

The Molecular Structure of Biphenyl and some of its Derivatives. II

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NON-ORTHO-SUBSTITUTED BIPHENYLS

Electron diffraction studies of biphenyl and some of its non-*ortho*-substituted derivatives have been carried out by the sector method, showing that the molecules have non-planar configurations in the gaseous state^{1,2}. It was, however, not possible in any of the cases treated to give the value of the angle φ between the two ring planes with very great accuracy. The best result was obtained by the investigation of 3,3'-dibromobiphenyl. It led to six practically independent values for the angle, the mean value being 54° and the fluctuation being 5° to either side. An accurate determination of the angle is very desirable; it would give us valuable information about the van der Waals distances between two hydrogen atoms. The 3,3',5,5'-tetrabromobiphenyl was expected to be well fitted for the purpose; experience, however, unfortunately showed that this was not true. The study of the 3,3',5,5'-tetrabromobiphenyl did not lead to a more accurate determination of the angle than the study of the dibromo-compound already mentioned. By comparing the two compounds 3,3'-dibromobiphenyl and 3,3',5,5'-tetrabromobiphenyl, it can easily be seen that the latter one contains the largest number of distances varying with the angle φ , but it also contains the largest number of distances which do *not* vary. The latter distances seem, unfortunately, to effect the electron diffraction pattern to a greater extent than do the former ones. In Fig. 1 the $\frac{\sigma(r)}{r}$ -curve for 3,3',5,5'-tetrabromobiphenyl is given. At about 8 Å the peaks in the curve seem to disappear. For $r > 8$ Å the fluctuations from the abscissa axis are very small and the reproducibility found by studying curves originating from different diagrams is unsatisfactory. Though this part of the curve also certainly gives evidence for the non-planarity of the

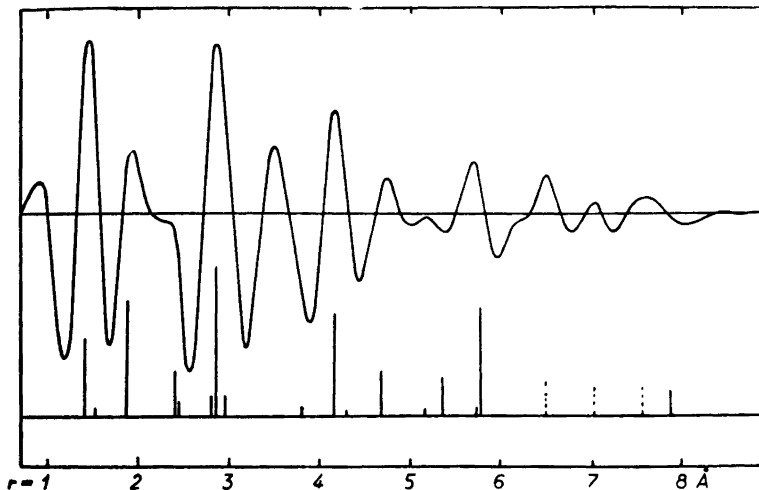


Fig. 1. $\frac{\sigma(r)}{r}$ -curve of 3,3',5,5'-tetrabromobiphenyl.

molecule, it has been omitted in the discussion because of its uncertainty. Studying the $\frac{\sigma(r)}{r}$ -curve for $r < 8 \text{ \AA}$ we see that the inner part of the curve is easily explained by inter-atomic distances which do not vary with φ . (Solid lines in the line diagram.) The three outer peaks can be ascribed mainly to distances which do vary with φ . (Dashed lines in the line diagram.) In Table 1 the positions of the maxima and the corresponding distances and

Table 1. Values characterizing the magnitude of the deviation from coplanarity of 3,3',5,5'-tetrabromobiphenyl.

Observed r -values	Distances	φ	
6.49 Å	$\text{Br}_3 - \text{C}_2'$	48°	mean value 49°
7.01 »	$\text{Br}_3 - \text{C}_5'$	40°	
7.61 »	$\text{Br}_3 - \text{C}_3'$	58°	

φ -values are given. For the last peak corrections for the fixed distance indicated have been carried through. The mean value of φ from these three peaks is found to be 49°.

Table 2. φ -values for different non-ortho-substituted biphenyls in the gaseous state.

