

628. *Studies in Spectroscopy. Part I. Steric Effects in Some Substituted Butadienes and cycloButanes.*

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The ultra-violet absorption spectra of 1:1:4:4-tetraphenylbutadiene and of the compounds (I) where R = Ph, *p*-C<sub>6</sub>H<sub>4</sub>Me, *p*-C<sub>6</sub>H<sub>4</sub>Pr<sup>1</sup>, and *p*-C<sub>6</sub>H<sub>4</sub>Bu<sup>b</sup> reveal appreciable steric effects in the molecules. Deductions are made concerning the configurations of the compounds.

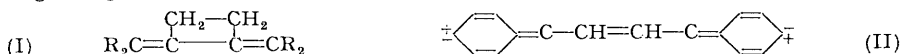
THE introduction of methyl groups into butadiene causes only small bathochromic shifts of about 50 Å for each methyl group, with only slight variation in intensity (Table 1). Introduction of a phenyl group at position 1 in butadiene, on the other hand, results

TABLE 1.

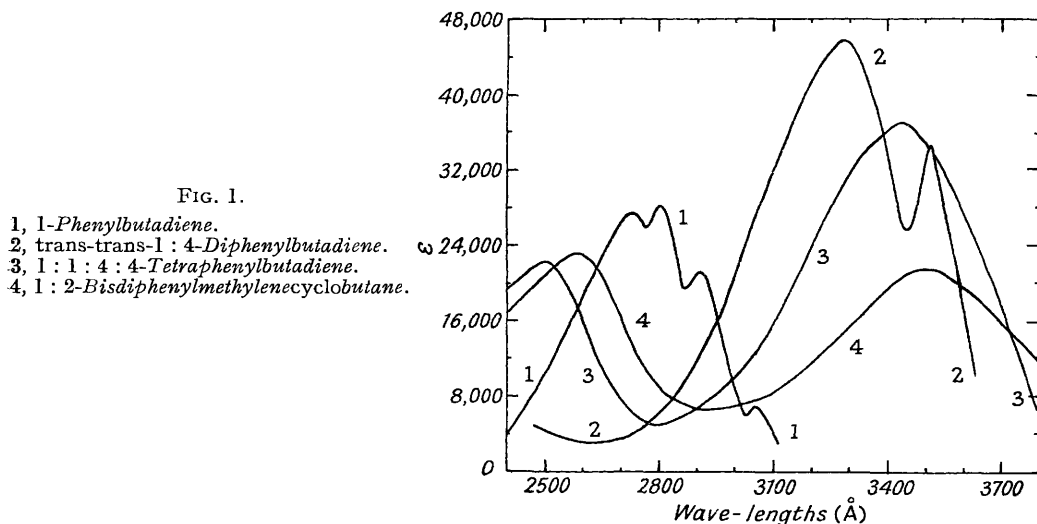
	$\lambda_{\max.}$	$\epsilon_{\max.}$		$\lambda_{\max.}$	$\epsilon_{\max.}$
Butadiene <sup>1</sup> .....	2170	20,900	2:3-Dimethylbutadiene <sup>3</sup>	2260	21,400
1-Methylbutadiene <sup>2</sup> .....	2235	25,500	1:4-Dimethylbutadiene <sup>2</sup>	2270	25,500
Isoprene <sup>1</sup> .....	2200	23,900			

The solvent was hexane in all cases. <sup>1</sup> Smakula, *Angew. Chem.*, 1934, **47**, 657. <sup>2</sup> Booker, Evans, and Gillam, *J.*, 1940, 1453. <sup>3</sup> Scheibe, *Ber.*, 1926, **59**, 1333.

in a large bathochromic shift with increase in the intensity of absorption relative to butadiene and appearance of multiple maxima (Fig. 1 and Table 2, p. 3287); in *trans-trans*-1 : 4-diphenylbutadiene the main absorption band has increased still further in intensity (with loss of fine structure), and moved to longer wave-length. The discrepancies in the values in the literature are probably due to isomerisation of *trans-trans*-1 : 4-diphenylbutadiene to the *trans-cis*- and *cis-cis*-forms on irradiation (Sandoval and Zechmeister, *J. Amer. Chem. Soc.*, 1947, **69**, 553; Pinkard, Wille, and Zechmeister, *ibid.*, 1948, **70**, 1938; Hirshberg, Bergmann, and Bergmann, *ibid.*, 1950, **72**, 5150).



