that still exists between curve A and D can easily be explained. First of all the normalisation necessary for carrying out the subtraction introduces uncertainties. Secondly, the form of the normal curves applied is somewhat uncertain. Thirdly, oscillations in the molecule from the equilibrium position will influence the curves, and moreover the influence on the various distances are different. The $\frac{\mathrm{d}r}{\mathrm{d}\varphi}$ values are considerably greater in the case of the variable C—F distances than in the case of the variable C—C distances. This can for instance easily explain the fact that the maxima at approximately 3.9 Å and 4.2 Å are broader and less pronounced in curve A than the corresponding maxima in curve D.

2-Fluorobiphenyl. In Fig. 5 the $\frac{\sigma(r)}{r}$ curve of 2-fluorobiphenyl is reproduced. In the line diagram we have given all C—C and C—F distances that do not vary with the angle φ. Apparently practically all details in the curve are explained by these distances. However, by correcting for the unvariable distances in the usual way applying the proper normal curves, peaks corresponding to variable distances have been found. The position of these peaks are tabulated in Table 1 together with φ values calculated from the corresponding distances. The numbering of the atoms in the molecule is seen from Fig. 6. This procedure leads us to the value of angle φ of 49° ± 5°. The variable distances which have not been included in Table 1 were either not reproducible or not separable.

Table 1. Variable distances in the 2-fluorobiphenyl molecule and φ values calculated from these distances.

C_2-C_8	3.67 Å	46.4°	
C_2-C_{11}	4.46 Å	54.6°	mean value 49.0°
C_2-C_9	4.86 Å	46.2°	
C_3-C_9	6.13 Å	48.6°	

For instance, the distance C_2—C_{12} can not be reproduced by subtraction because of the rather pronounced peaks in the neighbourhood of the r values at which this distance is supposed to occur. The distances F_2—C_8 and F_2—C_{11} are very close together and can therefore not be separated. However, correcting for the neighbouring distances we find that the mean value of the two distances in question should be 4.07 Å. The calculated mean distance assuming 49° gives 4.04 Å which must be regarded as a good correspondance.

4,4'-Difluorobiphenyl. Fig. 7 represents the $\frac{\sigma(r)}{r}$ curve of 4,4'-difluorobiphenyl. In Fig. 8 the difference between the curve of Fig. 7 and the $\frac{\sigma(r)}{r}$ curve of fluorobenzene is reproduced. The line diagram in Fig. 8 describes the position of the distances between the rings that do not vary with φ. The positions of the peaks corresponding to the variable distances are found in the same

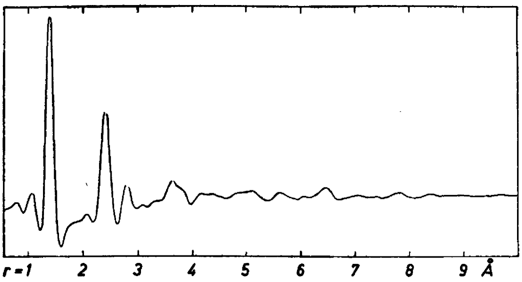

Fig. 7. $\frac{\sigma(r)}{r}$ *curve of 4,4'-difluorobiphenyl.*

Table 2. Variable distances in the 4,4'-difluorobiphenyl molecule and φ *values calculated from these distances.*

C_2-C_{12}	3.07 Å	45.6°	
C_2-C_8	3.69 Å	42.9°	mean value 44.2°
C_2-C_{11}	4.41 Å	43.4°	
C_2-C_9	4.87 Å	45.0°	

way as for 2-fluorobiphenyl and the resulting values are given in Table 2. We have studied the influence of the shape of the theoretical normal curve used in this procedure, as the shape in this case was believed to influence the determination rather much. We did find a certain variation for the single observed φ values. The mean value did, however, never vary more than a few tenths of a degree. In spite of the rather high reproducibility we believe that the total error in the determination of φ is about ± 5°.

DISCUSSION OF THE RESULTS

The results obtained are based upon the assumption also applied in earlier work of this kind, that the carbon rings in biphenyl derivatives do not deviate from the hexagonal symmetry. This assumption is probably not strictly correct. As a matter of fact detailed studies of the $\frac{\sigma(r)}{r}$ curve of 2,2'-difluorobiphenyl and of fluorobenzene seem to give indications of the existance of a small deviation, however, too small to influence the result very much. The determination of the φ values is further dependent upon the indirectly determined

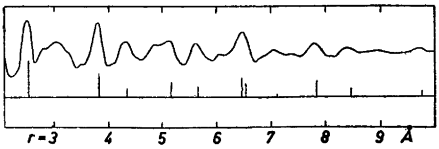

Fig. 8. Difference between the $\frac{\sigma(r)}{r}$ *curves of 4,4'-difluorobiphenyl and fluorobenzene.*

C—C bond linking the two rings together. Both these two sources of error have been taken into consideration in estimating the error range of ± 5°.

The deviation from coplanarity found in the three biphenyl derivatives under investigation is in good qualitative agreement with what one might expect from earlier studies in this field. The 4,4′-difluorobiphenyl should be expected to deviate from the coplanarity to the same extent as biphenyl and 1,3,5-triphenylbenzene, since the *ortho* hydrogen-hydrogen interaction is primarily believed to be responsible for the deviation. The φ values of 44.2° found for 4,4′-difluorobiphenyl is certainly in very good agreement with the values 45° and 46.4° found for biphenyl and 1,3,5-triphenylbenzene, respectively [1,3]. The φ value found for 2,2′-difluorobiphenyl is considerably smaller than the values of the corresponding chloro, bromo, and iodo compounds [2]. Going from the iodo towards the fluoro compound the following values were found: 79°, 75°, 74°, and 60°. The great gap between the chloro and the fluoro compound demonstrates that the steric effect introduced by fluorine is considerably less than for the other halogens. This is apparently still more pronounced in the case of 2-fluorobiphenyl the deviation of which is hardly greater than that of the non-*ortho* substituted biphenyls. If we apply the angles 45°, 49°, and 60° for biphenyl, 2-fluorobiphenyl, and 2,2′-difluorobiphenyl, respectively, we find the following closest packings: For H—H 2.47 Å, for H—F 2.55 Å and for F—F 2.85 Å. The values are in fair agreement with the van der Waals distances of Pauling which give the following values: 2.4 Å, 2.55 Å, and 2.70 Å.

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