Compound	φ
Biphenyl	45°
3,3'-Dibromobiphenyl	54°
3,3'-Dichlorobenzidine	52°
3,3',5,5'-Tetrabromobiphenyl	49°

In Table 2 we have listed the non-*ortho*-substituted biphenyls which have been studied by the electron diffraction method. The corresponding φ -values found are listed. If we now assume the actual angle to be the same for all the biphenyl derivatives of this type, φ can be given the value $50^\circ \pm 5^\circ$. If we further give the C—H-bond distance the value 1.05 ± 0.03 Å, the central C—C'-bond distance the value 1.50 ± 0.03 Å, and take into consideration the errors from all these three molecular parameters, but consider the C—C-bond distance in the ring to be correct, equal to 1.40 Å, we find the value for the 2,2'-H—H-distance to be 2.5 ± 0.2 Å. The value is perhaps somewhat larger than should be expected assuming the non-coplanarity to be caused by equilibrium between van der Waals forces and resonance phenomena. But considering the large limit of error it is not at all unreasonable.

I would like to draw attention to the fact that the calculation of the φ -value and consequently the 2,2'-H—H-distance is based upon the assumption that all the C—C-bond distances in the phenyl rings are the same. It has in several cases been claimed that this is far from correct. Fowweather and Hargreaves³ report, in the case of *m*-tolidine dihydrochloride, variations in the C—C-bond length ranging from 1.31 Å to 1.40 Å, and Smare⁴ finds in the case of 2,2'-dichlorobenzidine that the C—C-bonds are alternately long and short, with mean values 1.45 and 1.30 Å respectively. Both the investigations mentioned are based upon X-ray crystallographic work. We have, as will be mentioned later, never been able to observe such a great deviation by the electron diffraction method, though minor deviations can not be excluded. It is, on the other hand, easily seen that deviations of the type mentioned would not effect our calculation very much, and would not effect the main feature of the result at all.

ORTHO-SUBSTITUTED BIPHENYLS

It might also be worth while to study some *ortho*-substituted biphenyls to compare the molecular structure in the gaseous state with the result found in the crystals by the X-ray investigators. X-ray analysis of the crystal structure of *m*-tolidine dihydrochloride⁴ and 2,2'-dichlorobenzidine^{3,5} has shown that in each of these molecules the phenyl rings are rotated from the *cis*-planar configuration through approximately 36° in opposite directions around the central C—C'-bond, so that the angle between the ring planes is approximately 72° .

The structure of 2,2'-dichloro- and 2,2'-dibromobiphenyl has been studied by the sector method. The $\frac{\sigma(r)}{r}$ -curves of these compounds are to a great

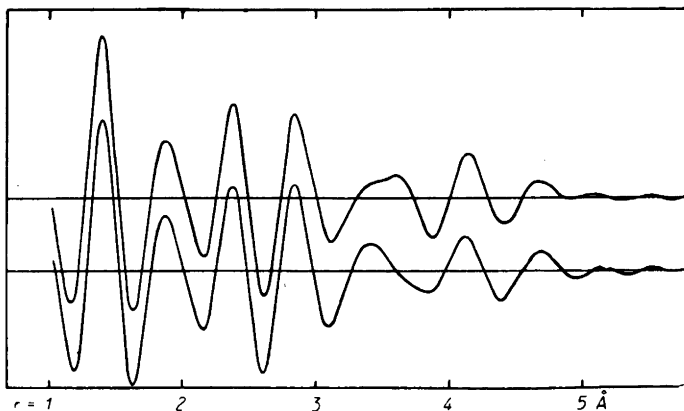


Fig. 2. The upper curve is the $\frac{\sigma(r)}{r}$ -curve of 2,2'-dibromobiphenyl, the lower one is the $\frac{\sigma(r)}{r}$ -curve of monobromobenzene.

extent composed of contributions from distances occurring within the phenyl rings. We should therefore assume that the $\frac{\sigma(r)}{r}$ -curve of 2,2'-dichlorobiphenyl ought to be very similar to the $\frac{\sigma(r)}{r}$ -curve of monochlorobenzene, and that the $\frac{\sigma(r)}{r}$ -curve of 2,2'-dibromobiphenyl ought to be similar to that of monobromobenzene. — In Fig. 2 the upper curve is the $\frac{\sigma(r)}{r}$ -curve of 2,2'-dibromobiphenyl, the lower one is that of monobromobenzene. The last curve has been multiplied by a factor of about 2 to get the proper normalization. The two curves are strikingly similar in the main features. The assumption made earlier that the phenyl rings in a biphenyl derivative are usually very nearly the same as the benzene ring itself is therefore shown to be reasonable. If, for instance, in the two curves we compare the peaks at 1.40 Å corresponding to the C—C-bond distance, we see no evidence of the existence of different C—C-bond lengths in the phenyl ring of the biphenyl derivative. In fact, a close inspection of the curves really shows that the peak mentioned is about 5 % wider for the 2,2'-dibromobiphenyl curve than for the bromobenzene curve. This is, however, easily explained by considering the contribution of the central C—C'-bond distance in the case of the 2,2'-dibromobiphenyl, the C—C'-bond distance being about 1.50 Å. The upper curve in

