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PHOTOELECTRON SPECTRA OF ORGANIC COMPOUNDS—VI

EXOCYCLIC METHYLENE COMPOUNDS[a]

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Abstract—The photoelectron spectra of methylene and dimethylene derivatives of bridged and unbridged cyclohexane and cyclohexene were recorded and interpreted on the basis of an LCBO model. The conjugative interaction is found to be appreciably smaller for exocyclic *cis*-dienes than for the corresponding endocyclic *cis*-dienes, whereas the homoconjugative interaction between exocyclic and endocyclic double bonds and between two endocyclic double bonds is about the same.

Olefins containing a double bond exocyclic to an alicyclic ring may differ in their physical and chemical properties considerably from their endocyclic counterparts. Thus, the relative instability of methylenecyclopentane and methylenecyclohexane with respect to their endocyclic isomers, which has been illustrated by comparison of their heats of hydrogenation,[1] as well as the difference in their C=C stretching frequencies as given in Table 1, may be attributed to angle-bending strain.

Although ionization potentials decrease with increasing ring size both for exocyclic and endocyclic double bonds, indicating for both series of compounds a π orbital destabilization by the inductive effect of the alkyl group[2] which increases with increasing ring size, the different stability of the endocyclic and exocyclic π orbital in small ring compounds is fairly well documented by the data of Table 1.

Similarly, exocyclic 1,2-dimethylene systems may differ in their properties from their endocyclic counterparts, as may be seen e.g. from the reactivity of *o*-quinodimethane[3] or from a comparison of the UV spectra of cyclohexadiene and dimethylenecyclohexane.[4]

We therefore studied the photoelectron spectra (PE) of methylene and 1,2-dimethylene derivatives of cyclohexane and cyclohexene, norbornane and norbornene and those of bicyclo[2.2.2]octane and bicyclo[2.2.2]octene in order to get more information about the electronic structure of exocyclic double bonds.

In particular, we are concerned with the following problems:

(a) The determination of the π interaction within an exocyclic diene system as compared with that of an endocyclic *cis* diene.

(b) The homoconjugative interaction between an exocyclic and an endocyclic double bond.

(c) The homoconjugative interaction between an exocyclic diene system and an endocyclic double bond.

RESULTS AND DISCUSSION

The vertical ionization potentials I_v as determined from the PE spectra may be equated with negative orbital energies within the framework of Koopmans' theorem.[5] Experimental I_v values for all compounds studied are collected in Table 2, whereas Figs 1–3 give correlation diagrams for π and σ levels of the derivatives of cyclohexane, norbornane and bicyclo[2.2.2]octane respectively.

Assignment of PE bands. From the data in Table 2 and Figs 1–3, the assignmment of the PE bands to ionizations from π and σ orbitals is fairly obvious: as was shown by Heilbronner *et al.*[6,15] double bonds cause a shift of the first σ bands in the PE spectra of hydrocarbons towards higher ionization potentials, this shift being to a first approximation proportional to the number of π bonds in the system. Thus, for all compounds considered the orbital sequence must be such that all π levels lie above the σ levels. For the cyclohexane and bicyclo[2.2.2]octane system, this σ stabilization is 0·30–0·35 eV per exocyclic or endocyclic double bond; only for 2,3 - dimethylenebicyclo[2.2.2]octane **17**, the σ stabilization is 0·1 eV larger than for 5 - methylenebicyclo[2.2.2]octene **16**. For the norbornane system on the other hand, there is a great difference between the σ stabilization due to an endocyclic double bond, which in this case amounts to 0·38–0·62 eV, and the other one to

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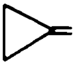
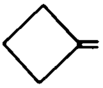
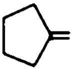
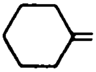
[*] For Part V see Ref 9.

Table 1. CC stretching frequencies and vertical π ionization potentials of small ring compounds with endocyclic or exocyclic double bonds

	ν_{CC}[cm^{-1}]^a	I(π)[eV]^b		ν_{CC}[cm^{-1}]^a	I(π)[eV]^c
	1525	9·86		1780	9·5
	1566	9·43		1678	9·19
	1614	9·18		1657	9·15
	1649	9·12		1651	—

[a] Ra-frequencies from B. Schrader, *Angew. Chem.* Internat Ed. 12, 884 (1973).

[b] PE values from P. Bischof and E. Heilbronner, *Helv. Chim. Acta* 53, 1677 (1970).

