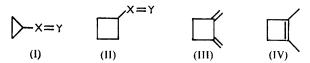
## **431**. The Auxochronic Effect of the cycloButane Ring. By J. J. WREN.

The ultraviolet spectra of three types of unsaturated cyclobutane compound reveal auxochromic effects attributable to the cyclobutane ring.

It has long been known 1 that the ultraviolet spectra of unsaturated cyclopropane compounds of the general type (I), when compared, for example, with those of corresponding isopropyl compounds, show bathochromic and hyperchromic effects due to the "unsaturated" character of the cyclopropane ring. A number of authors confirm or utilise this knowledge. 2,3,4 No study, however, appears to have been made of such effects



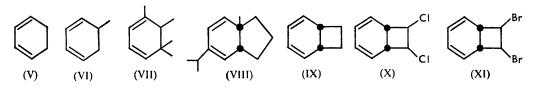
in the spectra of cyclobutane compounds. Robertson et al.4 showed that there are progressive bathochromic and hyperchromic displacements of B bands in the series, cyclohexyl-, cyclopentyl- and cyclopropyl-benzene (see Table 1), and attributed them to ring strain in the cyclopentyl and cyclopropyl compounds. Although cyclobutylbenzene was not included in their study, it can be inferred from their discussion that its spectrum should fit into this series between cyclopentyl- and cyclopropyl-benzene. In contrast, Mariella and

TABLE 1. Auxochromic effect of ring strain in cycloalkylbenzenes 4 (solvent: cyclohexane).

Compound	$\lambda_{\mathrm{max.}}$ (m $\mu$ )	ε	Compound	$\lambda_{\max}$ (m $\mu$ )	ε
isoPropylbenzene	259	197	cycloPropylbenzene	266.5	427
cycloHexylbenzene	<b>26</b> 0	202	Štyrene	282	802
cvcloPentylbenzene	262	251	•		

Raube 5 have shown that the position and intensity of the R bands for the lower cycloalkanones and cycloalkyl methyl ketones cannot be related to ring size. They went so far as to predict that cyclobutylbenzene would not fall into the scheme of Table 1, but it seems unreasonable to make such a prediction solely on the basis of the very weak ketone R bands.

Below is presented a study of five examples of the auxochromic effect of the cyclobutane ring in compounds of types (II), (III), and (IV).



(1) Roberts and Green <sup>3</sup> compared the ultraviolet spectra of various 2: 4-dinitrophenylhydrazones and demonstrated the effect of the cyclopropane ring on the spectrum of methyl cyclopropyl ketone dinitrophenylhydrazone. Our results for the cyclobutyl homologue are shown in Table 2. In order to standardise the  $\lambda_{max}$  and  $\varepsilon_{max}$  values with those of Roberts and Green, the spectrum of disopropyl ketone dinitrophenylhydrazone was also

Carr and Burt, J. Amer. Chem. Soc., 1918, 40, 1590.
 Klotz, ibid., 1944, 66, 88; Gillam and West, J., 1945, 95; Rogers, J. Amer. Chem. Soc., 1947, 69, 2544; Mariella, Peterson, and Ferris, ibid., 1948, 70, 1494; Sandoval, Rosenkranz, and Djerassi, ibid., 1951, 73, 2383; Smith and Rogier, ibid., p. 3840; Mariella and Raube, ibid., 1952, 74, 521.
 Roberts and Green, ibid., 1946, 68, 214.
 Robertson, Music, and Matsen, ibid., 1950, 72, 5260.
 Moriella and Paube, ibid., 1952, 74, 518.

<sup>&</sup>lt;sup>5</sup> Mariella and Raube, ibid., 1952, 74, 518.

examined. The values of  $\lambda_{max}$  for the two spectra were measured graphically and may be considered accurate within  $\pm 0.5$  m $\mu$ . The values in Table 2 show that the cyclobutane ring has a definite, though small, bathochromic effect (at least 1 mμ); the ε values are all similar, and do not appear to yield any useful conclusion.

(2) The bathochromic effect of alkyl substitution in the 5- and the 6-position of cyclohexa-1: 3-diene is normally small, as shown by comparison (Table 3) of the values of  $\lambda_{max}$ .