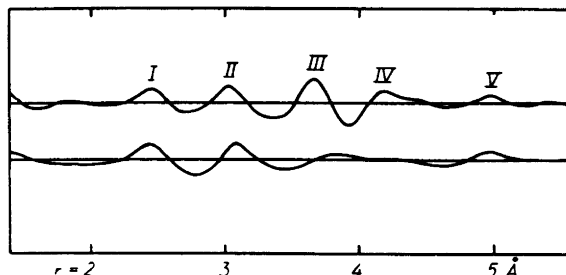


Fig. 3. The upper curve is the difference of the two curves of Fig. 2; the lower one is the theoretical $\frac{\sigma(r)}{r}$ -curve for distances between the two rings of the 2,2'-dibromo-biphenyl molecule, containing only distances which do not vary with φ .

Fig. 3 is the difference between the two curves in Fig. 2. This difference $\frac{\sigma(r)}{r}$ -curve contains contributions almost exclusively from the distances between atoms in different rings. These distances can be divided into two types: those which do not vary by rotation about the central C—C'-bond, and those which do vary. The contribution of the former kind to the difference $\frac{\sigma(r)}{r}$ -curve can therefore, for the purpose of determining the angle φ , be subtracted to advantage from the curve. The lower curve in Fig. 3 is a theoretically calculated difference curve containing only distances which are independent of φ . The molecular structure parameters chosen to be used in these calculations are as follows: C—C-bond distance in the ring = 1.40 Å, C—Br-bond distance = 1.88 Å, valency angles = 120°, C—H-bond distance

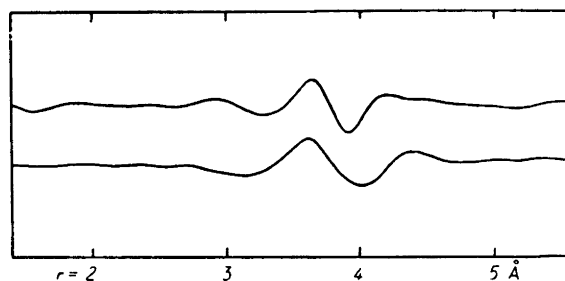


Fig. 4. The upper curve is the difference between the two curves of Fig. 3; the lower one is the $\frac{\sigma(r)}{r}$ -curve for distances in the 2,2'-dibromobiphenyl molecule which do vary with φ .

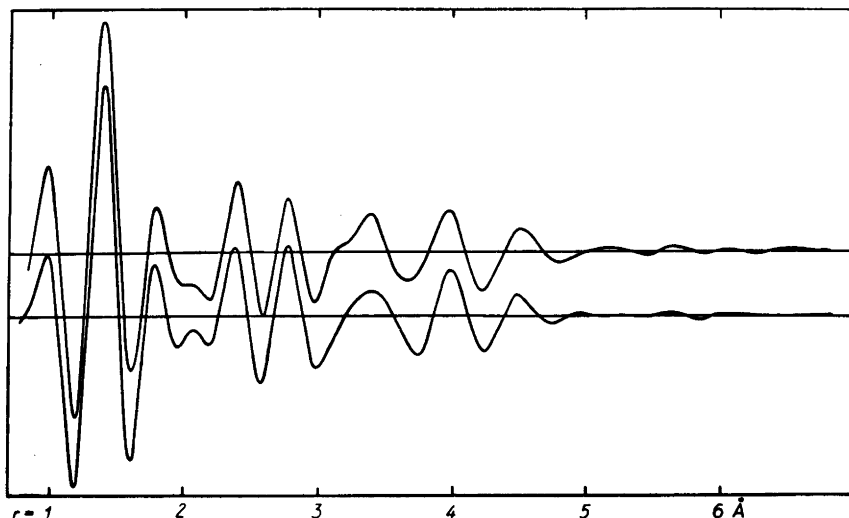


Fig. 5. The upper curve is the $\frac{\sigma(r)}{r}$ -curve of 2,2'-dichlorobiphenyl, the lower one is that of monochlorobenzene.