[c] PE values from D. W. Turner, C. Baker, A. D. Baker and C. R. Brundle, *Molecular Photoelectron Spectroscopy*, Wiley, Interscience, London (1970).

Table 2. Vertical ionization potentials of exocyclic methylene compounds and reference systems (all values in eV, vibrational fine structure in cm^{-1} in brackets)

		$I_1(\pi)$	$I_2(\pi)$	$I_3(\pi)$	$I(\sigma)$
Cyclohexane	1	—	—	—	10·32^a
Cyclohexene	2	9·11(1370)	—	—	10·67
Methylenecyclohexane	3	9·13(1370)	—	—	10·64
4-Methylenecyclohexene	4	9·27(1370)	9·49	—	11·0
1,2-Dimethylene-cyclohexane	5	8·92	9·85	—	10·98
4,5-Dimethylene-cyclohexene	6	9·00	9·21	10·13	11·28
Norbornane	7	—	—	—	10·17^a
Norbornene	8	8·97	—	—	10·55^a
2-Methylenenorbornane	9	9·04(1330)	—	—	10·56
5-Methylenenorbornene	10	9·01	9·38	—	11·18
2,3-Dimethylene-norbornane	11	8·41(1435)	10·20(1230)	—	10·70
5,6-Dimethylene-norbornene	12	8·48(1470)	9·02	10·35	11·29
Bicyclo[2.2.2]octane	13	—	—	—	9·71^a
Bicyclo[2.2.2]octene	14	9·07(1250)	—	—	10·04
2-Methylenebicyclo [2.2.2]octane	15	8·87(1300)	—	—	10·06
5-Methylenebicyclo [2.2.2]octene	16	8·97(1250)	9·34	—	10·43
2,3-Dimethylenebicyclo [2.2.2]octane	17	8·37(1420)	10·14(1210)	—	10·53
5,6-Dimethylenebicyclo [2.2.2]octene	18	8·33(1445)	9·06	10·38	10·71

[a] Values taken from P. Bischof, J. A. Hashmall, E. Heilbronner and V. Hornung, *Helv. Chim. Acta* 52, 1745 (1969); values for cyclohexene and bicyclooctene given by these authors are 9·12; 10·66 eV and 9·05; 10·03 eV respectively.

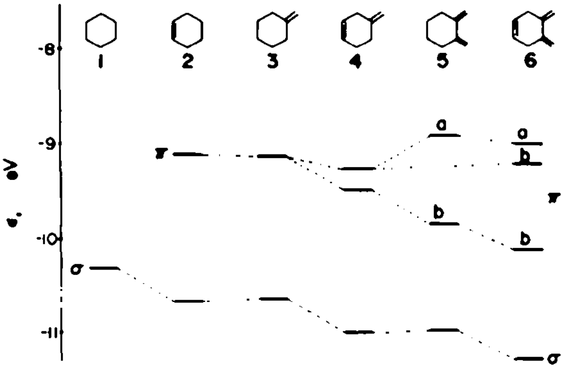


Fig 1. Correlation diagram for π and σ levels of methylene derivatives of cyclohexane and cyclohexene.

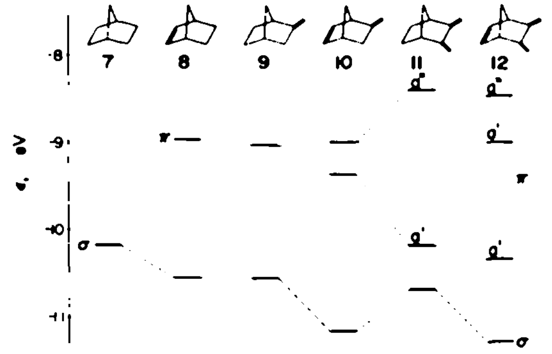


Fig 2. Correlation diagram for π and σ levels of methylene derivatives of norbornane and norbornene.

