

The Molecular Configuration of Diphenyl Ether as Revealed by Dipole Moment Data.

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(Received February 18, 1939.)

The dipole moments of 2,2'-dinitro-, 2,2'-diiodo- and 2,2'-dimethyl-diphenyl ethers were measured in benzene and hexane solutions at 27° and 50°. Four isomers of dimethyl-diphenyl ethers were also studied in benzene solution at 30°. The results obtained for them lead to the conclusion that each benzene ring is perpendicular to the other ring in the molecules considered.

It is not long ago that diphenyl ether, quite a familiar substance to chemists, was found to be playing an important role in the natural world, its skeleton being often found in extracts from plants etc. For instance the work of H. Kondo and his pupils⁽¹⁾ might be mentioned, who discovered the skeleton of this molecule in many alkaloids extracted from plants proper to Japan. In connection with this, Y. Asahina and his co-workers⁽²⁾ showed that diphenyl ether is also the mother structure of some acids which are found in lichens. Moreover, certain alkaloids, derivatives of diphenyl ether, have recently been found to be of special interest from the chemotherapeutical point of view.⁽³⁾ Thus, it has become necessary for pharmacutists as well as for chemists to make a research into the molecular configuration of diphenyl ether.

Many investigations of this substance are known from the side of pure physics and chemistry and many heated discussions have taken place about the valency angle of its oxygen atom. The paper of Hare and Mack⁽⁴⁾ is probably the first one relating to this angle. It was based on the collision area method, and gave the angle as 107°, but this value is not certain. We must mention next, the investigation by the dipole moment method, by which an abnormally large angle was deduced at first.⁽⁵⁾ But the interpretations of the results were severely criticized by Bennett,⁽⁶⁾ who concluded the angle of 109.5° as the more trustworthy. Afterwards, the problem of the valency angle was reexamined by Sutton and Hampson⁽⁷⁾ and the angle of diphenyl ether was determined as 128°±4°. ⁽⁸⁾

(1) Kondo and Tomita, *Arch. Pharm.*, **274** (1936), 65.

(2) Asahina and co-workers, *Ber.*, **66** (1933), 689, 893, 1031, 1215, etc.; see also Richter-Anschutz, "Chemie der Kohlenstoffverbindungen," Vol. II, 1, 394-398.

(3) Unpublished.

(4) Hare and Mack, *J. Am. Chem. Soc.*, **54** (1932), 4272.

(5) Hampson, Farmer, and Sutton, *Proc. Roy. Soc. (London)*, A, **143** (1933), 147; Bergmann and Tschudnowsky, *Z. physik. Chem.*, B, **17** (1932), 107; Smyth and Walls, *J. Am. Chem. Soc.*, **54** (1932), 3230.

(6) Bennett, *Trans. Faraday Soc.*, **30** (1934), 853.

(7) Sutton and Hampson, *ibid.*, **31** (1935), 945.

(8) Quite recently a revision of this angle was carried out by Coop and Sutton, by making a new determination of dipole moment in the vapour phase, *J. Chem. Soc.*, **1938**, 1869. The corrected value is 124°±5° which shows a better agreement with the value of Maxwell than their earlier one.

On the other hand, using the electron diffraction method, Maxwell and his co-workers⁽⁹⁾ obtained the value of $118^\circ \pm 3^\circ$, which lies between 128° and 109° (Fig. 1).

Contrary to the valency angle of oxygen, little attention has been paid to the problem of the structure of the molecule as a whole, i.e. about

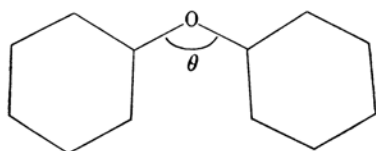


Fig. 1.

the orientation of each benzene nucleus in it. This is in sharp contrast to the development of study on the stereo-chemistry of diphenyl derivatives. Pauling,⁽¹⁰⁾ however, suggested in conversation with Sutton that the two benzene rings might be fixed in the same plane—a result which is expected if there be strong resonance

among the following structures A and B (Fig. 2). But there seemed no further support for it than the apparent widening of the angle of oxygen.⁽⁷⁾ The other structure which the organic chemists imagine instinctively to

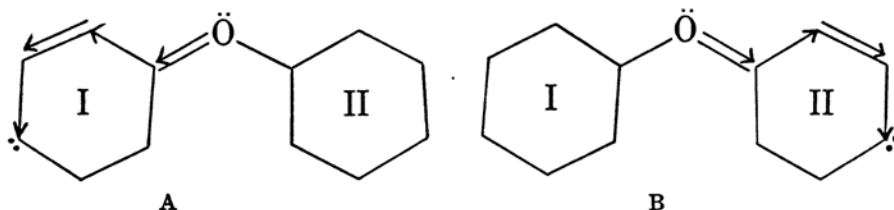


Fig. 2.

be stable is that the two benzene rings are perpendicular to the plane of the valency of oxygen. For instance, Smyth⁽¹¹⁾ seemed to hold this opinion when he spoke of the rotational vibration around this position.

Morino⁽¹²⁾ has recently made calculations on the interaction force between the H atoms of the neighbouring rings. One of the results is that the plane structure corresponds to a big increase in the potential energy and is unstable unless a pronounced resonance does occur. The second result is that Smyth's structure does not correspond to the lowest position of this potential energy, and that this condition is attained when one benzene ring is approximately perpendicular to the other (Fig. 3). The present investigation was undertaken in order to examine the suggestions of Pauling and Smyth in view of the recent research of Morino.

