Deviation from Coplanarity in the 1,3,5-Triphenylbenzene Molecule

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All biphenyl derivatives studied by electron diffraction so far show a deviation from the planar configuration in the gaseous state [1,2]. This is not only the case for the orthosubstituted but also for the meta- and para-substituted derivatives which X-ray crystallographic work has shown to consist of planar molecules. This apparent discrepancy is accounted for by taking into consideration the inter-molecular forces which are of much greater significance in the crystalline than in the gaseous phase. It is easily understood that a planar molecule might be preferred as a unit for the construction of a stable lattice, even if the isolated molecule itself is generally found in a non-planar configuration. The coplanarity of non-orthosubstituted biphenyls is accordingly not entirely caused by resonance phenomena as is generally believed. If this argument is correct it is not necessarily true that all non-orthosubstituted biphenyl molecules are planar in the crystalline state. In certain cases sufficient stability might be obtained to maintain the non-planarity characteristic of the isolated molecule even in the lattice.

In this connection the result obtained by Lonsdale [3] concerning sym. triphenylbenzene is of great interest. She finds that the molecule is probably non-planar in the crystalline state. The planes of the phenyl groups are rotated through 25° out of the plane of the central nucleus. In the opinion of the present author this deviation from coplanarity is not caused by the interaction between the meta-substituted phenyl groups, but by the interactions between the ortho-hydrogens in neighbouring rings. The shortest hydrogen-hydrogen distance between two of the outer phenyl groups in a planar molecule is about 3.3 Å, which is definitely so great as to exclude any possible van der Waals repulsion. The effect must be the same as that present in biphenyl and its meta- and para-substituted derivatives. The angle between the planes of
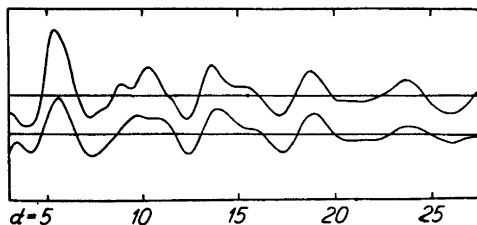
Fig. 1. (I_E/B_E-1) function for 1,3,5-tri-phenylbenzene (upper curve) and benzene (lower curve).

two adjacent phenyl rings should accordingly be approximately 50° in gaseous 1,3,5-triphenylbenzene, as found for other non-orthosubstituted biphenyls [2]. The fact that the angle seems to be smaller in the crystal is easily explained.

EXPERIMENTS AND CALCULATIONS

The 1,3,5-triphenylbenzene used in this work was prepared by heating acetophenone with aniline and iodine. The compound was recrystallized from glacial acetic acid and melted at 172° C.

Electron diffraction photographs were taken using an s^3 sector. At the same time new photographs of benzene were taken for comparison and subtraction purposes. In Fig. 1 the intensity curves of triphenylbenzene (upper curve) and benzene (lower curve) are given. The background is substracted in both cases. (N. B. the abscissa here is not the usual $s = \dfrac{4\pi}{\lambda} \sin \Theta$ but $d = \dfrac{2\pi}{\lambda} \tan 2\,\Theta$). In Fig. 2 the $\dfrac{\sigma(r)}{r}$ curves for the two compounds are given. They are calculated from the following relation:

$$\frac{\sigma(r)}{r} = \int\limits_{s=3}^{s=26} \left(\frac{I_E}{B_E} - 1 \right) s\ e^{-k\,s^2}\ B_T\ \sin\ rs\ ds$$

where I_E and B_E are the corrected experimental intensity and background respectively. B_T is $\Sigma_i[Z_i - f_i)^2 + S_i]$ summed over all atoms in the molecules, and k is here 0.007. — The corresponding normal curve [4] for the carbon-carbon distance was calculated using the relation:

$$N(\varrho) = \int\limits_{s=3}^{s=26} \left(1 - \frac{f_c}{Z_c} \right)^2 e^{-k\,s^2} \cos\ \varrho\ s\ ds$$

The Fourier inversion was carried out using I.B.M. calculating techniques [5].
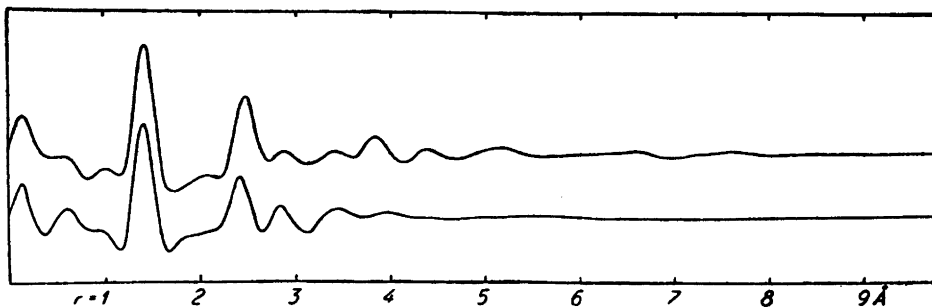
Fig. 2. $\dfrac{\sigma(r)}{r}$ *curve for 1.3.5-triphenylbenzene (upper curve) ond benzene (lower curve).*

