Conformation of Biaryls. Dipole Moment Measurements of o-Methylbiphenyls

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Since the structure of biphenyl in crystals had been determined by X-ray crystal analysis[1], it was a subject of interest for many workers to elucidate the conformation of substituted biphenyls by using various physical methods. As the result of extensive works on biphenyl derivatives especially halogenobiphenyls, their conformations have been determined under various conditions. By X-ray method planar structure was advanced for 3, 3′-dichlorobenzidine[2] in accordance with the conclusion of Dhar on biphenyl itself, of which the result can be compared with a skew conformation found for 2, 2′-dichlorobenzidine[3]. For the knowledge of the free molecules, electron diffraction investigation was undertaken, and it was reported that the biphenyls without any substituent at position 2 were also non-planar[4,5] as well as 2, 2′-dihalogenobiphenyls[6]. Dipole moment measurements of 2-halogeno-[7,8], 2, 2′-dihalogeno-[7,9] and 3, 3′-dihalogenobiphenyls[9] were also reported and rotated molecular conformations were advanced for each case and the mean angles were calculated. It seemed, however, that the information on the structure of 2, 2′-dialkylbiphenyls were very limited, only two examples were reported, at present. Namely, Hargreaves et al.[10] have reported the X-ray

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[1] N. R. Dhar, *Indian J. Physics*, **7**, 43 (1932). Cf. J. Hengstenberg and H. Mark, *Z. Krist.*, **70**, 283 (1929); G. L. Clark and L. W. Pickett, *J. Am. Chem. Soc.*, **53**, 167 (1931); N. R. Dhar, *Proc. Nat. Inst. Sci. India*, **15**, 11 (1949).

[2] J. Toussaint, *Acta Cryst.*, **1**, 43 (1948).

[3] D. L. Smare, ibid., **1**, 150 (1948).

[4] J. Karle and L. O. Brockway, *J. Am. Chem. Soc.*, **66**, 1974 (1944).

[5] O. Bastiansen, *Acta Chem. Scand.*, **3**, 408 (1949).

[6] Idem., ibid., **4**, 926 (1950).

[7] G. C. Hampson and A. Weissberger, *J. Am. Chem. Soc.*, **58**, 2111 (1936).

[8] A. C. Littlejohn and J. W. Smith, *J. Chem. Soc.*, 2456 (1953).

[9] Idem., ibid., 2552 (1954).

[10] F. Fowwether and A. Hargreaves, *Acta Cryst.*, **3**. 81 (1950); A. Hargreaves and W. H. Taylor, *J. Sci. Instruments*, **18**, 138 (1941).

crystal analysis of 2, 2′-dimethylbenzidine dihydrochloride and found that the compound has a rotated angle of 70.6°. Suzuki[11] has also computed the interplanar angle of biphenyls with methyl groups at position 2 (and 2′) based on the ultraviolet absorption spectra and found an angle of 70.5° for 2, 2′-dimethylbiphenyl.

While, in the course of synthetic studies of estrogenic biphenyl derivatives, it has been reported that 2, 2′-dimethylbiphenyls[12,13] failed to show a conjugation band of biphenyl system in the near ultraviolet region[14-16]. This result was explained by the steric interference of the two methyl groups which forced the benzene nuclei into non-planar arrangement, and the mean angle between the rings was assumed to be nearly perpendicular to each other.

In an effort to verify the above postulation, this communication records the results of the dipole moment measurement and the calculation of the interplanar angle of 2-methyl- and 2, 2′-dimethylbiphenyls. Dipole moment of 2, 2′-dimethylbiphenyl was reported to be 0.66 D[17]. The value, however, would not be large enough for the safer calculation of the angle, when one considered the small dipole moment found for toluene (0.34 D[18]) and the experimental error of this measurement. Thus for favorable compounds, 5, 5′-disubstituted 2, 2′-dimethylbiphenyls (II) were prepared from the corresponding iodo-compound (I) by the Ullmann reaction. Suitable substituents at the meta positions will increase the moment of the system and alter it markedly according to the rotation around the axis of the biaryl without affecting the steric environment. The method of preparations were described in the *Experimental Part.*

The measurement was carried out for a benzene solution at 25°C. The values found for the dimethylbiphenyls are given in Table I. The moments of benzene component used for the calculations were 1.94 D for *p*-chlorotoluene[19] and 4.52 D for *p*-nitrotoluene[20]. The calculated values for *cis*-planar and perpendicular conformations are given in Table I. As can be seen, the observed values for compound II (X=Cl and NO_2) were essentially the same for the calculated ones for the perpendicular arrangement as long as the rings are coaxial. The present results is in good agreement with the assumption derived from the ultraviolet absorption spectra of 2, 2′-dimethylbiphenyls[12,13].