= 1.05 Å, and the central C—C'-bond distance = 1.50 Å. By comparing the two curves in Fig. 3 we see that peak I, II, and V can be attributed mainly to distances independent of φ , while the peaks III and IV must be due to distances which vary with φ . In Fig. 4 the upper curve is the difference between the two curves in Fig. 3. A series of theoretical difference curves containing only distances varying by rotating about the central C—C'-bond has been calculated for different values of φ . ($\varphi = 0^\circ$ for the *cis*-form). A value of $\varphi = 75^\circ$ seems to lead to the best agreement with experimental data. The corresponding theoretical curve is given as the lower curve of Fig. 4. It has been multiplied by 0.5 to get a proper scale for the comparison with the upper curve. The real difference in the height of the main peak of the "experimental" and the theoretical curves of Fig. 4 can be explained by assuming that the molecule is not quite rigid. If the molecule is oscillating somewhat about the equilibrium position, the height of the main peak, which is due to the Br—Br distance, must of course decrease. The minor disagreement in the shape of the two curves in Fig. 4 can also be partly explained by the assumption of an oscillation as mentioned, but other effects might contribute to a certain extent.

For instance, the fact that the experimental $\frac{\sigma(r)}{r}$ -curves are calculated using the temperature factor $e^{-0.007s^2}$ while the normal curves (Viervoll⁶) used for

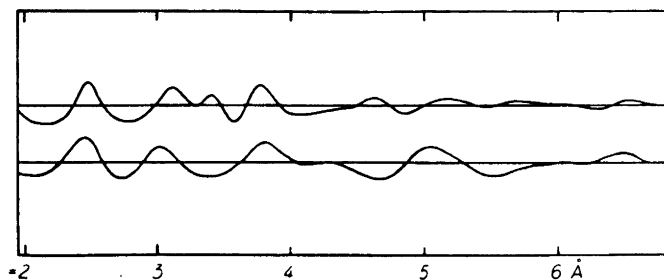


Fig. 6. The upper curve is the difference between the two curves of Fig. 5; the lower one is the theoretical $\frac{\sigma(r)}{r}$ -curve for distances between the two rings of the 2,2'-dichlorobiphenyl molecule, containing only distances which do not vary with φ .

the theoretical curves are calculated with the temperature factor $e^{-0.01s^2}$ will be of some importance.

The same procedure carried through for 2,2'-dibromobiphenyl and bromobenzene has been applied to the corresponding chloro-compounds. In Fig. 5 the upper curve is the experimental $\frac{\sigma(r)}{r}$ -curve of 2,2'-dichlorobiphenyl and the lower one that of monochlorobenzene. Here we also find the C—C-bond peak of the biphenyl derivative curve to be about 5 % wider than the corresponding peak of the chlorobenzene curve. The difference between the two curves of Fig. 5 is given as the upper curve in Fig. 6. The lower curve in this figure is the theoretical difference curve containing only distances which do not vary with the angle φ . The theoretical curve is calculated using a C—Cl-bond distance of 1.72 Å. The other parameters found to be in best agreement with experiments are the same as for the bromo-compound. — The curves of Fig. 7 are, as we see, a little more complicated than those of Fig. 4 to which they correspond. For 2,2'-dibromobiphenyl the halogen-halogen distance predominates, the carbon-halogen and the hydrogen-halogen distances being of less importance. In the case of 2,2'-dichlorobiphenyl, however, the carbon-halogen and the hydrogen-halogen distances must contribute to a relatively greater extent. This is easily seen in both the curves of Fig. 7. The φ -value which leads to the best agreement is, in this case, 74°. The Cl—Cl distance corresponds to peak I. On first inspection we might believe peak III to correspond to the Cl—Cl distance. This assumption leads to an angle of about 110°; however, resulting in a minimum at the r -value of peak I, it is easily excluded. In this case also the lower curve (Fig. 7) has been multiplied by 0.5 to make the height of the peaks comparable to those of the upper one.

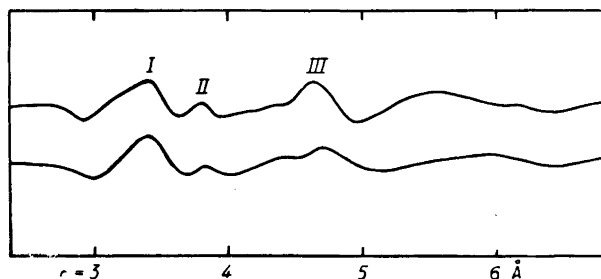


Fig. 7. The upper curve is the difference between the two curves of Fig. 6; the lower one is the $\frac{\sigma(r)}{r}$ -curve for distances in the 2,2'-dichlorobiphenyl molecule which do vary with φ .