The $\dfrac{\sigma(r)}{r}$ curve of benzene (Fig. 2) was multiplied by a factor so that the
ratio of the heights of the first peaks in the two curves should have the correct
theoretical value. Theoretically the normalization factor should be 4, but a
deviation from this value might be expected because of the uncertainty in the
drawing in of the background. As a matter of fact the factor was found to
be 4.4.

If we now assume that the rings in triphenyl-benzene have the same dimen-
sions as in benzene, the distances within the rings of triphenylbenzene can be
subtracted. This assumption is not of course strictly correct, but for the
purpose of determining the angle between the ring planes of triphenylbenzene
it may be regarded as a valid approximation. The upper curve of Fig. 3 shows
the difference between the two curves of Fig. 2. It is thus, to the approxi-
mation mentioned, and disregarding some unimportant carbon-hydrogen
contributions, the $\dfrac{\sigma(r)}{r}$ curve for triphenylbenzene containing only distances
between different rings. (The ordinate scale in Fig. 3 is twice that of Fig. 2.)
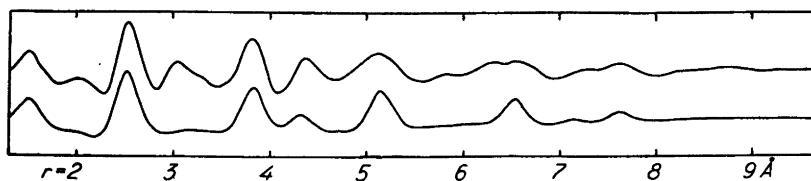

*Fig. 3. The upper curve is the difference between the two curves of Fig. 2. The lower curve
is the* $\dfrac{\sigma(r)}{r}$ *curve calculated for the unvariable distances between different rings in 1,3,5-
triphenylbenzene.*

Table 1. C—C distances occuring in the sym. triphenylbenzene. n and m refer to the numbers given in Fig. 4. N is the number of the times the particular type of distance occurs in the molecule. r_{nm} is the distance in Å.

Part I

C_n-C_m	N_{nm}	r_{nm}
* 1—2	24	1.40
1—3	24	2.42
1—4	12	2.80
1—7	3	1.52
1—8	12	2.53
1—9	12	3.82
1—10	6	4.32
10—2	12	5.16
10—3	12	6.53
10—14	3	7.12
7—13	3	5.06
7—16	6	7.61
10—16	3	9.91

Part II

C_n-C_m	N_{nm}	* r_{nm}	** r_{nm}
2—12	6	2.92	3.07
2—8	6	3.80	3.67
2—11	12	4.32	4.43
2—9	12	4.95	4.86
3—11	6	5.72	5.80
3—9	6	6.21	6.14
7—14	6	5.25	5.43
7—15	6	6.61	6.75
7—18	6	6.31	6.16
7—17	6	7.48	7.35
10—14	6	7.48	7.73
10—15	6	8.72	8.93
10—18	6	8.95	8.73
10—17	6	10.00	9.82

Part III

C_n-C_m	N_{nm}	* r_{nm}	** r_{nm}	** r_{nm}
12—14	3	5.06	5.71	5.41
12—15	6	6.31	6.91	6.68
12—18	6	6.61	6.44	6.68
12—17	6	7.61	7.52	7.72
11—18	6	7.99	7.78	7.98
11—17	6	8.95	8.81	8.99
11—15	3	7.48	8.05	7.86
9—18	6	8.72	8.53	8.35
9—17	3	9.91	9.69	9.53
8—18	3	7.48	7.32	7.11

* $\varphi = 0$
** $\varphi = 46.4°$

These distances can be devided into two kinds: 1) those which are constant during a rotation about the carbon-carbon bridges linking the rings together, and 2) those which vary with such a rotation. Using the normal curve mentioned above the contribution of the invariable distances has been calculated. The result is given as the lower curve in Fig. 3. The carbon-carbon bond distances in the ring are determined by the curves in Fig. 2 to be 1.40 Å, and
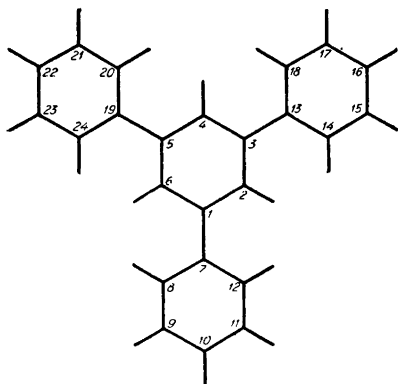