It should, however, be pointed out that the calculated values would be modified in a minor degree by considering the induction effects[8,9,21-23], which comprised the effects already present in the component benzene, the effect of each dipole on the second ring and the moment induced at each dipolar substituent by the presence of the other. These inductive effects will be rather large when the polar groups are located at ortho positions as in the case of 2, 2′-disubstituted biphenyls. Thus, the values of the angle for 2, 2′-dichlorobiphenyl were 88° when all induction effects were ignored but 69∼84° when they were considered[9]. However, as can be easily assumed, both values

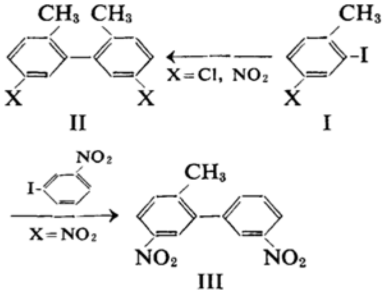

TABLE I. COMPARISON OF OBSERVED[a] WITH CALCULATED DIPOLE MOMENTS FOR 5, 5′-DISUBSTITUTED 2, 2′-DIMETHYLBIPHENYLS (II) AND 2-METHYL-3′, 5-DINITROBIPHENYL (III)

Compound	μ, D observed	μ, D, calculated Rings *cis*-planar	μ, D, calculated Rings perpendicular	Mean angle between planes of rings
II X=H	0.66[b]			
Cl	2.37	3.36	2.38	90°
NO_2	5.53	7.83	5.54	90°
III	4.55	7.35	5.21	104°

a) Benzene solution, at 25°C. b) See Ref. 17.

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[11] H. Suzuki, This Bulletin, 27, 597 (1954).
[12] T. Sato, ibid., 32, 1130 (1959).
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[16] Idem, ibid., 30, 958 (1957).
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were essentially the same for 3, 3′-disubstituted biphenyls[9], to which the present series are structurally related.

It is quite natural to consider that the conformation of 2-methylbiphenyl is located somewhat between 2,2′-dimethylbiphenyls (II) and biphenyl without ortho substituent owing to the decrease in steric hindrance given by the ortho substituent compared with compound II. The same measurement was applied to 2-methyl-3′, 5-dinitrobiphenyl (III) of which preparation was illustrated in the diagram and described in the *Experimental Part.* For the calculation of the theoretical moment of the system, dipoles moments of nitrobenzene and *p*-nitrotoluene were taken as 3.96[24] and 4.52D[20], respectively.

The observed value, 4.55 D, is smaller than the calculated ones for the conformations in which both rings are in *cis*-planar and perpendicular arrangement. These facts suggest that the molecule takes conformation in which two benzene rings are twisted further from the perpendicular position to *trans*-relationship in respect to two nitro groups. The observed value agreed with the calculated one for the conformation with the rings inclined at an angle of 104°. Therefore, the molecule can be regarded to have a slightly *trans*-arrangement with inclined benzene rings at an angle of 76°. The present result might be compared with the value found for 3, 3′-dinitrobiphenyl, which was reported to have a non-planar structure with an interplanar angle of 106°[9]. The reduction in the rotation angle found in compound III compared with the dimethyl compounds (II) was quite reasonable, but it remained unexplained whether the preferred *trans*-conformation of compound III was given by the steric effect of ortho groups or by the presence of meta substituents.

Experimental[25]

2, 2′-Dimethyl-5, 5′-dinitrobiphenyl (II, X=NO_2). —It was obtained by the Ullmann reaction of 2-iodo-4-nitrotoluene, b. p. 138~140°C/3 mmHg, m. p. 58°C (reported melting point is 58°C[26]) according to the modified method given in the literature[27]. One hundred grams (0.38 mol.) of 2-iodo-4-nitrotoluene and 150 g. of dry clean sand were preheated to 215°C and to this mixture was added with good stirring 100 g. (1.6 atoms) of activated copper bronze during one hour while the temperature was maintained at 215~220°C. It was then heated to 250°C and kept at that temperature for one and a half hour. After the reaction was over the mixture was poured onto dry sand and extracted with ethanol. The extract was recrystallized from acetic acid or acetone for several times with the aid of active charcoal. Pale yellow needles, m. p. 177~178°C, were obtained in a low yield.

5, 5′-Dichloro-2, 2′-dimethylbiphenyl (II, X=Cl). —Sixteen grams (0.063 mol.) of 4-chloro-2-iodotoluene, b. p. 108~109°C/10 mmHg, n^{19} 1.6231 obtained from 4-chloro-2-toluidine[28] according to Wroblewski[29] or from 2-iodo-4-toluidine[30] by Sandmeyer reaction was heated at 240~250°C with stirring and 20 g. (0.32 atom) of activated copper bronze was added over a period of one hour. The reaction mixture was then heated and kept at 280~290°C for forty minutes. It was extracted with acetone and the extract was distilled to give an oil which boiled first at 140~155°C/4 mmHg, and then at 142~144°C/3 mmHg., n^{20} 1.5961 on redistillation. Yield was 4 g. or 50% of the theory.

Found: C, 66.75; H, 4.74. Calcd. for $C_{14}H_{12}Cl_2$: C, 66.95; H, 4.82%.

2-Methyl-3′, 5-dinitrobiphenyl (III).—Under good stirring 15 g. (0.24 atom) of activated copper bronze was added to a mixture of 21 g. (0.080 mol.) of 2-iodo-4-nitrotoluene and 7.5 g. (0.030 mol.) of *m*-nitroiodobenzene in the course of thirty minutes, while the temperature was kept at 220~230°C. It was then heated to 240~250°C and kept for additional thirty minutes at that temperature. After the reaction was over, the mixture was extracted with acetone and the solution was treated with active charcoal. The solvent was evaporated and the remainder was recrystallized from ethanol for several times. Compound III was obtained as pale yellow plates, m. p. 145~146°C.

Found: N, 10.70. Calcd. for $C_{13}H_{10}O_4N_2$: N, 10.85%.

When the above reaction was conducted with an equimolar amount of iodo compounds the main product was found to be 3, 3′-dinitrobiphenyl.

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25) All boiling and melting points are uncorrected. The author wishes to thank Mr. T. Mizushima for microanalyse and Mr. M. Fujii for preparations of the materials.

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