Since the bathochromic shifts in the above compounds are due to increased conjugation, it might be expected that the introduction of more phenyl groups into the 1- and the 4-position of butadiene would lead to a further appreciable displacement of absorption maxima to the red, with increase in intensity. It has now been found, however, that the long-wave maximum of 1 : 1 : 4 : 4-tetraphenylbutadiene shows loss of fine structure, is of



lower intensity, and is displaced to the red by only 150 Å relative to the corresponding band of 1 : 4-diphenylbutadiene (Fig. 1 and Table 2). The bathochromic effect is that which might be expected from the introduction into 1 : 4-diphenylbutadiene of two weakly chromophoric groups, and the spectrum thus indicates that the introduction of the two further phenyl groups has had little effect on the resonance in the molecule.

This may be explained on the basis of interaction between adjacent phenyl groups in 1 : 1 : 4 : 4-tetraphenylbutadiene as is revealed by a scale diagram (Fig. 2). Appreciable interference between the *ortho*-hydrogen atoms of the phenyl groups *A* with *B* and *C* with *D*, with some interference involving the hydrogen atoms attached to  $C_{(2)}$  and  $C_{(3)}$  of the butadiene system with those of rings *B* and *C*, is apparent when the four phenyl groups are coplanar. The molecule can assume a less strained configuration if rings *B* and *C* are twisted out of the plane of the rest of the system, *i.e.*, out of the plane of the paper. Since these rings cannot contribute to resonance structures of type (II) in which near coplanarity is essential, the ultra-violet spectrum of 1 : 1 : 4 : 4-tetraphenylbutadiene is presumably composed of the 1 : 4-diphenylbutadiene spectrum (displaced to the red by 150 Å) plus the weak absorption of the two independently absorbing out-of-plane phenyl groups ( $\lambda$  ca. 2500 Å,  $\epsilon$  ca.  $2 \times 250$ ). The decrease in intensity on passing from the 1 : 4- to the 1 : 1 : 4 : 4-substituted butadiene system indicates that complete coplanarity of rings *A* and *D* and the butadiene system cannot be realised even if rings *B* and *C* are at right angles to the plane of the paper. There can obviously be no isomerisation on irradi-

ation of 1:1:4:4-tetraphenylbutadiene similar to that reported for 1:4-diphenylbutadiene.

The short-wave-length maximum of 1:1:4:4-tetraphenylbutadiene at 2490 Å is comparable to the butadiene maximum displaced to the red by 320 Å by the introduction of four groups. The short-wave-length maximum of 1:4-diphenylbutadiene [unrecorded by Hausser, Kuhn, and Smakula, and by Blout and Eager (refs. in Table 2)] should thus be at *ca.* 2330 Å, and similarly 1:1:4-triphenylbutadiene should have a spectrum similar to that of 1:4-diphenylbutadiene with maxima at *ca.* 2410 and 3360 Å ( $\epsilon$  *ca.* 21,000 and 40,000).

The ultra-violet spectrum of 1:1:4:4-tetraphenylbutadiene thus reveals another example of steric inhibition of resonance in systems containing the  $-\text{CH}=\text{CPh}_2$  group. Jones (*ibid.*, 1943, 65, 1820) has shown that 1:1-diphenylethylene has a spectrum similar to that of styrene and that tetraphenylethylene is spectroscopically similar to *trans*-stilbene. The introduction of a phenyl group into styrene to give 1:1-diphenylethylene caused a bathochromic shift approximately half that brought about in the long-wave-length band by the introduction of two phenyl groups into 1:4-diphenylbutadiene.