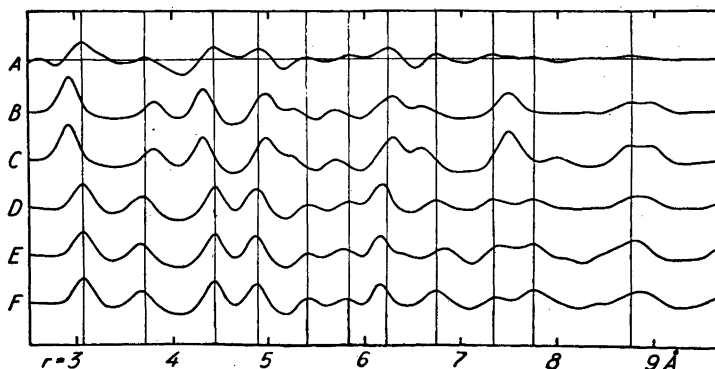*Fig. 4. A planar model for 1,3,5-triphenylbenzene.*

Fig. 5. Curve A is the $\dfrac{\sigma(r)}{r}$ *curve of 1,3,5-triphenylbenzene for the variable distances.*

Curves B—F are theoretical curves for various structures.

the bond distance between neighbouring carbon atoms from adjacent rings is determined from the upper curve in Fig. 3 to be 1.52 Å. (The corresponding distance for biphenyl, 3,3'-dibromobiphenyl, 3,3', 5,5'-tetrabromobiphenyl, and ortho-dibromobiphenyl is found to be 1.48, 1.49, 1.50, and 1.50 Å respectively [1,2], and all these measurements agree within the limits of their respective errors.) All carbon-carbon distances in triphenylbenzene used in the calculation of theoretical curves are given in Table 1. The numbering of the atoms in the table refers to the planar model of Fig. 4.

As might have been expected, the two curves in Fig. 3 show many similarities. The difference between them must contain contributions from all the carbon-carbon distances which vary when the angle φ between the planes of two adjacent rings is varied. This difference is given as the upper curve (A) of Fig. 5 and should be well suited for the determination of φ, since all the disturbing distances are removed. Curve A of Fig. 5 is now compared with corresponding theoretical curves for planar models, B and C. In B we have only taken into account the distances given in Part II of Table 1, while in C

Table 2. Angle φ calculated from four pronounced peaks of curve A, Fig. 5.

$C_n - C_m$	Distances for plane model	Observed values	Calculated φ-values	
2—12	2.92 Å	3.065 Å	45.2°	
2—11	4.32 »	4.425 »	46.6°	
2—9	4.95 »	4.88 »	41.0°	Mean value 46.4°
3—11	5.72 »	5.82 »	52.6°	

4

the rest of the variable distances have been included. The general appearance of the theoretical curves is very much the same as that of curve A as most of the peaks in A have corresponding peaks in B and C. The positions of the peaks of the theoretical curves, however, by no means coincide with those of curve A. We must therefore abandon the planar model.

Most of the peaks in the difference curve are composed of contributions from two or more distances. To calculate the angle φ from direct measurements of the positions of the peaks in curve A is therefore not straight-forward. To find φ we have chosen the four peaks whose positions are given in Table 2. Each of these peaks is virtually caused by only one distance. We thus get four independent measurements of φ giving an average value $\varphi = 46.4°$. Of course the positions of the four peaks chosen are not entirely uninfluenced by neighbouring distances.

It can easily be shown, for instance, that the maximum at 5.82 Å is markedly influenced by other distances than 3—11. This explains the high value of φ calculated from this particular peak.

If we now use the value $\varphi = 46.4°$ to calculate the carbon-carbon distances and theoretical difference curves of the type under discussion we get curves D, E, and F. Curve D contains only contributions from the distances given in Part II of Table 1, while E and F include the rest of the variable distances. E is calculated for a propeller-shaped model and F for a model where the meta-phenyl groups are statistically arranged in relation to each other but in such a way that the angle between each of them and the central nucleus is 46.4°. Taking into consideration the fact that we are dealing with difference curves,

Table 3. *Deviation between experimental and theoretical positions of the maxima for a planar and a non-planar ($\bar{\varphi} = 46.4°$) structure.*