Here, therefore, as for the bromo-compound, there also seems to be an oscillation about the equilibrium position. The curves in this case give, however, still further indications for the existence of an oscillation: If we compare the relative height of the peaks of the curves of Fig. 7, remembering the factor 0.5, we see that peak I in the "experimental" curve (upper curve) is reduced considerably more than peak III, the last one being in fact only negligibly reduced. Now is peak I essentially due to the Cl—Cl distance while peak III is due to two Cl—C distances. By a rotation of, say, 10° from the equilibrium position, the Cl—Cl distance is increased or decreased about 0.18 \AA , while one of the Cl—C distances contributing to peak III is *increased* about 0.06 \AA and the other one is *decreased* by the same amount. It is therefore obvious that an oscillation about the equilibrium position must influence the height of peak I more than the height of peak III. This effect might be used to get a rough idea of the magnitude of the oscillation.

The 2,2'-diiodobiphenyl has also been studied. The electron diffraction diagrams taken were, however, not very good, and we got few diagrams, due to the small amount of substance available. The experiments ought therefore to be repeated. It might, however, be mentioned that the $\frac{\sigma(r)}{r}$ -curve calculated shows the peaks which are expected due to the fixed distances, and in addition to that a pronounced peak appears at 3.82 \AA . It can reasonably be interpreted as an I—I distance corresponding to a φ -value of about 79° .

If we include the 2,2'-diiodobiphenyl we can summarize our results in Table 3. In the fourth column the effective halogen-halogen radii found by our investigations are given. They are compared with the Pauling van der Waals radii⁷ given in the fifth column. The latter are somewhat greater than the

Table 3. Values characterizing the amount of deviation from the coplanarity of some *ortho*-substituted biphenyls.

Compounds	φ	Halogen-halogen distances	Halogen-halogen radii	Pauling v.d. Waals radii	Difference
2,2'-Dichlorobiphenyl	74°	3.46 Å	1.73 Å	1.80 Å	0.07 Å
2,2'-Dibromobiphenyl	75°	3.62 »	1.81 »	1.95 »	0.14 »
2,2'-Diiodobiphenyl	79°	3.82 »	1.91 »	2.15 »	0.24 »

radii found by us. The difference increases in going from the chloro- to the iodo-compound.

The determination of the φ -value of the *ortho*-substituted biphenyls is probably more accurate than for the non-*ortho*-substituted biphenyls. The probable error of the halogen-halogen distance is presumably less than 0.05 Å. Taking into consideration the possible errors in the determination of the other parameters necessary for the calculation of the φ -value, we can conclude that the probable error of φ is about 5° or perhaps somewhat less than that. In this case also, however, an accurate estimation of the errors is rather difficult.

The φ -values found above are in good agreement with those found for the 2,2'-dichlorobenzidine by the X-ray investigation already mentioned. The φ -values for gaseous 2,2'-dichlorobiphenyl and solid 2,2'-dichlorobenzidine are, in fact, the same, within the limits of errors.

It might be objected that a comparison of a biphenyl derivative with the corresponding benzidine derivative is not permissible because of the additional resonance possibility caused by the amino groups in the latter type of compound. It is my opinion, however, that the φ -value of the *ortho*-substituted molecules under discussion is mainly determined by the interaction of the *ortho*-atoms, and is consequently not very much influenced by resonance phenomena.

The fact that the *ortho*-substituted biphenyls treated above, show a molecular structure more similar to the *cis*-form than to the *trans*-form seems perhaps a little surprising at first. According to Pauling⁷ the electronegativities of hydrogen, carbon, and chlorine are 2.1, 2.5, and 3.0 respectively. This means that a repulsive force ought to act between two chlorine atoms and an attractive force ought to act between a hydrogen atom and a chlorine atom, both effects favouring a *trans*-form and decreasing the dipole moment of the molecule. Hampson and Weissberger⁸, who have studied the dipole moment of 2-, 3-, and 4-mono-chlorobiphenyl and 2,2'-, and 3,3'-dichlorobiphenyl, were led to the conclusion that *London forces* play an important rôle in deter-