Steric inhibition of resonance has also been established for 1:2-disubstituted cyclo-

FIG. 2.

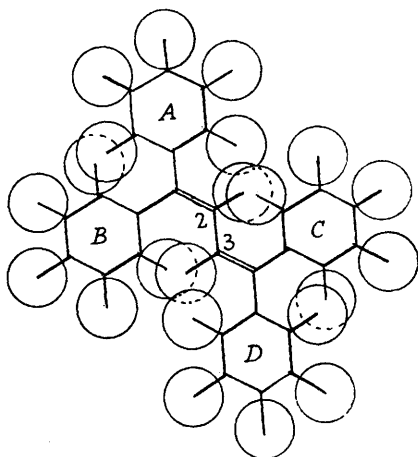
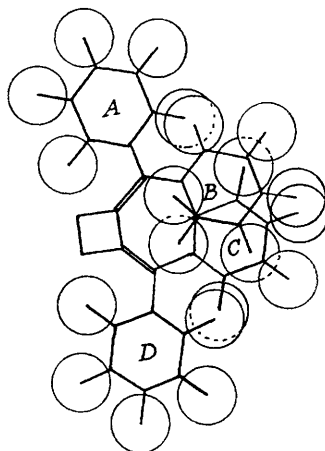


FIG. 3.



butane derivatives of type (I) where R is phenyl, *p*-tolyl, *p*-isopropylphenyl, or *p*-*tert*-butylphenyl. These compounds may be regarded as butadiene in which  $C_{(2)}$  and  $C_{(3)}$  form part of the *cyclobutane* ring, and when R = Ph the tetraphenyl compound is clearly closely related to 1:1:4:4-tetraphenylbutadiene. Its spectrum (Fig. 1 and Table 2) shows that the band at shorter wave-length (2580 Å,  $\epsilon$  23,000) has the same intensity as that for tetraphenylbutadiene; the bathochromic shift of 90 Å can be attributed to the introduction of two alkyl groups into butadiene (regarding the *cyclobutane* ring as spectroscopically equivalent to two methyl groups). The long-wave-length band (3510 Å,  $\epsilon$  21,400) has undergone a similar expected bathochromic shift of 80 Å relative to tetraphenylbutadiene, but there is a considerable decrease in the intensity of absorption compared with di- and tetra-phenylbutadienes. This can be attributed to additional steric inhibition of resonance caused by introduction of the *cyclobutane* ring. A scale diagram (Fig. 3) shows the marked overlap between rings A and B, C and D, and B and C, if all the phenyl groups are coplanar.

The rotation of rings B and C through 90° about the bond joining them to the butadiene system still gives interference (Fig. 4; cf. 1:1:4:4-tetraphenylbutadiene where a similar rotation gives a strain-free configuration). The steric interaction in the *para*-positions of rings B and C of the *cyclobutane* compound could be relieved if these rings were forced apart by increase in bond angles (*e.g.*, if angles  $\alpha$  and  $\alpha'$  increased by about 8°, or if angles  $\gamma$  and  $\gamma'$  were also increased) and/or by change in bond length.

If the compound (I; R = Ph) had a configuration similar to that shown by Fig. 4, the substitution of groups in the *para*-position of rings *B* and *C* would increase considerably the steric effect. Furthermore, if the groups were sufficiently large the strain would be relieved only if none of the benzene rings were coplanar with the butadiene system, and a marked change in absorption spectrum and in the fluorescence exhibited by this type of compound should be observed. Introduction of alkyl groups into the *para*-position showed spectroscopically that the rings *B* and *C* cannot be at 90° to the plane of the cyclobutane ring. The spectra of the compounds in question (Table 2) show bathochromic shifts and slight increases in intensity of absorption relative to the compound where R = Ph,

FIG. 4.