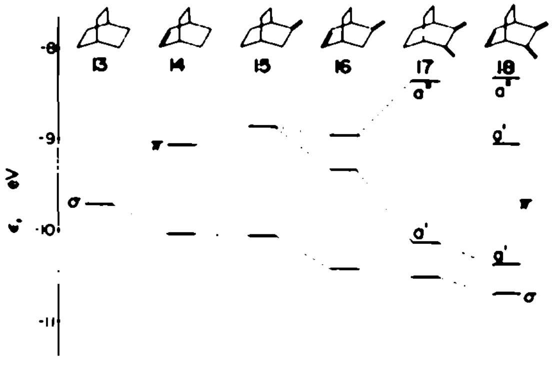


Fig 3. Correlation diagram for π and σ levels of methylene derivatives of bicyclo[2.2.2]octane and bicyclo[2.2.2]octene.

exocyclic double bonds, being of the order of 0·14–0·39 eV.

This difference can be rationalized in terms of the 2s-character of the σ-frame, the highest occupied MO of the boat cyclohexane structural part of the molecule being the "ribbon orbital"[7] of a_2 symmetry: ring strain in the norbornane system should have the effect of decreasing the C═C—C angle of an endocyclic double bond, thus increasing the 2s-character of the CC σ bond adjacent to the double bond, i.e. increasing the 2s-character of the σ-frame. The opposite holds for the exocyclic double bonds. The lacking sensitivity of the cyclohexane and bicyclooctane system towards these effects demonstrates fairly well the negligible angular strain the these compounds.

The assignment of the first PE bands to ionizations from π orbitals is confirmed by the vibrational fine structure, as may be seen from Table 2. All monoenes show a vibrational spacing of approximately 1370–1250 cm^{-1}, which can be attributed to the C═C stretching mode of the ion.[8] For the exocyclic dienes two different vibrational spacings of approximately 1450 cm^{-1} and 1225 cm^{-1} are observed for the first two PE bands, corresponding to the antisymmetric and the symmetric C═C stretching mode. In the trienes, only the first bands shows a fine structure, the spacing being again 1450 cm^{-1}.

Basis orbitals and their interaction. Methylenecyclohexene **4** and the corresponding norbornane and bicyclooctane derivatives **10** and **16** show two π ionization potentials separated by 0·22–0·37 eV, thus indicating only a small homoconjugative interaction between exocyclic and endocyclic double bonds.

The two π ionization potentials for the diexomethylene compounds are separated by 0·9 eV for the cyclohexane derivative **5** and 1·8 eV for the bridged species **11** and **17**; this difference in π interaction between **5** and the corresponding bridged compounds may be attributed to the fact that the *cis*-diene system is expected to be non-planar in the chair cyclohexane structure of **5**, but more or less coplanar in the boat cyclohexane structure of **11** and **17**. The trienes **6**, **12** and **18** finally, show three ionizations potentials at nearly the same values as were observed for the corresponding exocyclic and endocyclic double bonds (*cf* Figs 1–3).

In order to get quantitative data for the interaction between the different kinds of double bonds we apply a linear combination of bonding orbital (LCBO) approach[9] within the frame of the HMO approximation. We start by assigning basis orbital energies E_p to the different kinds of π orbitals, which, of course, can not be done unequivocally. In general, E_p values differ only slightly from the E_p° values belonging to the π orbital of the corresponding monoenes, i.e. $E_p = E_p^\circ + \delta_p$, with $\delta_p = -0{\cdot}35$ eV for conjugated and $\delta_p = -0{\cdot}17$ eV for homoconjugated double bonds, as determined by Heilbronner *et al.*[10] from the PE spectra of monocyclic polyenes.

On the assumption that the basis π orbitals of both double bonds of a diene system are perturbed to the same extent, the corresponding δ can be evaluated according to Heilbronner[11] from

$$\delta = -\frac{1}{2}\sum_{j=1,2}(I_j' - I_j^\circ). \qquad (1)$$

where the I_i° are the observed π ionization potentials of the appropriate monoene and the I_i' are those of the diene. Values for δ and E obtained in this way from the monomethylene alkenes **4**, **10** and **16** are given in Table 3 for p = *endo*. The corresponding interaction term $H_{exo,endo}$ was obtained from the experimental ionization potentials by means of the relation

$$\Delta I = I_2 - I_1 = \sqrt{(E_p - E_q)^2 + 4H_{pq}^2}. \qquad (2)$$

The values for E_{exo} and $H_{exo,exo}$ were determined similarly from the data of the diexomethylene compounds **5**, **11** and **17** (*cf* Table 3).