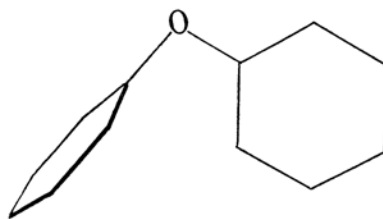


Fig. 3.

Experimental.

In order to realise the aim thus outlined, it was decided to measure dipole moments in solution and to do this over a wide range of temperature

(9) Maxwell, Hendricks, and Mosley, *J. Chem. Phys.*, **3** (1935), 699.

(10) Cited in the paper of Sutton and Hampson, *Trans. Faraday Soc.*, **31** (1935), 945.

(11) Smyth and Walls, *J. Am. Chem. Soc.*, **54** (1932), 3230.

(12) Private communication; the details of his calculation will appear shortly.

with the use of as many solvents as possible. Attention had also to be given to the choice of the solute substances; and 2,2'-dinitro- and 2,2'-diiodo-diphenyl ethers (m.p. 115° and 66° respectively) were prepared⁽¹³⁾ in the present research, the reason being that these substances can be obtained in the form of pure crystals and also because they have many advantages over their position isomers in the discussion of molecular structure. Five isomers of dimethyl-diphenyl ethers, the pure samples of which had been prepared by Dr. Tomita⁽¹⁴⁾ and were kindly given to us, were also studied for comparison.

Full details of the present research, i.e. the apparatus, the data of dielectric constants and densities, preparations of materials and their purity etc. will not be described here, because they may be found in other places.⁽¹⁵⁾ In the following tables the results are summarized in six columns: (1) The sample employed as solute, (2) the temperature in °C., (3) the solvent employed, (4) the polarisation, (5) the dipole moment calculated from $P - MR_D$, (6) the dipole moment calculated after Groves-Sugden,⁽¹⁶⁾ viz. $P - 1.05 MR_D$.

The results of these tables present many features. One is the small solvent effect as seen from the difference between the apparent moments in solution. This gives a clear proof that the observed moments are fairly trustworthy and moreover, that benzene does not exert such an anomalous solvent action to the solute as it does on ethylene chloride.⁽¹⁷⁾ From this, one can safely expect that the small temperature coefficient of moment in benzene is reliable. Moreover, one may notice that the difference between μ and μ' is quite small in the case of dinitro- and diiodo-compounds. There-

Table 1.

| Substance | t°C. | Solvent | P (c c) | μ (D) | μ' (D) |
|------------------------------|------|------------------------|---------|-----------|------------|
| 2,2'-Dimethyl-diphenyl ether | 27 | Benzene | 75.2 | 0.83 | 0.73 |
| | 50 | „ | 74.4 | 0.84 | 0.73 |
| | 27 | Hexane | 74.7 | 0.82 | 0.72 |
| 2,2'-Dinitro-diphenyl ether | 27 | Benzene | 970 | 6.64 | 6.62 |
| | 50 | „ | 890 | 6.57 | 6.56 |
| | 27 | Dioxan ⁽¹⁸⁾ | 992 | 6.72 | 6.70 |
| 2,2'-Diiodo-diphenyl ether | 27 | Benzene | 230 | 2.72 | 2.69 |
| | 50 | „ | 225 | 2.78 | 2.74 |
| | 27 | Hexane | 228 | 2.70 | 2.67 |

(13) Higasi and Uyeo, *J. Chem. Soc. Japan*, **60** (1939), 204.(14) Tomita, *J. Pharm. Soc. Japan*, **57** (1937), 76.(15) Apparatus, Higasi, this Bulletin, **13** (1938), 158. The data of dielectric constants and densities, Uyeo and Higasi, *J. Chem. Soc. Japan*, **60** (1939), 199, 204. Preparation of Materials, Higasi and Uyeo⁽¹³⁾, Tomita⁽¹⁴⁾.(16) Groves and Sugden, *J. Chem. Soc.*, **1935**, 971.(17) Mizushima, Morino, and Higasi, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **25** (1934), 159.

(18) 2,2'-Dinitro-diphenyl ether is hardly soluble in hexane, so dioxan was employed as solvent instead of hexane. As this solvent may not be so neutral as hexane, allowance must be made of its specific action on the moment.

Table 2.

| Substance | $t^{\circ}\text{C.}$ | Solvent | $P(\text{c.c.})$ | $\mu(\text{D})$ | $\mu'(\text{D})$ |
|--|----------------------|---------|------------------|-----------------|------------------|
| 3,3'-Dimethyl-diphenyl ether | 30 | Benzene | 101.0 | 1.40 | 1.35 |
| 4,4'-Dimethyl-diphenyl ether ⁽¹⁹⁾ | " | " | 104.6 | 1.46 | 1.41 |
| 3,4'-Dimethyl-diphenyl ether | " | " | 102.0 | 1.42 | 1.36 |
| 3,4-Dimethyl-diphenyl ether | " | " | 109.0 | 1.53 | 1.49 |

fore, it is evident that the error arising from atomic polarisation is insignificant in these molecules. For dimethyl-diphenyl ethers, however, this error becomes rather serious on account of their small moments.