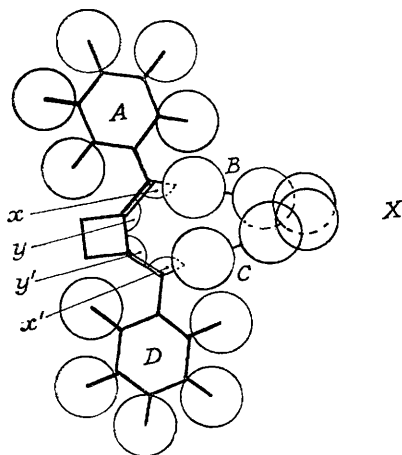
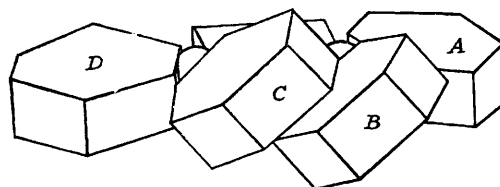


FIG. 5.



which can be explained only by the extra conjugation in the butadiene system due to groups in the *para*-positions such as Bu<sup>t</sup> contributing fully to resonance; that is to say, the butadiene system and two of the 1:4-substituted phenyl groups remain virtually coplanar. The maxima would have shifted to shorter wave-length if there had been appreciable non-planarity of the butadiene system involving rings *A* and *D*.

An alternative configuration for compounds of this type must therefore be sought and models show that the near coplanarity indicated by the absorption spectra can be maintained if rings *B* and *C* are parallel and at an angle to the rest of the system, as indicated in Fig. 5 by the edge-on view in the plane of the paper from *X* in Fig. 4.

It will, however, be noted that the intensities of the long-wave-length maxima of the cyclobutane derivatives are less than the corresponding maxima for tetraphenylbutadiene.

TABLE 2

	First max.		Second max.		Fluorescence
1-Phenylbutadiene <sup>1</sup> .....	2710	28,000	2230	12,000	Unrecorded
	2800	28,300	2330	8,500	
	2900	27,000			
	3050	6,000			
1:4-Diphenylbutadiene <sup>2</sup> .....	3280	41,000	Unrecorded		Deep blue
	3500	35,000			
1:4-Diphenylbutadiene <sup>3</sup> .....	3280	52,700	Unrecorded		
	3450	34,000			
Tetraphenylbutadiene .....	3430	37,250	2490	22,800	Deep blue
(I; R = Ph) .....	3510	21,400	2580	23,000	Intense green
(I; R = C <sub>6</sub> H <sub>4</sub> Me) .....	3580	23,000	2610	28,400	Yellow-green
(I; R = <i>p</i> -C <sub>6</sub> H <sub>4</sub> Pr <sup>1</sup> ) .....	3630	23,400	2620	30,000	Intense green
(I; R = <i>p</i> -C <sub>6</sub> H <sub>4</sub> Bu <sup>t</sup> ) .....	3650	27,200	2630	32,200	Intense yellow

The solvent was ethanol in all cases. <sup>1</sup> Braude, Jones, and Stern, *J.*, 1947, 1087; Smakula, *loc. cit.*; Grummitt and Christopher, *J. Amer. Chem. Soc.*, 1949, **71**, 4157. <sup>2</sup> Hausser, Kuhn, and Smakula, *Z. physikal. Chem.*, 1935, *B*, **29**, 384. <sup>3</sup> Blout and Eager, *J. Amer. Chem. Soc.*, 1945, **67**, 1315.

A slight distortion of the butadiene system involving rings *A* and *D* of the *cyclobutane* compounds from the planar configuration giving maximum resonance interaction must therefore be involved even when the configuration shown by Fig. 5 is adopted. Models show that if rings *A* and *D* are twisted slightly out of the plane of the butadiene system, rings *B* and *C* can then be so disposed that their *p*-positions are not opposite one another and hence space is provided for the large substituent in, for example, the *tert.*-butyl compound. It is clear that a molecule represented by Fig. 5 should exhibit optical activity and experiments to demonstrate this are in hand.