Using these parameters, the ionization potentials of the trienes **6**, **12** and **18** were calculated by solving for each case the 3 × 3 secular problem. The results are given in Table 3 together with the experimental values. As is seen, the agreement is such that we expect the values for the interaction terms H_{pq}, determined by the procedure described above, to be rather reliable. If we expand the bond orbitals ϕ_p in terms of atomic orbitals φ_μ, we can express H_{pq} in terms of the LCAO coefficients and the resonance integral $\beta_{\mu\nu}$. As all coefficients equal $\pm 1/\sqrt{2}$, we find for the homoconjugative interaction between exocyclic and endocyclic double bonds $\beta_{\mu\nu} = -0{\cdot}22$ eV in the case of the cyclohexene derivatives and $\beta_{\mu\nu} = -0{\cdot}36$ eV and $\beta_{\mu\nu} = -0{\cdot}31$ eV for the norbornene and the bicyclooctene system. The differences may be correlated with the distances between the homoconjugated π centers. Similarly, for the conjugative interaction within the exocyclic diene system, we find $\beta_{\mu\nu} = -0{\cdot}93$ eV, $\beta_{\mu\nu} = -1{\cdot}80$ eV and $\beta_{\mu\nu} = -1{\cdot}77$ eV for the three series of compounds. The low value for the cyclohexane series is consistent with the assumption of the chair conformation[12] with non-coplanar exomethylene gruops; also, the greater flexibility of the bicyclooctane system, as compared with that of norbornane is reflected in the observed values.

Assuming an angle ϑ for the twisted diene systems, the resonance integral is given by

$$\beta_{\mu\nu} = \beta^0_{\mu\nu} \cos\vartheta; \qquad (3)$$

taking the dimethylenenorbornane value as $\beta^0_{\mu\nu} = -1{\cdot}80$ eV we find ϑ values of approximately 60° and 10° for dimethylenecyclohexane and dimethylenebicyclooctane respectively, in very good agreement with expectations from Dreiding models.

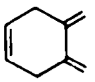
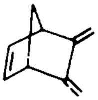
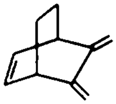
Introducing another double bond reduces the σ-frame-flexibility of compound **5** as well as that of compound **17**, thus reducing the deviation from coplanarity of the exocyclic diene system. This effect is demonstrated fairly well by the PE spectra of the trienes, which show that for **6** and **18** the splitting $I_3(\pi)$–$I_1(\pi)$ is appreciably larger than the splitting $I_2(\pi)$–$I_1(\pi)$ for the dienes **5** and **17**, whereas for **11** and **12** both splittings are of comparable size.

Orbital assignment. From the work of Heilbronner *et al.*[11] it is known that in the case of the symmetrical bicyclo[2.2.n]dienes, the effect of "through bond"-interaction[13] increases with increasing n such that for large n an unusual ordering of π levels is found, with the antisymmetric combination (b_2 in C_{2v}) below the symmetric one (a_1 in C_{2v}), whereas for n = 1 and n = 2, the natural order with the a_1 below the b_2 orbital is observed. Therefore we may ask, whether similar through bond interactions are to be expected for the dimethylene alkenes studied in the present paper. The answer should be no for the following reasons:

(a) Dimethylenecyclohexene is likely to exist in a chair conformation being less suited for through bond interaction than the fairly planar conformation of 1,4-cyclohexadiene.

(b) The reduced symmetry in dimethylenealkenes as compared with the corresponding dienes has the effect that CH orbitals of suitable symmetry

Table 3. Basis orbital energies $E_p = E_p^\circ + \delta_p$, interaction energies H_{pq} as well as calculated and experimental π-ionization potentials all in eV

Compound		LCBO parameters δ_p	E_p	$H_{exo,p}$		Ionization potentials $I_1(\pi)$	$I_2(\pi)$	$I_3(\pi)$
	p = *endo* p = *exo*	−0·26 −0·25,	−9·37 −9·38,	−0·11 · 0·46,	calc: exp:	8·92 9·02	9·32 9·21	9·90 10·13
	p = *endo* p = *exo*	−0·19 −0·26,	−9·16 −9·30,	−0·18 −0·90	calc: exp:	8·41 8·48	9·10 9·02	10·26 10·35
	p = *endo* p = *exo*	−0·18, −0·38,	−9·25, −9·25,	−0·15, −0·88,	calc: exp:	8·37 8·33	9·20 9·06	10·19 10·38

can interact with all three π orbitals, thus making an inversion of the orbital sequence rather unlikely.