It may be concluded, therefore, that the moments of the above molecules are not much affected by solvent,⁽²⁰⁾ temperature, and also by the choice of atomic polarisation, and if dimethyl-diphenyl ethers should be regarded as an exception, these are affected only by the last.

Discussion.

For convenience' sake we shall first discuss the results of Table 1. And then, using the conclusions drawn from them, we shall discuss the dipole moments of isomeric dimethyl-diphenyl ethers (Table 2).

Free Rotation and Contour Map of Moment. The molecule of 2,2'-disubstituted diphenyl ether has four polar linkages, i.e. two C—O bonds and two C—X bonds (X being the substituent), but we may represent the two C—O bond moments by its resultant (μ_1) which bisects the valency angle of the oxygen atom (Fig. 4). According to the classical view of organic chemistry, this molecule has two axes of rotation, so that for describing the intramolecular configuration, two parameters, θ_1 and θ_2 are necessary which will be defined as follows.

Consider a Cartesian co-ordinate system (Fig. 5) and let the Z axis coincide with the direction of μ_1 and choose the YZ plane on the C—O—C plane. Now, each substituent is capable of rotation around the corresponding C—O line, the azimuths of rotation θ_1 and θ_2 for μ_2 , right and left respectively, will be defined as follows: θ_1 and θ_2 are zero, when they lie on the YZ plane on the right side of the corresponding C—O line, and the positive sense is taken as in the left hand screw (see Fig. 5).

(19) The result for 4,4'-dimethyl-diphenyl ether may be compared with that of Hampson, Farmer, and Sutton, *Proc. Roy. Soc. (London)*, A, **143** (1933), 147. They gave it $P = 104.5 \text{ c.c.}$ at 25°C. which corresponds to $P = 103.8 \text{ c.c.}$ at 30°C. The dipole moment of this substance was newly determined in the vapour phase by Coop and Sutton, *J. Chem. Soc.*, **1938**, 1869. The result was $\mu = 1.44 \text{ D.}$ and P_2 at 30° estimated from it is 108.0 c.c.

(20) It may be too bold to say so without any corresponding data in the vapour phase. But according to the theory of solvent effect, this error would not be serious—not so serious at least as 4,4'-disubstituted diphenyl ether.

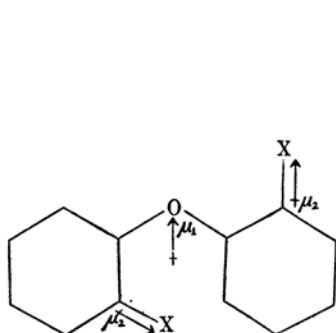


Fig. 4.

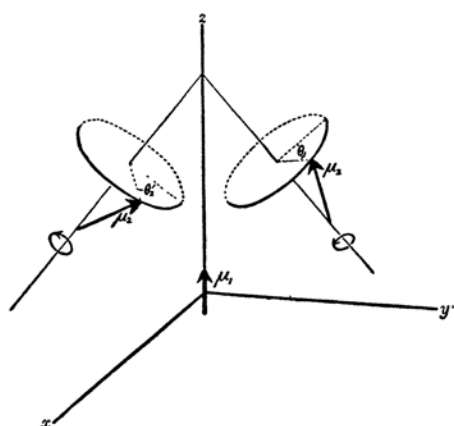


Fig. 5.

And the moment of a molecule as a whole, μ can be expressed by the following relation.

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}} \quad (1)$$

where

$$\left. \begin{aligned} \mu_x &= \mu_2(\sin \theta_1 + \sin \theta_2) \sin 60^\circ \\ \mu_y &= \mu_2(\cos \theta_1 + \cos \theta_2) \sin 60^\circ \cos \varphi \\ \mu_z &= \mu_1 + 2\mu_2 \cos \varphi \cos 60^\circ + \mu_2 \sin \varphi (\cos \theta_1 - \cos \theta_2) \sin 60^\circ \end{aligned} \right\} \quad (2)$$

where φ denotes half of the valency angle of oxygen.

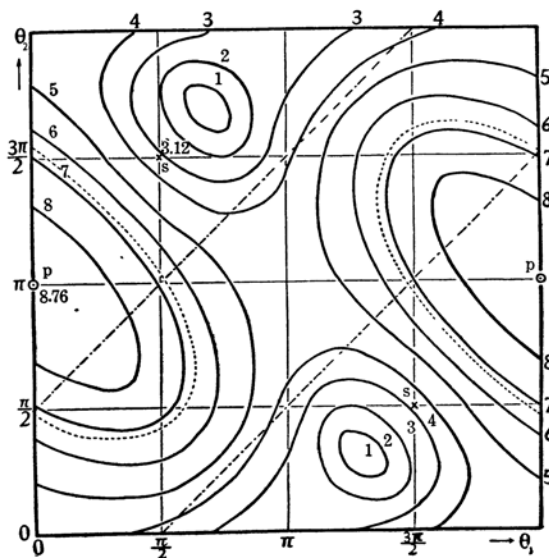


Fig. 6. 2,2'-Dinitro-diphenyl ether: $\mu_1 = 1.14\text{D}$, $\mu_2 = 3.80\text{D}$.