Table 2. Absorption maxima of 2: 4-dinitrophenylhydrazones in 95% ethanol.

Dinitrophenylhydrazone of	М. р.	Colour	$\lambda_{\text{max.}}$ $(m\mu)$	ε	Source
Acetone	125126·5°	Yellow	360	21,100	Ref. 3
cycloPentanone	144 - 145	,,	363	21,500	,,
Ďi <i>iso</i> propyl ketone	91 - 92	,,	363	22,000	,,
,,	92.5 - 93	Yellow-orange	363	23,100 *	Present work
cycloButyl methyl ketone	$129 - 129 \cdot 5$	Orange	364	22,300 †	**
Methyl <i>cyclo</i> propyl ketone	149 - 150	Orange-red	367	23,500	Ref. 3"
Mesityl oxide	198.5 - 199.5	Red	379	23,000	,,

\* Mean of two determinations.

† Mean of three determinations.

Table 3. Bathochromic effect of the cyclobutane ring in bicyclo[4:2:0] octa-2:4-dienes.

Compound	$\lambda_{\text{max.}}$ $(m\mu)$	ε	Solvent	Ref.	Compound	$\lambda_{\mathrm{max.}} (\mathrm{m}\mu)$	ε	Solvent	Ref.
(V)	256	8000	Hexane?	a	(IX)	<b>274</b>	3340	cycloHexane	$\boldsymbol{e}$
(VI)	<b>26</b> 0	4910	Ethanol	$\boldsymbol{b}$	$(\mathbf{X})$	270	<b>564</b> 0	,,	f
(VII)	263	<b>46</b> 00	Hexane?	С	(XI)	270	<b>364</b> 0	,,	f
(VIII)	258	4000	Ethanol	d	, ,				

a, Braude and Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, New York, 1955, p. 155. b, Booker, Evans, and Gillam, J., 1940, 1453. c, Fisher, Goldblatt, Kniel, and Snyder, Ind. Eng. Chem., 1951, 43, 671. d, Conroy, J. Amer. Chem. Soc., 1952, 74, 491, 3046. e, Cope, Haven, Ramp, and Trumbull, ibid., p. 4867. f, Cope and Burg, ibid., p. 168.

published for this compound (V), for 5-methylcyclohexa-1: 3-diene (VI), for α-pyronene (VII), and for picrotoxadiene (VIII). However, the values reported by Cope et al. for the compounds, (IX), (X), and (XI) show bathochromic effects of 10 mu or more, which must be attributed to the cyclobutane rings of these compounds.

(3) The spectrum of cyclobutene-1: 2-dicarboxylic acid (XII) in water is notable in having a well-defined maximum at 235 mu (\$\pi\$ 10,600), whereas the longest-wavelength maximum for maleic acid is reported at 210 mμ (ε 32,000).6 The bathochromic displacement of 25 mu is 2.5 times what would be expected if the two methylene groups of the cyclobutene ring in (XII) were spectroscopically equivalent to two alkyl groups. Similarly, the spectrum of the dimethyl ester of the acid (XII) in methanol shows a maximum at 232 m $\mu$  ( $\varepsilon$  8700): this may be compared with the values,  $\lambda_{max}$ , 194 m $\mu$  ( $\varepsilon$  22,000), and  $\lambda_{max}$ 198 mμ (ε 26,000), reported respectively for hexane solutions of the dimethyl and di-(-)menthyl esters of maleic acid.6 More recent measurements of the spectra of diethyl

$$CO_2H$$
 $CO_2H$ 
 $CO_2$ 

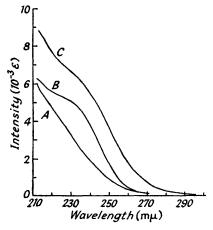
maleate and diethyl citraconate in 95% ethanol 7 show that they have no maxima above 210 mu. This agrees with the earlier data, and shows that alkyl substitution on the

ethylenic carbon atoms gives no "abnormal" bathochromic shifts.