(c) Considering the π system of the dimethylenecycloalkenes as being composed of the π systems of ethylene and butadiene as in Fig 4, we see that the principal effect of a through bond interaction would be to destabilize the π MO of lowest energy, thus reducing the splittings $I_3(\pi)$–$I_1(\pi)$ and $I_3(\pi)$–$I_2(\pi)$; this effect is clearly not observed in the PE spectra.

We therefore conclude that for all three trienes **6**, **12** and **18**, the sequence of the π orbitals is such that the highest π ionization potential corresponds closely to the symmetric π orbital of the exocyclic diene system, the next one to the endocyclic double bond (both a′ in C_s), and the first ionization potential corresponds to the antisymmetric diene orbital (a″ in C_s), as is confirmed by the vibrational frequency $\nu \approx 1450\,\mathrm{cm}^{-1}$ of the first PE band, which may be attributed to the antisymmetric C=C stretching of the diene system.

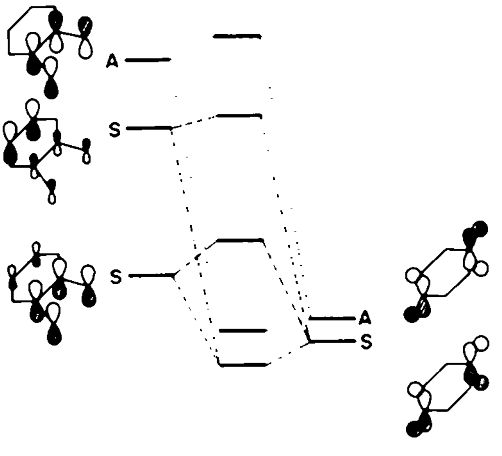


Fig 4. Orbital interaction in dimethylene cycloalkenes.

CONCLUSIONS

From the spectra of 1,3-cycloalkadienes,[2] values of $\beta_{\mu\nu} = -2{\cdot}16$ to $-2{\cdot}5$ eV were found by Heilbronner *et al.* for the resonance integral, showing that as long as the π system is coplanar, the interaction between two ethylene π bonds is about the same for endocyclic *cis*-dienes as for *trans*-butadiene, where $\beta_{\mu\nu} = -2{\cdot}5$ eV.[14] In contrast to these results, we found in the present investigation that the corresponding interaction in exocyclic dimethylene compounds is considerably smaller, being described appropriately by $\beta_{\mu\nu} = -1{\cdot}8$ eV. The double bonds of exocyclic dienes thus appear to be appreciably more localized than their endocyclic counterparts, which might be due mainly to angular distortions caused by steric interactions among the methylene hydrogens of the exocyclic double bonds.

Similarly, the homoconjugative interactions in exocyclic methylene- and dimethylenealkenes are found to be small. The values $\beta_{\mu\nu} = -0{\cdot}22$ eV for the cyclohexene derivatives, and $\beta_{\mu\nu} = -0{\cdot}36$ eV and $\beta_{\mu\nu} = -0{\cdot}31$ eV for the norbornene and bicyclooctene derivatives determined in this work, should be compared with $\beta_{\mu\nu} = -0{\cdot}5$ eV for 1,4-cyclohexadiene, $\beta_{\mu\nu} = -0{\cdot}48$ eV for norbornadiene and $\beta_{\mu\nu} = -0{\cdot}29$ eV for bicyclooctadiene;[15] the agreement for the norbornane and bicyclooctane derivatives is very good, whereas for the methylenecyclohexenes, the numerically low value $\beta_{\mu\nu} = -0{\cdot}22$ eV may be explained again by the deviation from coplanarity of the π system.

The fact that in spite of these $\beta_{\mu\nu}$ values, the effect of homoconjugation on the orbital energies of the trienes is almost negligible, is easily understood from the orbital diagram in Fig 4: by reason of symmetry, only the lower π MO of the diene can interact with ethylenic π MO, and these two orbitals are separated by more than 1 eV.

These PE results are very nicely confirmed by the UV spectra of the 1,2-dimethylenalkanes and -alkenes as shown in Fig 5: the non-coplanarity of the π system of the cyclohexane derivatives **5** and **6** is demonstrated by the value $\lambda_{max} = 216$ nm, whereas the negligible homoconjugative interaction between the exocyclic diene and endocyclic ethylene π system in the trienes **6**, **12** and **18** is apparent from the fact that there is no bathochromic shift nor an appreciable intensity change going from the exocyclic dienes to the trienes. Indeed, the dimethylenenorbornene **12** has its λ_{max} at slightly shorter wavelengths than the diene **11**, thus showing the increased strain of this system.