mining the inner configuration of the molecules. The three types of forces determining the structure of 2,2'-, and 3,3'-dichlorobiphenyl are, according to Hampson and Weissberger: a) Electrostatic repulsions and attractions, b) quantum mechanical attractions (London forces), and c) quantum mechanical repulsions (impenetrability of colliding atoms). To these we might add a fourth effect caused by resonance phenomena. This effect might, however, as earlier emphasized, be of less importance for the 2,2'-derivatives. In order to study the theoretical dipole moments of 2,2'-, and 3,3'-dichlorobiphenyl Hampson and Weissberger calculated the London forces between the two chlorine atoms. This procedure is essentially correct for the 2,2'-dichlorobiphenyl, but for the 3,3'-dichlorobiphenyl the 2,2'-hydrogen interaction, which was not at all taken into consideration by Hampson and Weissberger, must in fact be of much greater importance than the 3,3'-chloro interaction. — In the case of the 3,3'-compound Hampson and Weissberger believe the two phenyl rings to rotate almost unhindered about the central C—C'-bond. A completely free rotation leads to a dipole moment of 1.90 D, and if the weak chlorine-chlorine interaction is taken into consideration the calculated value is 1.89 D. The structure is, however, not at all unambiguously determined by the dipole moment measurement. The assumption made earlier² that the non-*ortho*-substituted biphenyls are non-planar with a φ -value of about 50° and with a fifty-fifty contribution of the *cis*- and the *trans*-like forms, also leads to a dipole moment of 1.89 D. For comparison the experimental value reported is 1.80 D. The calculated value is based upon Hampson and Weissberger's measurement of the dipole moment of 3-chlorobiphenyl (1.64 D). If the value for chlorobenzene is used (1.55 D), a still better agreement is obtained.

For 2,2'-dichlorobiphenyl a dipole moment calculation based upon Hampson and Weissberger's value for 2-chlorobiphenyl (1.45 D) and the φ -value given in this work (74°) leads to a value of 2.00 D. The measured value is 1.91 D. The agreement is very good, considering not only the rough approximation made when assuming a rigid model but also both the errors of the dipole moment determinations of 2-chlorobiphenyl and 2,2'-dichlorobiphenyl and the errors in our determination of the φ -value.

SUMMARY

Electron diffraction investigations of 3,3',5,5'-tetrabromobiphenyl, 2,2'-dichloro-, 2,2'-dibromo-, and 2,2'-diiodobiphenyl have been carried through. The first of these compounds shows a deviation from the coplanarity of about the same magnitude as was found earlier for other non-*ortho*-substituted bi-

phenyls². — For the three *ortho*-substituted compounds under investigation the angle between the two ring planes is found to be 74°, 75°, and 79° respectively, the deviation from the *cis*-form being less than from the *trans*-form. The agreement with X-ray investigations and dipole moment measurements is very good, and well within the limits of error.

I should like to express my gratitude to Professor Dr. O. Hassel for his interest in my work and to Dr. William S. Emerson at the Monsanto Chemical Co, Dayton, Ohio, who has kindly supplied me with the 2,2'-dichlorobiphenyl. The other compounds studied in this investigation were purchased from L. Light & Co Ltd. Old Bowry Laboratories, Wraysbury, England. — I must also acknowledge my indebtedness to *Norges Teknisk-Naturvitenskapelige Forskningsråd* and the Fulbright Foundation for financial aid for a journey to U. S. A. during which the present investigation was finished. — A great deal of the elaborate calculation work has been carried through on I. B. M. machines which have kindly been placed at the disposal of the Chemical Department of the University in Oslo.

LITERATURE

1. Bastiansen, O. *Om noen av de forhold som hindrer den fri dreibarhet om en enkeltbinding*. Bergen (1949).
2. Bastiansen, O. *Acta Chem. Scand.* **3** (1949) 408.
3. Fowweather, F., and Hargreaves, A. *Acta Cryst.* **3** (1950) 81.
4. Smare, D. L. *Acta Cryst.* **1** (1948) 150.
5. Hargreaves, A., and Taylor, W. H. *J. Sci. Instrum.* **18** (1941) 138.
6. Viervoll, H. *Avhandling Norske Videnskaps-Akad. Oslo I Mat.-Naturv. Kl.* (1941) no. 5, *Acta Chem. Scand.* **1** (1947) 120.
7. Pauling, L. *The nature of chemical bond*. (1939).
8. Hampson, G. C., and Weissberger, A. *J. Am. Chem. Soc.* **58** (1936) 2111.

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