Exp. positions of maxima	Calculated positions $\varphi = 0°$	$\lvert \varDelta \rvert$ $\varphi = 0°$	Calculated positions $\varphi = 46.4°$	$\lvert \varDelta \rvert$ $\varphi = 46.4°$
3.06 Å	2.93 Å	0.13 Å	3.06 Å	0.00 Å
3.71 »	3.81 »	0.10 »	3.67 »	0.04 »
4.43 »	4.32 »	0.11 »	4.43 »	0.00 »
4.88 »	4.98 »	0.10 »	4.87 »	0.01 »
5.40 »	5.25 »	0.15 »	5.43 »	0.03 »
5.82 »	5.70 »	0.12 »	5.82 »	0.00 »
6.23 »	6.28 »	0.05 »	6.17 »	0.06 »
6.74 »	6.58 »	0.16 »	6.75 »	0.01 »
7.34 »	7.48 »	0.14 »	7.34 »	0.00 »

$$\overline{\lvert \varDelta \rvert} = 0.12 \text{ Å} \qquad \overline{\lvert \varDelta \rvert} = 0.017 \text{ Å}$$

where essential and easily reproducible information is subtracted leaving only a fraction of the original information contained in the experimental intensity curve, we think that the correspondence between curve A and the curves D—F is remarkably good. The degree of correspondence of the positions of the maxima is shown in Table 3 in which the Δs represent the differences in Å between the positions of the peaks for the pairs of curves A & B and A & D. The average $|\Delta|$ value is found to be 0.12 Å between curves A and B and only 0.017 Å between curves A and D.

DISCUSSION OF THE RESULTS

All the theoretical difference curves are calculated on the assumption of rigid molecules. One might expect this assumption to be a rather unsatisfactory working hypothesis, particularly when a well pronounced restricted rotation about the equilibrium position would be expected. It is, of course, difficult to obtain a complete picture of the amount of restrited rotation in a molecule of such high complexity from electron diffraction data. This much can, however, be said: by comparing the two curves A and D we see that the heights of corresponding peaks are not very different, though we can as a general rule say that the peaks of curve D are more pronounced and higher than those of curve A. This is to be expected if restricted rotation occurs. Furthermore we see by inspecting the curves D, E, and F that D agrees best with curve A although E or F would be expected to be better on theoretical ground, assuming a rigid molecule. E and F include all carbon-carbon distances that are included in the semi-experimental curve A. Internal rotation should, however, reduce the contribution of the various types of distances to a different degree. In calculating curve D we have only considered carbon-carbon distances varying with rotation about one single carbon-carbon bond. In E and F the rest of the carbon-carbon distances are included, and these distances would be expected to be influenced more by restricted rotation as they vary with rotation about two single bonds. For instance if we rotated through an angle 3.5° from the value of 46.4° which we have used in our calculation, we find that a distance of the type 2—12 will vary by about 0.03 Å, while a distance of the type 12—14 will vary by about 0.08 Å.

The above arguments indicate that some restricted rotation certainly occurs, but that it is of limited amplitude. Hence the rigid model can be used as a reasonable approximation.

Comparing the curves E and F we see that curve F gives the better agreement with curve A. Although the difference between curves E and F might be of the order of magnitude of the errors in curve A, we should like to point

out that the model corresponding to F is more likely from a chemical point of view than that corresponding to curve E. As has been pointed out earlier, two meta phenyl groups would not be expected to influence each other to any appreciable extent. A statistical arrangement should accordingly be more probable than the symmetrical propeller-like model with a three-fold axis of symmetry. Even if this is true in the gaseous state, however, there is no reason to suppose that it should be the case in the solid state. The symmetrical form of the molecule might conceivably pack better into a crystal than the dis-ordered form.

Finally we should say something about the accuracy of the determination of the angle φ. The value 46.4° is not, of course, particularly accurate: it is only the average of the values of Table 2, of which at least the result for the distance 3—11 is unreliable. To estimate the error we could have calculated curves corresponding to curve D for a whole series of φ-values. This is, how-ever, a very long and tedious method, and the same result can be obtained more simply by studying the influence of the variation in φ on the most pronounced peaks. By doing so we find that the error in the determination is less than 5°. We therefore feel that we can safely state that the angle φ is 46° ± 5°.

This value is, within the limits of error, the same as has been found for biphenyl and its meta- and para-derivatives by electron diffraction [1,2]. There is, however, some reason to believe that small differences do exist. For in-stance the limits of the errors for the φ-value obtained for 3,3'-dibromobiphenyl (54° ± 5°) do certainly overlap with those found for sym. triphenylbenzene, but the average values are rather different. We believe that the difference is a real one, though its precise interpretation does not seem to be straight-forward.

SUMMARY

The structure of 1,3,5-triphenylbenzene has been studied by the electron diffraction sector method. By using the subtraction procedure it has been shown that the molecule is non-planar. The angle between two adjacent ring planes is found to be 46° ± 5°.

LITERATURE

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