

249. *The Electric Dipole Moments of 1 : 2-5 : 6-Dibenzocyclooctadiene and o-Xylene.*

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Electrical-polarisation measurements on benzene solutions of 1 : 2-5 : 6-dibenzocyclooctadiene, at 25°, indicate that 25—35% of the solute is in the polar C_{2v} conformation.

X-RAY analysis¹ shows that in the crystalline state 1 : 2-5 : 6-dibenzocyclooctadiene (I) exists in the *trans*-conformation. On the other hand, measurements² of electric dipole moments show that the structurally somewhat similar disalicylide (II) in benzene solution exists in the *cis*-conformation, as do also di(thiosalicylide)³ (III), the lactone of 2'-hydroxydibenzyl-2-carboxylic acid⁴ (IV), and 1 : 6-dichlorocycloocta-1 : 5-diene⁵ (V). In order to

¹ Davidson, quoted by Baker, Banks, Lyon, and Mann, *J.*, 1945, 27.

² Edgerley and Sutton, *J.*, 1951, 1069.

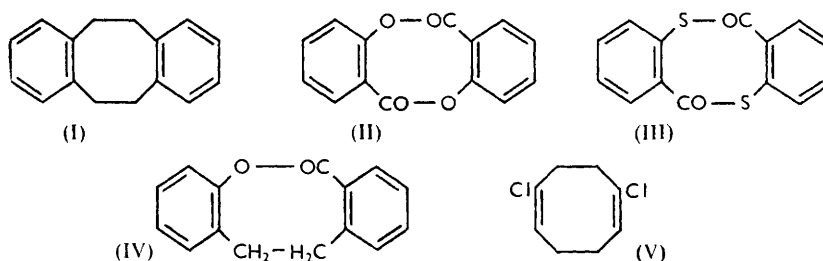
³ Saxby and Sutton, quoted by Baker, El Nawawy, and Ollis, *J.*, 1952, 3163.

⁴ *Idem*, quoted by Baker, Ollis, and Zealley, *J.*, 1952, 1447.

⁵ Roberts, *J. Amer. Chem. Soc.*, 1950, **72**, 3300.

elucidate the conformation of 1 : 2-5 : 6-dibenzocyclooctadiene in solution, we have measured its electric dipole moment in benzene at 25°, and also that of *o*-xylene.

For *o*-xylene, $\tau P - R_D$ is 8.0 ± 0.5 c.c. and, if ΔP is taken⁶ as 1.9 c.c., μ can be calculated to be 0.54 D. This agrees well with the value we have recalculated from



Tiganik's measurements,⁷ *viz.*, 0.53 D, using the modified Halverstadt-Kumler⁸ procedure and the value for ΔP quoted above.

For 1 : 2-5 : 6-dibenzocyclooctadiene, $\tau P - R_D$ is 9.4 ± 0.5 c.c., and ΔP is likely to be between 2 and 4 c.c., *i.e.*, about twice as great as for *o*-xylene, so that μ lies between 0.50 and 0.60 D. A comparative run with the non-polar substance *p*-xylene ($\tau P = 37.28$ c.c., $\epsilon P = 36.20$ c.c.) showed that the above-determined value for ϵP is well outside the error due either to technique or to atom polarisation.

This indicates (i) that the substance in solution is not all in the non-polar, *trans*-conformation (C_i point group) (Fig. 1 of ref. 1), (ii) that it is not all in the polar, *cis*-conformation (C_{2v} point group) (Fig. 1B of ref. 1) which, when the moment of *o*-xylene is taken to be 0.54 D (see above) and it is assumed that the valency angles in the methylene groups are tetrahedral, would have a calculated moment of 1.01 D and an orientation polarisation of 20.84 c.c.

The polarisation data are consistent with the view that 25–35% of the substance is in the C_{2v} form. The result is rather sensitive to the value chosen for the moment of *o*-xylene, for if the latter is taken as 0.62 D (the value for the gas³) the percentage range becomes 20–28%, and also to the value assumed for ΔP , an increase of 1 c.c. therein leading to a decrease of about 4 in the percentage.

Baker, Banks, Lyon, and Mann¹ have illustrated another conformation (Fig. 1A of ref. 1) which can be made by twisting the C_{2v} *cis*-form. This is of point group D_2 and should be both non-polar and enantiomorphous. There is thus the possibility of *four* conformational entities in solution, as well as, of course, intermediate forms. Baker, Banks, Lyon, and Mann¹ expressed the opinion, after examination of ordinary molecular models, that the rigid *trans*-conformation could be converted into the mobile *cis*-conformation only by passage through a highly strained intermediate or by breaking and re-forming a bond.

It does not seem possible to compare precisely the stabilities of these various conformations: there are two ethane residues in the molecule, and in all four conformations the bonds are eclipsed in each residue, so that one needs to know the relative interaction energies of two eclipsed C-H bonds, of two eclipsed C-Ph bonds, and of one C-H bond eclipsed by a C-Ph bond. The details of the numbers and kinds of eclipsed pairs for each conformation are in the annexed Table.

Eclipsed pairs of bonds.