Attempts to prepare *cyclobutane* derivatives in which R = 9-anthryl, and in which the butadiene type of resonance would be expected to be destroyed still further, failed; this is possibly because of steric factors involved in their formation.

The interatomic distances used in the diagrams are taken from Pauling's "Nature of the Chemical Bond," p. 220, and the angles of the *cyclobutane* ring are assumed to be 90°.

#### EXPERIMENTAL

M.p.s are corrected.

*Apparatus.*—The spectra were measured on a Beckmann D.U. spectrophotometer; determinations were carried out in duplicate and the mean of the results is reported.

1 : 1 : 4 : 4-Tetraphenylbutane-1 : 4-diol.—This was prepared from diethyl succinate. It crystallises from chloroform in colourless needles, m. p. 206—207°. Dehydration by the method of Wittig and von Lupin (*Ber.*, 1928, **61**, 1627) gave 1 : 1 : 4 : 4-tetraphenylbuta-1 : 3-diene, m. p. 207—208° (Valeur, *Bull. Soc. chim.*, 1903, **29**, 683; *Compt. rend.*, 1903, **136**, 694).

*cyclobutane Derivatives.*—These were prepared from diethyl *trans-cyclobutane*-1 : 2-dicarboxylate by treatment with the appropriate Grignard reagent and dehydration of the resulting carbinols (Alberman and Kipping, *J.*, 1951, 781). It is interesting that in the case of the *p*-tolyl compound the hydrocarbon, and not the carbinol, was isolated directly from the product of interaction of the ester and the Grignard reagent.

1 : 2-Bisdiphenylmethylenecyclobutane. (See Alberman and Kipping, *loc. cit.*)

1 : 2-Bisdi-*p*-tolylmethylenecyclobutane. The ester (2 g.) in ether was added to a Grignard solution from *p*-bromotoluene (8.6 g.) and magnesium (1.2 g.). After decomposition with ice and ammonium chloride in the usual way and steam-distillation, the residue (a yellow glass) crystallised from alcohol as a fluorescent microcrystalline powder. Recrystallisation from alcohol-benzene gave fine yellow needles of the *diene*, m. p. 214° (3 g.) (Found: C, 92.3; H, 7.7. C<sub>34</sub>H<sub>32</sub> requires C, 92.7; H, 7.3%).

1 : 2-Bisdi-*p*-isopropylphenylmethylenecyclobutane. The carbinol from the ester (1 g.), *p*-bromocumene (5 g.) and magnesium (0.6 g.) formed colourless prisms from alcohol, m. p. 182—183° (decomp.). Dehydration yielded the *diolefin* as jagged plates (from alcohol-benzene), m. p. 148—149° (Found: C, 91.1; H, 8.5. C<sub>42</sub>H<sub>48</sub> requires C, 91.3; H, 8.7%).

1 : 2-Bisdi-*p*-*tert.*-butylphenylmethylenecyclobutane. The carbinol from the ester (1 g.), *p*-bromo-*tert.*-butylbenzene (5.3 g.) (Marvel, *J. Amer. Chem. Soc.*, 1939, **61**, 2771) and magnesium (0.6 g.) crystallised from alcohol-benzene as colourless needles, m. p. 252° (2.3 g.) (Found: C, 85.5; H, 9.4. C<sub>46</sub>H<sub>60</sub>O<sub>2</sub> requires C, 85.7; H, 9.3%). Dehydration yielded the *diolefin* as yellowish blades (from benzene), m. p. 283—284° (Found: C, 91.0; H, 9.4. C<sub>46</sub>H<sub>56</sub> requires C, 90.8; H, 9.2%).

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