Comparison of the spectra of the acid (XII) and a homologue, or of simple derivatives, is suggested. cycloHexene-1: 2-dicarboxylic anhydride (XIII) was prepared in low yield

Wassermann and Smakula, Z. phys. Chem., 1931, A, 155, 366.
 Stafford, Shay, and Francel, Analyt. Chem., 1954, 26, 656.

by Baeyer's method.<sup>8</sup> It is, however, much more stable to hydrolysis than maleic anhydride and can be recrystallised from water; the acid itself has been described, 8,9 but loses water very readily, and there would thus be ambiguity in the interpretation of its spectrum. On the other hand, esterification of the anhydride might cause migration of the double bond, so that the diester obtained might be of doubtful purity. Several attempts to prepare an anhydride from cyclobutene-1: 2-dicarboxylic acid (XII) failed to give a crystalline product: this accorded with Perkin's observations, 10 and ruled out comparison of the spectra of the anhydrides. [The difference in ease of anhydride formation in the two cases is very striking, and may be attributed to ring strain which would exist in the anhydride of (XII).] There remained the possibility of comparing the spectra of the anions of the acids, in aqueous alkali, and the Figure shows these curves. Although curve C shows no maximum above 213 mu, the level of absorption is much higher than for curve B, and this can only be due to the effect of the cyclobutane ring.



Ultraviolet spectra of the ions of (A) maleic acid, (B) cyclohex-1-ene-1:2-dicarboxylic acid ( $\lambda_{\text{infl.}}$  225 m $\mu$ ;  $\epsilon$  5300), and (C) cyclobut-1-ene-1:2-dicarboxylic acid ( $\lambda_{\text{infl.}}$  228 m $\mu$ ; ε 6700); solvent, 0·1N-aqueous sodium hydroxide.

(4) Several 1: 2-dimethylenecycloalkanes have recently been synthesised, and these are listed in Table 4, with their ultraviolet absorption data, and those for buta-1: 3-diene and 2: 3-dimethylbuta-1: 3-diene for comparison.

TABLE 4. Ultraviolet absorption data for 1: 2-dimethylenecycloalkanes and analogues.

Compound	$\lambda_{\mathrm{max}}$ (m $\mu$ )	ε	Solvent	Ref.
Buta-1: 3-diene	217	20,900	Hexane	h
2:3-Dimethylbuta-1:3-diene (XIV)	<b>226</b>	21,400	Hexane	i
,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,, ,,	<b>226</b>	21,300	Methyl <i>cyclo</i> hexane	j
1: 2-Dimethylenecyclohexane (XV)	<b>220</b>	10,050	Hexane or cyclohexane?	k
4-Methyl-1: 2-dimethylenecyclohexane	Just below 220	_	,, ,,	l
4:5-Dimethyl-1:2-dimethylenecyclohexane	,,		,, ,,	m
1: 2-Dimethylenecyclopentane (XVI)	,,		,, ,,	n
1: 2-Dimethylenecyclobutane (XVII)	246	10,230	,, ,,	0
	<b>237</b>	9,770		
	(255 *	6.460)		

h, Smakula, Angew. Chem., 1934, 47, 657. i, Scheibe, Ber., 1926, 59, 1333. j, Scheibe and Pummerer, ibid., 1927, 60, 2163. k, Bailey and Golden, J. Amer. Chem. Soc., 1953, 75, 4780. l, Bailey, Rosenberg, and Young, ibid., 1954, 76, 2251. m, Bailey and Sorenson, ibid., p. 5421. n, Blomquist and Verdol, ibid., 1955, 77, 1806.

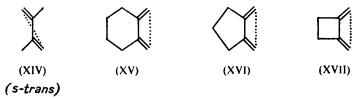
On the basis of Woodward's rules,  $^{11}$   $\lambda_{max}$  for 1:2-dimethylene cyclohexane (XV) might be expected at ca. 10 m $\mu$  nearer the red than  $\lambda_{max}$  for 2:3-dimethylbuta-1:3-diene (XIV) since both double bonds of the former are exocyclic. However, the observed value for

<sup>&</sup>lt;sup>8</sup> Baeyer, Annalen, 1890, 258, 145.

Alder and Backendorf, Ber., 1938, 71, 2199; Alder and Schumacher, Annalen, 1949, 564, 96.

<sup>&</sup>lt;sup>10</sup> Perkin, J., 1894, 950. <sup>11</sup> Woodward, J. Amer. Chem. Soc., 1942, 64, 72.

