28. *Benzcyclooctatetraenes. Part V. The Absorption Spectra of Tetraphenylene and* 1 : 2 : 3 : 4 : 5 : 6-*Tribenz*-$\Delta^{1:3:5:7}$-cyclo*octatetraene in Relation to their Structures.*

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A close similarity between the absorption spectra of tetraphenylene and 2 : 2′-diphenyldiphenyl is interpreted as indicating that in the former compound the central *cyclo*octatetraene ring contributes little, if at all, to the resonance of the structure as a whole. This finding, implying as it does a non-planar structure for tetraphenylene, is supported by the fact that interpretation of the results of the *X*-ray crystallographic analysis of tetraphenylene has not been possible on the basis of its planar formulation. It gives support to the view that *cyclo*octatetraene itself is non-planar and non-aromatic in type. The absorption spectrum of 1 : 2 : 3 : 4 : 5 : 6-tribenz-$\Delta^{1:3:5:7}$-*cyclo*octatetraene likewise shows none of the attributes of a compound containing condensed aromatic rings.

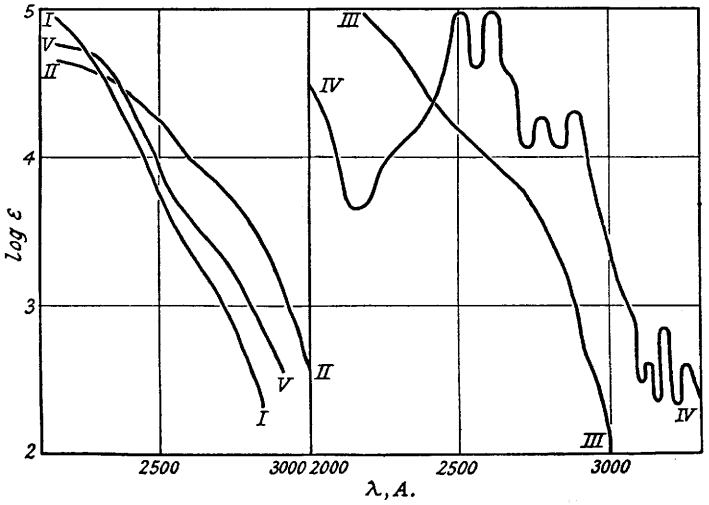
An objective in the present series of investigations has been to establish whether or not the *cyclo*octatetraene ring in compounds of the benz*cyclo*octatetraene type contributes materially to their resonance. If they could be established as typical planar polynuclear aromatic compounds, then there would be strong presumptive evidence for a planar resonant formulation of *cyclo*octatetraenoid systems generally. Alternatively, if such compounds could be established as definitely not of this type, then support would be obtained for the non-planar, non-resonant formulation of *cyclo*octatetraenes.

Sufficient data relating to tetraphenylene (Rapson, Shuttleworth, and van Niekerk, Part III, J. 1943, 326) and to 1 : 2 : 3 : 4 : 5 : 6-tribenz-$\Delta^{1:3:5:7}$-*cyclo*octatetraene (Shuttleworth, Rapson, and Theal Stewart, preceding paper) are now available to indicate that these substances are not typical planar polynuclear aromatic compounds containing condensed aromatic rings. Thus the relationship between the absorption spectra (see figure) of tetraphenylene (I) and 2 : 2′-diphenyldiphenyl (II) can be compared with that between the absorption spectra of 2-phenyldiphenyl (III; Pickett, Walter, and France, *J. Amer. Chem. Soc.*, 1936, **58**, 2298) and triphenylene (IV; Mohler and Sorge, *Helv. Chim. Acta*, 1939, **22**, 230). Whereas the presence of the central *cyclo*hexatriene ring in triphenylene causes a profound difference between its absorption spectrum and that of 2-phenyldiphenyl, the presence of the central *cyclo*octatetraene ring in tetraphenylene causes no such difference between its absorption spectrum and that of 2 : 2′-diphenyldiphenyl. The deduction seems clear

that in tetraphenylene the *cyclo*octatetraene ring contributes little to the resonance, and that a non-planar structure for the tetraphenylene molecule is probable.

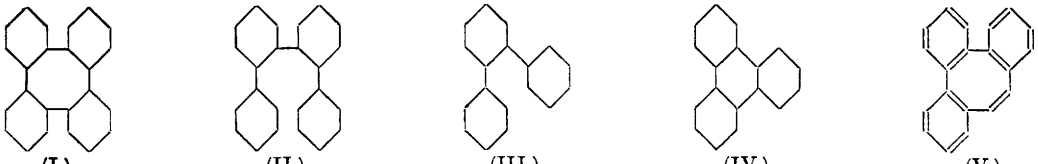
The close resemblance of the absorption spectrum of 1 : 2 : 3 : 4 : 5 : 6-tribenz-$\Delta^{1:3:5:7}$-*cyclo*octatetraene (V) to those of (I) and (II) indicates that similar conclusions can be drawn in the case of this compound.

These findings are in agreement with the results of *X*-ray studies of tetraphenylene; for Prof. R. W. James and Dr. J. N. van Niekerk have reported that the interpretation of their *X*-ray data has not been possible on the basis of a planar formulation, particularly when the three principal refractive indices of the crystal are taken



Absorption spectra of tetraphenylene (I), 2 : 2′-*diphenyldiphenyl* (II), 2-*phenyldiphenyl* (III), *triphenylene* (IV), *and* 1 : 2 : 3 : 4 : 5 : 6-*tribenz*-$\Delta^{1:3:5:7}$-cyclo*octatetraene* (V).

into account. Dr. L. O. Brockway (private communication) has obtained similar results in electron-diffraction studies.



(I.) (II.) (III.) (IV.) (V.)

Experimental.

Hydrocarbons.—Tetraphenylene (Rapson, Shuttleworth, and van Niekerk, *loc. cit.*) was recrystallised to purity from benzene, and heated till free from solvent. 1 : 2 : 3 : 4 : 5 : 6-Tribenz-$\Delta^{1:3:5:7}$-*cyclo*octatetraene (Shuttleworth, Rapson, and Theal Stewart, *loc. cit.*) and 2 : 2′-diphenyldiphenyl (Bowden, J., 1931, 1111) were recrystallised to purity from alcohol.

Absorption Spectra.—These were determined in both *n*-hexane and absolute ethyl alcohol; that of tetraphenylene was determined also in *cyclo*hexane. In no case was any significant variation in absorption with change of solvent noted. The curves have been constructed from 60—70 observations in respect of each solvent. A Hilger E_3 quartz spectrograph was used in conjunction with a sector photometer.

Molecular extinction coefficients (ε) were obtained from the relationship $\log I_0/I$ = density = εcd, where I_0 is the intensity of the incident light, I that of the transmitted light, c the concentration in g.-mols./l., and d the thickness of the layer of solution in cm.

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[*Received, December 7th*, 1943.]