EXPERIMENTAL

The PE spectra were recorded on a modified PS 16 PE spectrometer of Perkin-Elmer Ltd. (Beaconsfield, England). The spectra were calibrated with an Ar/Xe mixture as internal standard.

The UV spectra were recorded at 24°C on a Cary 12 UV spectrometer, using n-hexane solns of approximately 5×10^{-3} mole/l.

All compounds studied were purified by gas chromatography through a 10′ × ¼″ column packed with silicone gum rubber SE–30 on 45/60 A/W DMCS Chromosorb P (Varian Aerograph Co.), using a N_2 flow rate of 32 ml/min.

The dimethylene compounds **5**, **6**, **11** and **17** were prepared by ester pyrolysis as reported by Bailey *et al.*[16]

4-*Methylenecyclohexene* **4** was obtained similarly by pyrolysis of the acetate of 3-cyclohexene-1-carbinol at 450° in a combustion tube described by Bailey and Rosenberg:[16] 30 g of the acetate gave 9·3 g of 4-methylenecyclohexene, b.p. 58°/100 mm (lit.[17] b.p. 58°/110 mm). The product was identified by comparison of the IR- and NMR spectra with published data.[17]

2-*Methylenebicyclo*[2.2.1]*heptane* **9** was prepared by pyrolysis from the acetate of *endo*-2-bicyclo[2.2.1]heptylcarbinol according to Belikova *et al.*:[18] b.p. 123°/760 mm (lit.[18] b.p. 123°/750 mm); IR: 3070(m), 2940(s), 2870(s), 1665(m), 1450(m), 1430(m), 1300(m),

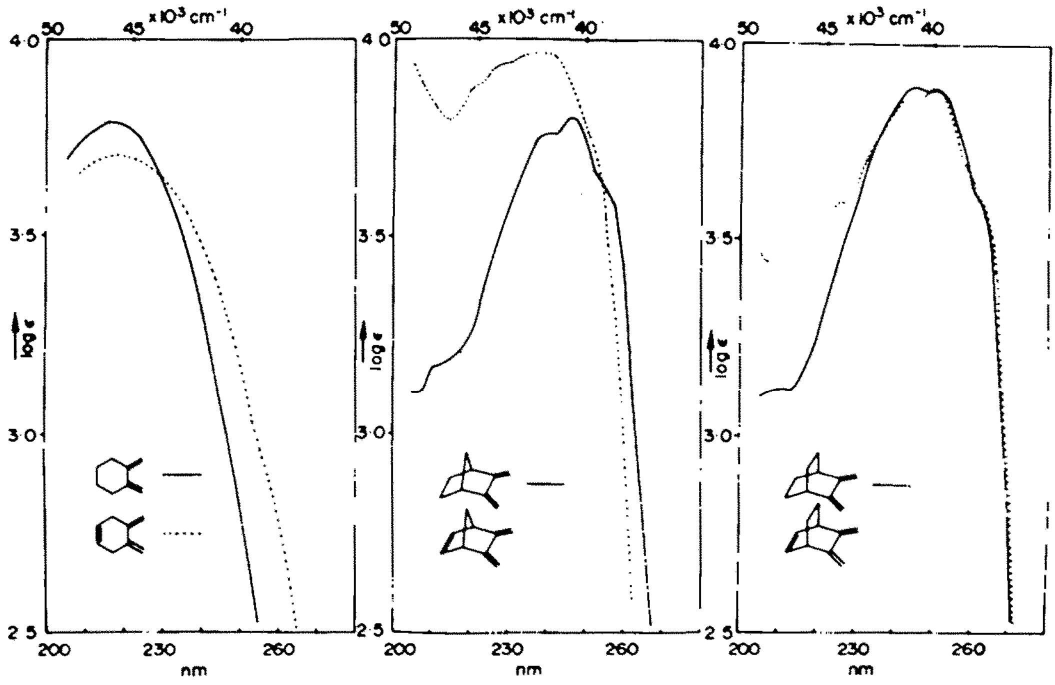


Fig 5. UV spectra of dimethylene derivatives of cycloalkanes and cycloalkenes.