Conformation	CH and CH	CH and CPh	CPh and CPh
C_i (<i>trans</i>)	2	4	0
D_2	2	4	0
C_{2v} (<i>cis</i>)	4	0	2

⁶ Hurdis and Smyth, *J. Amer. Chem. Soc.*, 1942, **64**, 2212.

⁷ Tiganik, *Z. phys. Chem.*, 1931, **B**, **13**, 425.

⁸ Everard, Hill, and Sutton, *Trans. Faraday Soc.*, 1950, **46**, 417.

Other repulsions, *e.g.*, van der Waals's, appear to be least for the *trans*-conformation. In the *cis*-model the benzene rings have overlapping π -electron clouds, and in the D_2 conformation two hydrogen atoms in each ethane residue interfere with two in the other ethane residue.

If there is no great difference in stability we may expect that, at equilibrium, 25% of the substance is in the polar C_{2v} conformation, 25% is in the non-polar C_i conformation, and 50% is in the non-polar D_2 forms. Our measurements and assumptions indicate between 25 and 35% of the polar C_{2v} conformation; but all that can safely be said is that some polar *cis*-form is present in the solution.

No change of polarisation with time could be detected, the minimum period between making of the solution and taking of the first observation being of the order of 5 min. The energy of activation for establishment of equilibrium between the conformational entities therefore appears to be less than 15—20 kcal./mole. This may be because the interatomic repulsions in the stable conformations are greater than in intermediate ones, and partly compensate for the bond strains in the latter.

Roberts⁵ has calculated that the energy barrier between the boat and the chair conformation of 1 : 6-dichlorocycloocta-1 : 5-diene is 9 kcal./mole, while that between the boat and the skew conformation is 3—14 kcal./mole. Thus the conformations ought to be readily interconvertible at room temperature. His polarisation measurements indicate that at least 85% of the molecules are in the boat conformation despite a dipole-dipole repulsion in this form of approximately 500 cal./mole. He concludes that this predominance of the boat conformation is best accounted for by secondary valency forces. These may, of course, be considerably modified in the dibenzo-derivative, just as the formation of the transition state may be affected by a stiffening of the molecule by the benzene rings.

Another example which appears relevant is the formation of the cycloocta-1 : 5-diene complexes $C_8H_{12}PtCl_2$ and $C_8H_{12}PdCl_2$ by reaction of the diolefin with K_2PtCl_4 and Na_2PdCl_4 respectively.⁹ These are best formulated as chelate complexes in which the hydrocarbon has the boat conformation.¹⁰ The reaction for the latter complex is rapid—"a yellow precipitate is formed almost at once"—so conversion of the cyclooctadiene in this case, if necessary, is evidently rapid.

EXPERIMENTAL

The 1 : 2-5 : 6-dibenzocyclooctadiene was kindly sent by Professor A. C. Cope, and had m. p. 108.5° (cf. ref.¹). Its purity was checked further by analysis (Found: C, 92.1; H, 7.7. $C_{16}H_{16}$ requires C, 92.3; H, 7.7%) and by infrared spectroscopy which showed that no appreciable amount of methanol was present.

1 : 2-5 : 6-Dibenzocyclooctadiene				<i>o</i> -Xylene			
10^6w	ϵ	v	$10^5\Delta n_D$	10^6w	ϵ	v	$10^5\Delta n_D$
2186	2.2736	1.1443	16	4049	2.2743	1.1446	0
3677	2.2745	1.1438	32	5697	2.2748	1.1446	2
5862	2.2755	1.1435	51	7508	2.2755	1.1447	1
7503	2.2763	1.1431	66	10165	2.2765	1.1446	1

$\epsilon = 2.2726 + 0.486w$; $v = 1.1447 - 0.213w$; $\Delta n_D = -0.00001 + 0.089w$; $\epsilon^P = 67.58$ c.c.; $\tau^P = 76.94$ c.c.

$\epsilon = 2.2727 + 0.371w$; v and Δn_D show very small variation with w . $\epsilon^P = 35.66$ c.c.; $\tau^P = 43.62$ c.c.

o-Xylene (from Messrs. L. Light and Co.) was used without further purification. Not only is the moment of *o*-xylene small and the experimental error in μ consequently large, but the principal impurities (*m*- and *p*-xylene, and ethylbenzene) all have small moments, so that relatively large amounts of these impurities would not vitiate the determination; *e.g.*, 3% of

⁹ Chatt, Vallarino, and Venanzi, *J.*, 1957, 2496.

¹⁰ Jensen, *Acta Chem. Scand.*, 1953, 7, 866, 868.

p-xylene impurity would lead to an error of only 0.01 D. The sample had n_D^{25} 1.5031 (lit.,¹¹ 1.5029) and d_{25}^4 0.8759 (lit.,¹¹ 0.87596).

Other details of the measurements and the nomenclature have been described.¹²

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¹¹ Weissberger, Proskauer, Riddick, and Toops, "Organic Solvents," 2nd edn., Interscience Publ. Inc., New York, 1955.

¹² Katritzky, Randall, and Sutton, *J.*, 1957, 1769.