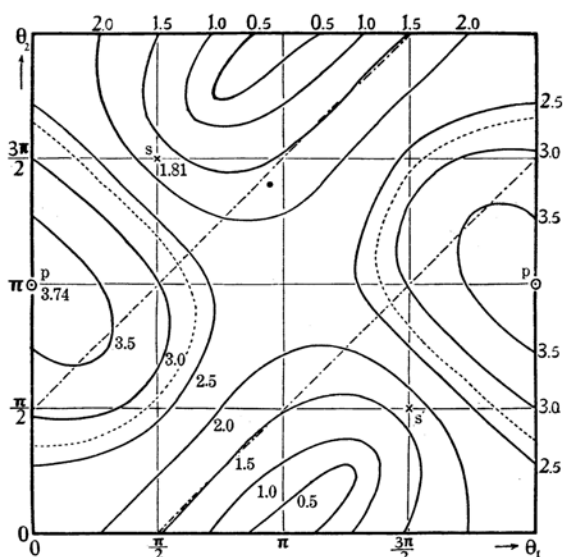


Fig. 7. 2,2'-Diiodo-diphenyl ether: $\mu_1 = 1.14\text{D}$, $\mu_2 = 1.30\text{D}$.

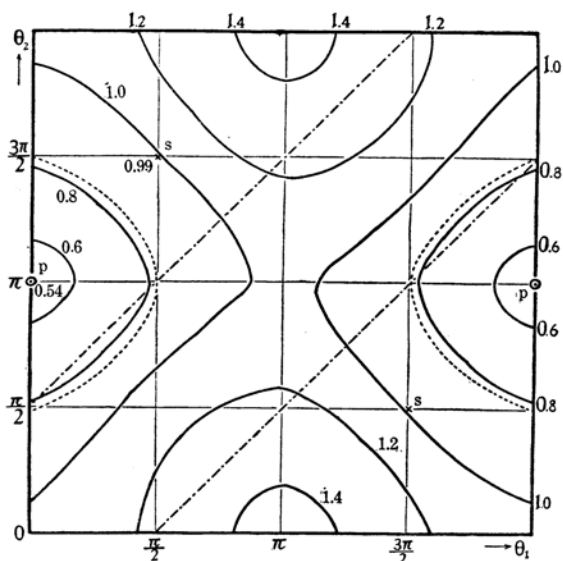


Fig. 8. 2,2'-Dimethyl-diphenyl ether: $\mu_1 = 1.14\text{D}$, $\mu_2 = -0.30\text{D}$.

As μ_1 , μ_2 and φ can be estimated, we can easily calculate the total moment μ as a function of θ_1 and θ_2 . The results of the calculation by this way are shown in the three contour maps of dipole moment (see Fig. 6, 7, and 8). The assumptions which were made in this calculation are as follows. (1) Half of the oxygen valency angle, $\varphi = 118^\circ/2$; (2) the resultant moment of two C-O bond moments, $\mu_1 = 1.14\text{D}$; ⁽²¹⁾ (3) the C-X bond moment, $\mu_2 = 3.80\text{D}$ (X = NO₂), 1.30D (X = I), -0.30D (X = CH₃).

(21) According to the new determination by Coop and Sutton, *J. Chem. Soc.*, **1938**, 1869, the moment of diphenyl ether in the vapour phase is 1.14D .

It is clear that the reliability of the contour maps (Fig. 6, 7, and 8) is dependent upon the validity of these assumptions as well as that of the above equations. Therefore, we shall discuss these more carefully afterwards. But in the following, we shall assume that the contour maps are fairly correct, and using them we shall discuss the molecular configuration of diphenyl ether.

The Plane Formula of Pauling. There are three plane formulae for disubstituted diphenyl ether, i.e., A, B, and C (Fig. 9). In the case of 2,2'-disubstituted compounds, however, the structures B and C should be excluded on account of big repulsion.

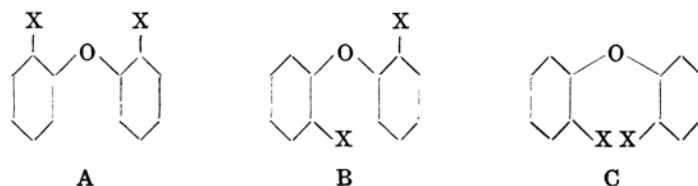


Fig. 9.

No explanation will be needed for the structure C. On constructing a model⁽²²⁾ of a 2,2'-disubstituted molecule, it will be also understood why the structure B is untenable. For instance, at a model of 2,2'-diiododiphenyl ether, one would find the distance between I and H atoms (of the neighbouring ring), if they are in the structure B, much smaller than the H-I distance of the chemically combined atoms. For dinitrodiphenyl ether the N-H distance for B would be estimated as 0.3 Å in contrast to the N-H distance of 1.0 Å of the combined atoms. Therefore, it is quite evident that a considerable repulsion occurs at this structure.⁽²³⁾

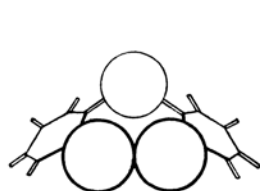
Thus the only possible structure is A which corresponds to a point, $\theta_1 = 0$, $\theta_2 = \pi$ in the contour maps (marked by \odot in Fig. 6, 7, 8). And the moments at this position are calculated as 8.76D, 3.74D, 0.54D for dinitro-, diiodo-, and dimethyl-diphenyl ethers, respectively, while the observed moments are 6.64D, 2.72D, and 0.83D, respectively. The differences are certainly too large to be explained as experimental errors.