 $\lambda_{max}$  is at 16 m $\mu$  shorter wavelength than that calculated, and the value of  $\varepsilon$  is roughly one half that for the butadiene (XIV). This difference closely resembles that well known between cis- and trans-isomers. The latter is attributable to the greater length of the resonating system in the trans-configuration, and agrees with Mulliken's theoretical deductions. 12 In the 1:2-dimethylenecycloalkanes, the diene systems cannot assume trans-configurations. The spectral data in Table 4 for 1:2-dimethylenecyclohexane, its 4-methyl and 4:5-dimethyl derivatives, and 1:2-dimethylenecyclopentane (XVI) are readily explained in this way.



(Dotted lines represent the overall lengths of the resonating systems.)

Molecular models show that there is little or no ring strain in compounds (XV) and (XVI), but, of course, compound (XVII) is even more strained than cyclobutane itself. This strain must account for the bathochromic shift of ca. 27 mu which its spectrum shows compared with those of the other 1: 2-dimethylenecycloalkanes listed in Table 4.

(5) Earlier, in this laboratory, the spectrum of 1: 2-bisdiphenylmethylenecyclobutane (XVIII) was studied. 13 Its maximum at longest wavelength shows a bathochromic shift of 8 m $\mu$  compared with that of 1:1:4:4-tetraphenylbuta-1:3-diene (XIX), and this was then attributed to the spectroscopic equivalence of the contribution of the cyclobutane ring to that of two alkyl groups. However, the structural change involved is analogous to the change from buta-1:3-diene to 1:2-dimethylenecyclobutane (XVII), which causes a bathochromic shift of approximately 30 mμ and a reduction of εmax, by half. (As explained above, this spectral change is mainly due to the characteristic effect of the cyclobutane ring system.) The relatively small bathochromic shift (8 mμ) associated with the change from (XIX) to (XVIII) is explained by increased steric interaction of the phenyl groups in the latter compound, resulting in a hypsochromic contribution.

The effect of the strained cyclobutane system in all examples may be attributed to the increased delocalisation of the  $sp^3$  electrons.

## EXPERIMENTAL

M. p.s are corrected. Ultraviolet spectra were measured on Unicam SP 500 spectrophotometers.

Diisopropyl Ketone 2:4-Dinitrophenylhydrazone.—This was obtained as yellow-orange rectangular plates, m. p. 92.5-93°, after two recrystallisations from 95% ethanol.

cycloButyl Methyl Ketone 2: 4-Dinitrophenylhydrazone.—A specimen of m. p. 121-121.5° (prepared by Dr. K. B. Alberman) was recrystallised once from light petroleum (b. p. 60—70°) and twice from 95% ethanol; this gave orange plates, m. p. 129-129.5° unchanged by further recrystallisation (Found: C, 51.6; H, 4.9; N, 20.3. C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>N<sub>4</sub> requires C, 51.8; H, 5.1; N, 20.1%). Earlier preparations of this compound were probably impure, since m. p.s 119.9— 121.3° (uncorr.5), and 123.9—126.9° (corr.14) were reported for it. Its infrared spectrum bore close resemblances to that of disopropyl ketone dinitrophenylhydrazone.

Dimethyl cycloButene-1: 2-dicarboxylate.—This was prepared from cis-cyclobutane-1: 2-dicarboxylic anhydride by Perkin's method.<sup>10</sup> Hydrolysis yielded the acid (XII) as rods, m. p. 178—178.5°, after recrystallisation, first from dioxan, then from water.

cycloHexene-1: 2-dicarboxylic Anhydride (XIII).—Phthalic anhydride was reduced with

<sup>&</sup>lt;sup>12</sup> Mulliken, J. Chem. Phys., 1939, 7, 364.

<sup>Alberman, Haszeldine, and Kipping, J., 1952, 3284.
Overberger and Lebovits, J. Amer. Chem. Soc., 1954, 76, 2722.</sup> 

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sodium amalgam according to Baeyer's method, to give cyclohexene-2: 3-dicarboxylic acid, m. p. 214—215°. At 220—230° this gave the anhydride, (XIII), which was recrystallised from water, distilled, then recrystallised from light petroleum (b. p. 40—50°) in ca. 2% overall yield (m. p. 71·5—72°; lit., 9 74°).

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