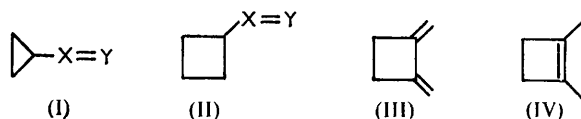


431. The Auxochromic Effect of the cycloButane Ring.

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 known¹ 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



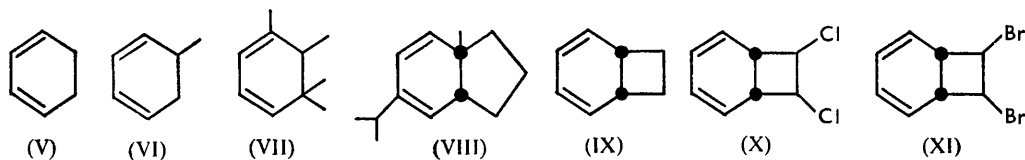
in the spectra of *cyclobutane* compounds. Robertson *et al.*⁴ showed that there are progressive bathochromic and hyperchromic displacements of *B* bands in the series, *cyclohexyl-*, *cyclopentyl-* and *cyclopropyl-benzene* (see Table I), and attributed them to ring strain in the *cyclopentyl* and *cyclopropyl* 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 I. Auxochromic effect of ring strain in cycloalkylbenzenes⁴ (solvent: cyclohexane).

Compound	$\lambda_{\max.}$ (m μ)	ϵ	Compound	$\lambda_{\max.}$ (m μ)	ϵ
<i>iso</i> Propylbenzene	259	197	<i>cyclo</i> Propylbenzene	266.5	427
<i>cyclo</i> Hexylbenzene	260	202	Styrene	282	802
<i>cyclo</i> Pentylbenzene	262	251			

Raube⁵ 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 I, 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 Green³ 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 $\epsilon_{\max.}$ values with those of Roberts and Green, the spectrum of *diisopropyl* ketone dinitrophenylhydrazone was also

¹ Carr and Burt, *J. Amer. Chem. Soc.*, 1918, **40**, 1590.

² 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.

³ Roberts and Green, *ibid.*, 1946, **68**, 214.

⁴ Robertson, Music, and Matsen, *ibid.*, 1950, **72**, 5260.

⁵ Mariella and Raube, *ibid.*, 1952, **74**, 518.

examined. The values of λ_{\max} , for the two spectra were measured graphically and may be considered accurate within $\pm 0.5 \mu\mu$. The values in Table 2 show that the *cyclobutane* ring has a definite, though small, bathochromic effect (at least $1 \mu\mu$); 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 λ_{\max} .

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

Dinitrophenylhydrazone of	M. p.	Colour	λ_{\max} , ($\mu\mu$)	ϵ	Source
Acetone	125—126.5°	Yellow	360	21,100	Ref. 3
<i>cyclo</i> Pentanone	144—145	"	363	21,500	"
Diisopropyl ketone	91—92	"	363	22,000	"
"	92.5—93	Yellow-orange	363	23,100 *	Present work
<i>cyclo</i> Butyl methyl ketone ...	129—129.5	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.

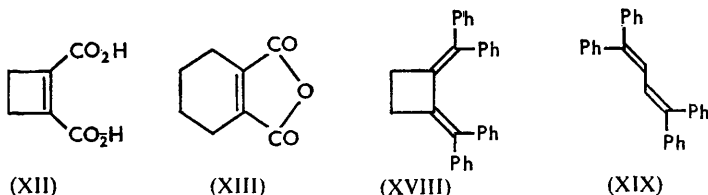
TABLE 3. Bathochromic effect of the cyclobutane ring in bicyclo[4 : 2 : 0]octa-2 : 4-dienes.

Compound	λ_{\max} , ($\mu\mu$)	ϵ	Solvent	Ref.	Compound	λ_{\max} , ($\mu\mu$)	ϵ	Solvent	Ref.
(V)	256	8000	Hexane?	a	(IX)	274	3340	<i>cyclo</i> Hexane	e
(VI)	260	4910	Ethanol	b	(X)	270	5640	"	f
(VII)	263	4600	Hexane?	c	(XI)	270	3640	"	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-methyl*cyclohexa-1 : 3-diene* (VI), for α -pyrone (VII), and for picrotoxadiene (VIII). However, the values reported by Cope *et al.* for the compounds, (IX), (X), and (XI) show bathochromic effects of $10 \mu\mu$ 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 $235 \mu\mu$ (ϵ 10,600), whereas the longest-wavelength maximum for maleic acid is reported at $210 \mu\mu$ (ϵ 32,000).⁶ The bathochromic displacement of $25 \mu\mu$ 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 $232 \mu\mu$ (ϵ 8700) : this may be compared with the values, λ_{\max} , $194 \mu\mu$ (ϵ 22,000), and λ_{\max} , $198 \mu\mu$ (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

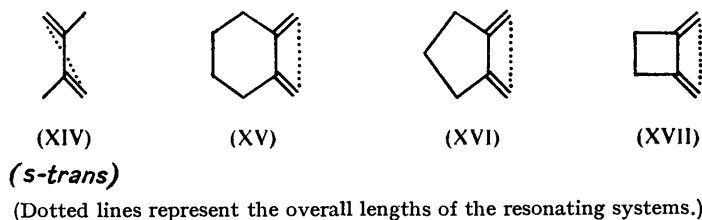


maleate and diethyl citraconate in 95% ethanol⁷ show that they have no maxima above $210 \mu\mu$. This agrees with the earlier data, and shows that alkyl substitution on the ethylenic carbon atoms gives no "abnormal" bathochromic shifts.

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

⁶ Wassermann and Smakula, *Z. phys. Chem.*, 1931, **A**, **155**, 366.⁷ Stafford, Shay, and Francel, *Analyt. Chem.*, 1954, **26**, 656.

λ_{\max} , is at 16 $m\mu$ shorter wavelength than that calculated, and the value of ϵ 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.



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 $m\mu$ 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 $m\mu$ and a reduction of ϵ_{\max} , 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 $m\mu$) 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. $C_{12}H_{14}O_4N_4$ 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 diisopropyl ketone dinitrophenylhydrazone.

Dimethyl cycloButene-1:2-dicarboxylate.—This was prepared from *cis-cyclobutane-1:2-dicarboxylic anhydride* by Perkin's method.¹⁰ 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

¹² Mulliken, *J. Chem. Phys.*, 1939, 7, 364.

¹³ Alberman, Haszeldine, and Kipping, *J.*, 1952, 3284.

¹⁴ Overberger and Lebovits, *J. Amer. Chem. Soc.*, 1954, 76, 2722.

sodium amalgam according to Baeyer's method,⁸ 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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