The Configuration according to Smyth. If we neglect the mutual interaction between the substituent groups, according to Smyth, there should be two probable configurations of disubstituted diphenyl ether; i.e. trans (D) and cis (E) forms (see Fig. 10) and the molecule might be supposed to be vibrating near both positions. In the 2,2'-disubstituted compounds, however, the substituents X approach each other and a big repulsion results at the cis position. For example, in 2,2'-diiodo-diphenyl ether the

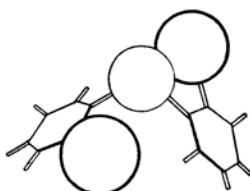
(22) A molecular model can be easily constructed with the use of data found in books like Stuart, "Molekülstruktur," Sidgwick, "Covalent Links in Chemistry." See also Pauling and Huggins, *Z. Krist.*, **84** (1933), 205.

(23) In order to make this structure stable, the valency angle of oxygen should be widened to a great extent, more than ca. 160°.

I—I distance becomes 2\AA for the E structure, while that of the combined atoms is 2.7\AA . In the molecule of 2,2'-dinitro-diphenyl ether, the O—O



E (cis-form)



D (trans-form)

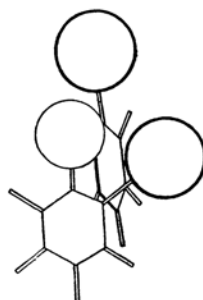


Fig. 10. Molecular model according to Smyth of 2,2'-disubstituted diphenyl ether.

○ Oxygen atom. ○ Substituent.

Fig. 11. Molecular model according to Morino of 2,2'-disubstituted diphenyl ether.

distance for E becomes less than 1.9\AA , which is certainly larger than that of the combined atoms 1.2\AA , but smaller than that of closest packing 2.72\AA . Therefore this position seems to be also improbable.

As a conclusion from the above, we may say that the trans form D has a much lower potential energy than cis form E and it will be sufficient to consider vibrations near this position which corresponds to the points $\theta_1 = \frac{\pi}{2}$, $\theta_2 = \frac{3\pi}{2}$ and $\theta_1 = \frac{3\pi}{2}$, $\theta_2 = \frac{\pi}{2}$ (marked with \times in the contour diagrams).

If the vibration has a small amplitude, we may expect at inspection of the map that the moment will not differ very much from that for the structure D. Therefore, for 2,2'-dinitro-, diiodo-, and dimethyl-diphenyl ether, the moments of 3.1D, 1.8D and 1.0D are estimated respectively. The difference between these and the observed moments are much more pronounced.

The Molecular Configuration according to Morino. The potential due to the repulsion between H atoms of the neighbouring rings was carefully traced by Morino of the Chemical Institute and it was found that the lowest valley in the potential diagram lies on two straight lines $\theta_2 = \theta_1 \pm \frac{\pi}{2}$ in the contour map—approximately speaking, one benzene ring is situated perpendicular to the other.

If all the positions on these lines are equally probable, the mean moment $\bar{\mu}$ is calculated as follows by putting $\theta_2 = \theta_1 \pm \frac{\pi}{2}$ in equation (1).

$$\bar{\mu}^2 = \frac{\int_0^{2\pi} \mu^2 d\theta_1}{\int_0^{2\pi} d\theta_1} \quad (3)$$

This definite integral is easily evaluated, and the resultant equation is

$$\bar{\mu}^2 = (\mu_1 + \mu_2 \cos \varphi)^2 + 1.5\mu_2^2 \quad (4)$$

Putting $\varphi = 59^\circ$, $\mu_1 = 1.14\text{D}$, $\mu_2 = 3.80\text{D}$, 1.30D , -0.30D for $-\text{NO}_2$, $-\text{I}$, $-\text{CH}_3$ respectively, the following values shown in the third column of the table are obtained.

Table 3.

| Substance | Observed value | Calculated moment | | |
|---|----------------|-------------------|---------|-------|
| | | Morino | Pauling | Smyth |
| 2,2'-($\text{NO}_2\text{C}_6\text{H}_4$) ₂ O | 6.64D | 5.59D | 8.76D | 3.1D |
| 2,2'-(IC_6H_4) ₂ O | 2.72D | 2.41D | 3.74D | 1.8D |
| 2,2'-($\text{CH}_3\text{C}_6\text{H}_4$) ₂ O | 0.83D | 1.05D | 0.54D | 1.0D |

Although, the calculated moments do not show close agreement with the experimental values, the differences between them are not so marked as in the cases of the Pauling and Smyth structures.

In the above calculation we assumed that any position on the lines of $\theta_2 = \theta_1 \pm \frac{\pi}{2}$ is equally probable.⁽²⁴⁾ But this assumption becomes certainly invalid when a big atom or group is introduced to the 2,2'-position. For instance, the structure F would be rather improbable on account of great repulsion (Fig. 12). The dipole moment at this position, $\theta_1 = \pi$, $\theta_2 = \frac{3\pi}{2}$ ($\theta_2 = \theta_1 + \frac{\pi}{2}$), $\theta_1 = \pi$, $\theta_2 = \frac{\pi}{2}$ ($\theta_2 = \theta_1 - \frac{\pi}{2}$) is much smaller than the average value, viz. 3.72D, 1.52D for dinitro- and diiodo-diphenyl ether, while it is larger than the average value in the case of dimethyl-diphenyl ether, i.e. 1.25D.

