Tetrahedron Letters No.46, pp. 4133-4135, 1965. Pergamon Press Ltd.
Printed in Great Britain.

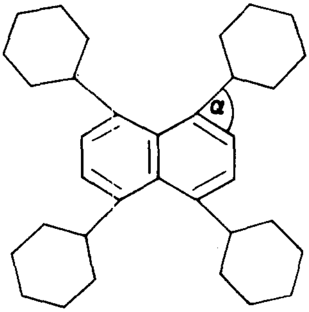
THE CONFORMATION OF 1,4,5,8-TETRAPHENYLNAPHTHALENE.

Mordecai Rabinovitz, Israel Agranat and Ernst D. Bergmann
Department of Organic Chemistry, Hebrew University, Jerusalem

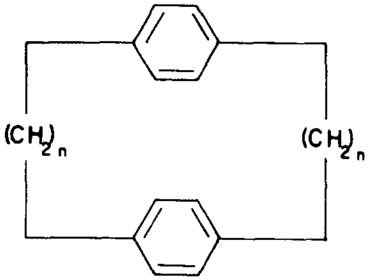
(Received 20 September 1965)

The ultraviolet spectrum of 1,4,5,8-tetraphenylnaphthalene (I) shows certain unexpected features (1,2) which undoubtedly are related to the inability of the four phenyl rings to arrange themselves in the plane of the naphthalene system. A possible conformation of the molecule would be one in which all the four phenyl rings are twisted out of the naphthalene plane, as has been suggested for rubrene (5, 6, 11, 12 -tetraphenylnaphthacene) by Jaffé and Chalvet (3). Thus the molecule would resemble that of the paracyclophans (II) in which the aromatic rings are facing each other and thus permit transannular delocalisation of the π-electrons (4). As in the case of II, this effect should be detectable in the N.M.R. spectrum of the hydrocarbon I. The symmetry of this compound makes the interpretation of the spectrum particularly easy.

Indeed, the expected shift to higher field has been observed (5). The N.M.R. spectrum shows a singlet at $\tau = 2.80$ (4 hydrogen atoms), a triplet at $\tau = 3.00$ (4 hydrogen atoms) and a doublet at $\tau = 3.23$ (16 hydrogen atoms). This doublet which is shifted by $\tau = 0.7$ as compared with 1-phenylnaphthalene (6), corresponds well to the shift of $\tau = 0.87$, observed in the paracyclophans, as compared with benzene. The singlet at $\tau = 2.80$ is to be ascribed to the four hydrogen atoms in the β-positions of the naphthalene nucleus; these hydrogen atoms are thus fully equivalent.



I



II

The triplet at $\tau = 3.00$ is obviously associated with four hydrogen atoms of the phenyl rings. If we assume that the angle in I is smaller than 90^0, it would be understandable that the transannular interaction of the <u>para</u>-hydrogen atoms of the phenyl rings is smaller than that of the <u>ortho</u>- and <u>meta</u>-hydrogen atoms. Thus the triplet is assigned to the four <u>para</u>-hydrogen atoms.

It is true that at $\tau = 3.23$ a <u>singlet</u> would have been expected; the appearance of a doublet seems to point to the existence of a magnetic asymmetry in the molecule, which might well be associated with the <u>para</u>-hydrogen atoms of the four phenyl rings. Indeed, the singlet at $\tau = 3.15$ observed in the less strained molecule of 1.8-diphenylnaphthalene (6) shows that the phenyl rings are perpendicular to the naphthalene plane,unlike as in (I).

Analogous observations have been made for 1-9-diphenylanthracene, 1,9,10-triphenylanthracene and 1,4,9,10-tetraphenylanthracene (7). It is noteworthy that in these cases, the following absorptions for phenyl protons have been observed: τ = 3.08 and 3.10; τ = 2.81 and 3.09, and τ = 3.02 and 3.10, respectively. Further studies on similar systems, now in progress, are likely to shed more light on the interactions which have been observed.

REFERENCES

1. Ch. Dufraisse, *Compt.Rend.Acad.Sci.*, **258**, 1507 (1964).

2. E.D. Bergmann, Sh. Blumberg, P. Bracha and Sh. Epstein *Tetrahedron*, **20**, 195 (1964).

3. H.H. Jaffé and O. Chalvet, *J. Amer. Chem. Soc.*, **85**, 1561 (1963).

4. D.J. Cram and L.A. Singer, *J. Amer. Chem. Soc.*, **85**, 1084 (1963).

5. The spectrum was measured in deuteriochloroform, tetramethylsilane serving as internal standard.

6. H.O. House, R. W. Magin and H.W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963).

7. S.C. Dickermann, D. De Souza and P.H. Wolf, *J. Org. Chem.*, **30**, 1981 (1965).