Therefore, if this structure is excluded in the above calculation the resulting moments would approach the observed values. Therefore, we may consider as follows: each benzene ring can rotate around the corresponding C-O axis on the two conditions: (1) one ring is almost perpendicular to the other and (2) the rotation near the position F is not allowed.

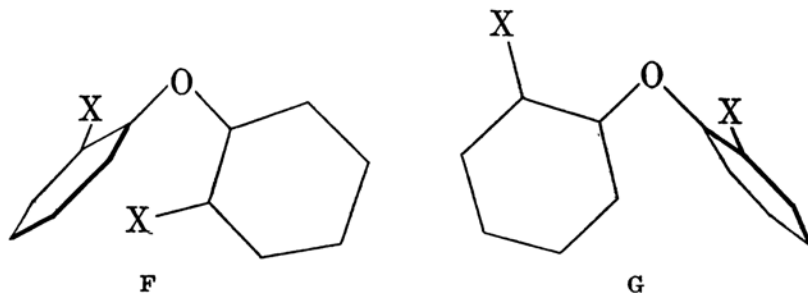


Fig. 12.

(24) This condition is satisfied in the case of diphenyl ether, but not necessarily so in the case of its derivatives.

In the contour map of dipole moment, we denoted the positions which correspond to the observed moment by the dotted lines (....) and the $\theta_2 = \theta_1 \pm \frac{\pi}{2}$ relation by (---) lines. It should be noted that the crossing of two dotted lines is always found near the positions $\theta_1 = \frac{\pi}{2}$, $\theta_2 = \pi$ or $\theta_1 = \frac{3\pi}{2}$, $\theta_2 = \pi$ in each map for the three substances. This is an interesting fact which should not be overlooked as a mere coincidence. The simplest explanation for it is, of course, to suppose that the molecule considered has the solid structure G (Fig. 12) corresponding to the position $\theta_1 = \pm \frac{\pi}{2}$, $\theta_2 = \pi$. (See also the model in Fig. 11.)

Alternatively, we may assume rotational vibration near this position. Because any vibration near it, (if its amplitude be small), would not much alter the value of average moment from that at G. Moreover, this vibrational structure explains the small temperature coefficient of dipole moment, because the increase in amplitude which should accompany the rise of temperature will not exert a very marked influence on the average dipole moment which is easily understood from the nature of the contour map.

The Dipole Moments of Dimethyl-diphenyl Ethers. So far, we have considered, 2,2'-disubstituted compounds only. Next, we shall discuss the results of the other derivatives of diphenyl ether in a few words. We can treat them just as we did before, and in the following table we show the comparison of the observed and calculated values (as the error due to the atomic polarisation is most serious in them, both μ and μ' are tabulated).

The observed moments show fairly good agreement with the mean moments calculated according to Morino. In this calculation, we assumed any position satisfying $\theta_2 = \theta_1 \pm \frac{\pi}{2}$ is equally probable. This as-

Table 4.

| | Observed moment | | Calculated moment | |
|------------------------------|-----------------|--------|-------------------|-------------------------|
| | μ | μ' | Morino | Pauling ⁽²⁵⁾ |
| 3,3'-Dimethyl-diphenyl ether | 1.40D | 1.35D | 1.35D | 0.76D 1.33D 1.84D |
| 3,4'-Dimethyl-diphenyl ether | 1.42D | 1.36D | 1.40D | 1.12D 1.68D |
| 3,4-Dimethyl-diphenyl ether | 1.53D | 1.49D | 1.46D | 1.27D 1.48D |
| 4,4'-Dimethyl-diphenyl ether | 1.46D | 1.41D | 1.45D | 1.46D |

(25) The following values are assumed in this calculation:

$$\theta = 125^\circ, \mu_1 = 1.14\text{D}, \mu_2 = -0.35\text{D}$$

sumption can be justified in these cases because the substituents are separated far from the neighbouring benzene rings and also from each other, i.e. the repulsion force is expected to be small.

From the same reason, there are a few possible plane structures deduced from Pauling's theory which differ in dipole moment, and the observed moments lie between the corresponding maximum and minimum values.⁽²⁵⁾ But this is insignificant, because the Pauling structure was found to be rather contradicting in the above case of 2,2'-disubstituted diphenyl ether.

Notes on Assumptions. (1) *The valency angle of oxygen.* In the above discussion the valency angle of oxygen was assumed to be 118° .⁽⁹⁾ What becomes if the angle be different from the assumed value, will be the next problem to be solved. If the widening of the angle did occur, Pauling's structure might be right after all? In order to answer this question, the following table may be found helpful in which the values of bond moments which are needed for Pauling's and Smyth's structure are given for different values of the valency angle.

Table 5.⁽²⁶⁾

| Valency angle of oxygen | μ (C-NO ₂) | | μ (C-I) | |
|----------------------------|----------------------------|-------|-------------|-------|
| | Pauling | Smyth | Pauling | Smyth |
| 90° | 3.16 | 7.79 | 0.90 | 2.24 |
| 100° | 2.92 | 8.56 | 0.83 | 2.46 |
| 110° | 2.78 | 9.58 | 0.79 | 2.76 |
| 120° | 2.74 | 11.00 | 0.78 | 3.16 |
| 130° | 2.78 | 13.00 | 0.79 | 3.74 |
| 140° | 2.92 | 16.10 | 0.83 | 4.62 |
| 150° | 3.16 | 21.22 | 0.90 | 6.10 |

The bond moments assumed in the present paper are as follows: μ (C-NO₂) = 3.80, μ (C-I) = 1.30, μ (Ph₂O) = 1.14. The same value for μ (Ph₂O) is employed in the calculation of Table 5.

At a glance at the above table it is evident that Smyth's structure can be ruled out, because it corresponds to a too big bond moment even when the angle decreases to 90° . On the other hand the bond moments for Pauling's structure are smaller than the value ordinarily proposed. With the widening of the angle, this difference gets smaller indeed, but even at $\theta = 150^\circ$ it is still of a magnitude for which some explanation⁽²⁷⁾ is required.

(26) The moments are expressed in Debye units, i.e. 10^{-18} e.s.u.

(27) The interaction moments which account for this will be

$$\delta\mu(\text{C-NO}_2) = 0.64\text{D} \quad \delta\mu(\text{C-I}) = 0.48\text{D}.$$

And if we take the moments of nitrobenzene and iodobenzene in the vapour phase, 4.23D and ca. 1.6D as the standard, $\delta\mu(\text{C-NO}_2)$, $\delta\mu(\text{C-I})$ will be 1.07D and 0.7D respectively. (Continued to the next page.)

(2) *Induction effect.* In the above discussion we neglected entirely the induction effect in the first approximation. But this effect on the bond moments of the molecule can be easily estimated⁽²⁹⁾ and in the following table the results of estimation are shown.

Table 6.⁽²⁶⁾ Induction effect on bond moment.

| Substance | Calculated moment without correction of induction | Calculated moment with correction of induction effect |
|---|---|---|
| 2,2'-(NO ₂ ·C ₆ H ₄) ₂ O | 8.74 | 8.49 |
| 2,2'-(I·C ₆ H ₄) ₂ O | 3.74 | 3.05 |
| 2,2'-(CH ₃ ·C ₆ H ₄) ₂ O | 0.54 | 0.54 |

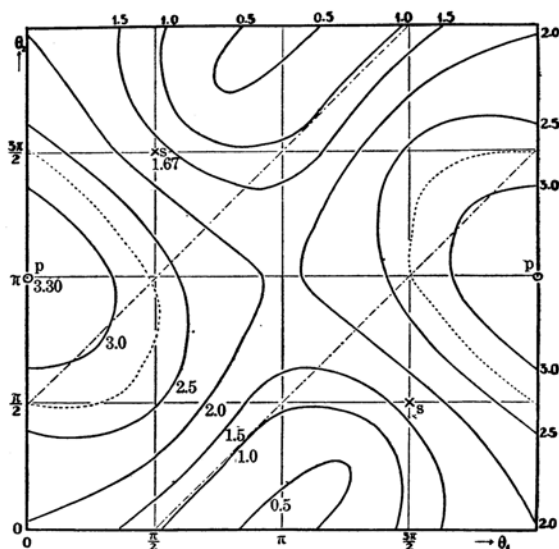


Fig. 13. 2,2'-Diiodo-diphenyl ether: $\mu_1 = 1.10D$, $\mu_2 = 1.10D$.

It should be emphasized that the induction effect in 2,2'-dinitro-diphenyl ether is too small to be considered. Therefore if the change of bond moment be needed for this molecule it is clear that induction effect

On the other hand, we must recall that the group moment μ (C—X) was assumed to lie on the C—X line in eq. (2). This assumption is certainly valid, when no interaction of moment occurs. But if such an interaction as considered by Sutton, *Trans. Faraday Soc.*, **31** (1935), 945, occurs, we must employ $\sin(60^\circ + \delta)$, $\cos(60^\circ + \delta)$ instead of $\sin 60^\circ$, etc. in the above equations. And if we confine our attention to the plane formula, the change in the angle of oxygen will bring about the same result as the introduction of δ , viz., the widening of the angle can be interpreted as the finite value of δ .

Therefore the writers do not regard this as a complete proof that the plane structure is improbable.

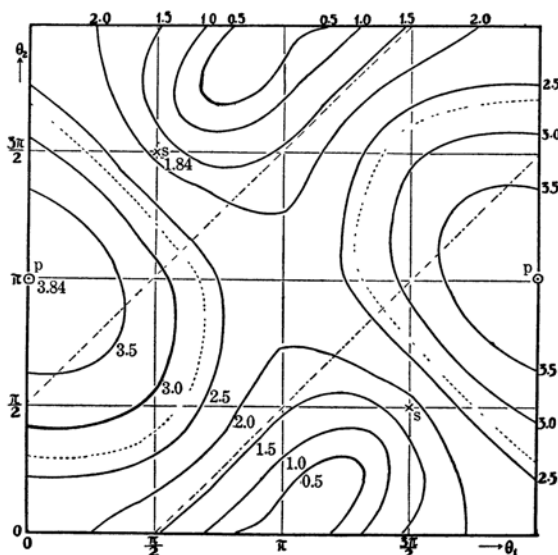
alone⁽²⁸⁾ cannot account for it. In the molecule of 2,2'-diiodo-diphenyl ether, however, a rather significant effect is expected from the big polarizability of iodine atom. Therefore a contour diagram of this molecule was constructed with the use of $\varphi = 59^\circ$, $\mu_1 = 1.10\text{D}$, $\mu_2 = 1.10\text{D}$ instead of $\mu_2 = 1.30\text{D}$ (Fig. 13). The comparison of it with Fig. 7 shows that almost the same conclusions can be drawn from here too.

(3) *Further test of bond moment.* In the following table the values of the bond moments assumed in the present paper are compared with those of Smallwood and Herzfeld⁽²⁹⁾ and also with the moments of $\text{C}_6\text{H}_5\text{X}$.⁽³⁰⁾

Table 7.⁽²⁶⁾

| Bond | Bond moment assumed value μ_2 | 4,4'-(X·C ₆ H ₄) ₂ O | | Bond moment Smallwood ⁽²⁹⁾ | $\mu(\text{C}_6\text{H}_5\text{X})^{(30)}$ |
|-------------------|-----------------------------------|--|---|---------------------------------------|--|
| | | Calc. with μ_2 | Observed | | |
| C—NO ₂ | 3.80 | 2.78 | $\begin{cases} 2.79(10) \\ 2.62(7) \end{cases}$ | 3.75 | $\begin{cases} 3.98(\text{B}) \\ 4.23(\text{G}) \end{cases}$ |
| C—I | 1.30 | 0.55 | — | 1.25 | 1.38(B) |
| C—CH ₃ | 0.30 | 1.45 | 1.46 | 0.43 | 0.37(G) |

Determinations in gas phase, and in benzene solution are indicated by G and B, respectively.

Fig. 14. 2,2'-Diiodo-diphenyl ether: $\mu_1 = 1.14\text{D}$, $\mu_2 = 1.35\text{D}$.

(28) The interaction effect besides induction arises from "resonance" or "electromerism," and it seems fair not to disregard this. But it seems rather difficult to treat this effect quantitatively, except making some arbitrary allowance for it. This allowance was introduced to a certain extent, indeed, in the consideration of the various contour maps. (Fig. 13, 14, 15, and 16. See also foot-note 27.) The effect of "resonance" on the vector additivity of bond moment is often very important in aromatic compounds. "Other effect" of disubstituted benzene should be reexamined on this ground. We intend to treat this problem quantitatively in a near future, and there we shall discuss the topic of the present paper again.

(29) Smallwood and Herzfeld, *J. Am. Chem. Soc.*, **52** (1930), 1919.

(30) A Table of Dipole Moments, Appendix, *Trans. Faraday Soc.*, **30** (1934).

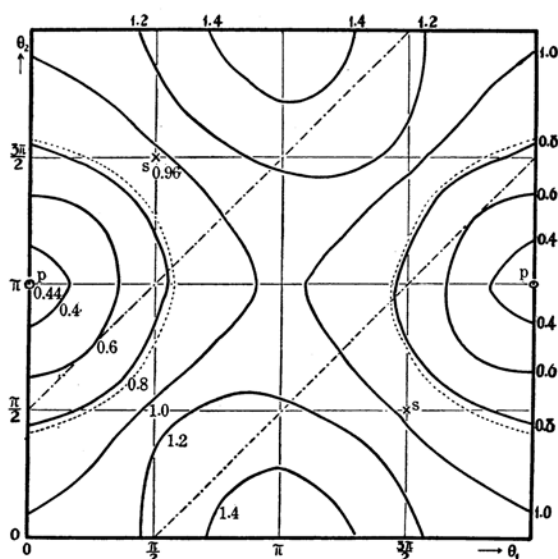


Fig. 15. 2,2'-Dimethyl-diphenyl ether: $\nu_1 = 1.14D$, $\nu_2 = -0.35D$.

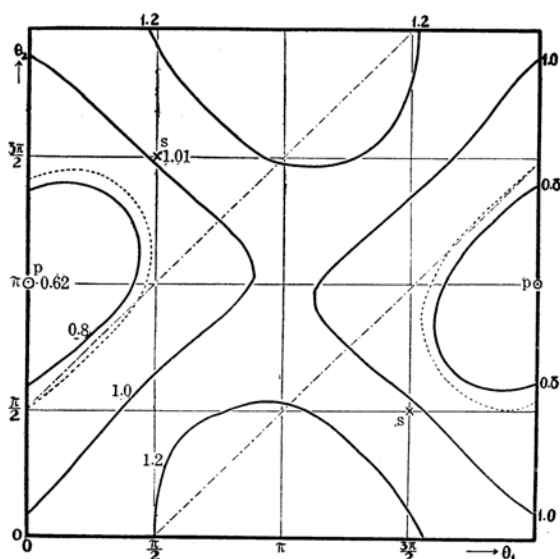


Fig. 16. 2,2'-Dimethyl-diphenyl ether: $\nu_1 = 1.14D$, $\nu_2 = -0.26D$.

The values of the present paper are near those employed by Smallwood and Herzfeld. In the middle column of the same table the moments of 4,4'-(X-C₆H₄)₂O are shown. The calculated values were obtained with the use of the bond moments in the present paper. It should be noticed that they are in good agreement with the observed moments.

A further examination of this problem was made by drawing the contour maps with the choice of other bond moments (Fig. 14, 15, and

16). It is certain from this that the change in bond moment so far as it is small, does not alter the essential conclusions reached in the above discussion.

In conclusion the writers wish to thank Professor E. Ochiai and Professor S. Mizushima for many valuable suggestions in connection with the present investigation. They are also indebted to Dr. Tomita for the gift of materials, and to Dr. Morino for kind discussions.

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