870(s) cm⁻¹. NMR δ(CCL/TMS): 4·77/4·52 (2H), 2·65/2·32 (2H), 1·98 (2H) 1·66/1·50 (2H), 1·33 (4H). Mass spectrum: M⁺ = 108 = M.W.

2 - *Methylenebicyclo*[2.2.2]*octane* **15** was prepared under the same conditions: pyrolysis of 10 g acetate of *endo* - 2 - bicyclo[2.2.2]octylcarbinol at 550° gave 3·8 g 2 - methylenebicyclo[2.2.2]octane, b.p. 51°/22 mm; IR: 3060(m), 2940(s), 2860(s), 1650(m), 1450(m), 1430(m), 1230(m), 910(m), 875(s) cm⁻¹. NMR δ(CCL/TMS): 4·68/4·53 (2H), 2·28 (2H), 2·18 (2H), 1·58 (8H). Mass spectrum: M⁺ = 122 = M.W.

Methylenecyclohexane **3** was obtained from cyclohexanone by a standard Wittig-reaction.[19]

5,6 - *Dimethylenebicyclo*[2.2.1]*heptene* - 2 **12** was prepared by Hock's[20] method of dehydrochlorination from *trans* - 5,6 - dichloromethylbicyclo[2.2.1]heptene - 2 as described by Toda *et al.*;[21] IR-, NMR- and mass spectra agree with the data given by these authors.

5 - *Methylenebicyclo*[2.2.2]*octene* - 2 **16** was obtained by a modification of this method: to a mixture of 10 g KOH in 30 ml DMSO and 4 ml water in a Claisen flask which was heated to 180°, a soln of 10 g of 5 - bromomethylbicyclo[2.2.2]octene - 2 in 30 ml DMSO was added dropwise over a period of 2 h under vigorous stirring. As the reaction proceeded, oily products were distilled out under a gentle stream of nitrogen and collected in a flask cooled in an ice bath. The collected products were washed with water, extracted with ether, and the combined ether layers were dried over sodium sulfate. After removal of the drying reagent and the ether, the products were fractionally distilled to yield 3·5 g of 5 - methylenebicyclo[2.2.2]octene - 2, b.p. 145° (lit.[22] b.p. 80°/80 mm). IR: 3030(m), 2940(s), 2850(m), 1660(m), 1625(w), 1440(w), 1355(m), 1175(m), 885(s), 860(m) cm⁻¹. NMR δ(CCL/TMS): 6·08/6·02 (2H), 4·7/4·5 (2H), 2·98/2·65 (2H), 2·12 (2H), 1·47 (4H). Mass spectrum: M⁺ = 120 = M.W.

5 - *Methylenebicyclo*[2.2.1]*heptene* - 2 **10** was obtained from 5 - bromomethylbicyclo[2.2.1]heptene - 2 under the same conditions: b.p. 116°/760 mm (lit.[21] b.p. 60°/100 mm). IR: 3070(m), 2980(s), 2940(m), 2865(m), 1665(m), 1570(w), 1435(m), 1335(m), 900(m), 875(s), 835(m) cm⁻¹. NMR δ(CCL/TMS): 6·03 (2H), 4·95/4·66 (2H), 3·12/2·92 (2H), 2·13/1·82 (2H), 1·50 (2H). Mass spectrum: M⁺ = 106 = M.W.

5,6 - *Dimethylenebicyclo*[2.2.2]*octene* - 2 **18** was prepared by a detosylation under the same conditions as described above for the preparation of compound **16**: 12 g of the ditosylate of 5,6 - bicyclo[2.2.2]octene - 2 - dicarbinol (m.p. 57°) gave 2·5 g of 5,6 - dimethylenebicyclo[2.2.2]octene - 2, b.p. 162°/760 mm (lit.[22] b.p. 68°/12 mm). IR: 3080(m), 3045(m), 2950(s), 2900(m), 2860(m), 1620(m), 1445(w), 1425(w), 1140(w), 880(s), 850(m), 740(s), 680(s) cm⁻¹. NMR δ(CCL/TMS): 6·22 (2H), 5·07/4·70 (4H), 3·17 (2H), 1·52 (4H). Mass spectrum: M⁺ = 132 = M.W.

Preparation of starting materials. 3 - Cyclohexene - 1 - carbinol was prepared by reduction of 3 - cyclohexene - 1 - carboxaldehyde[24] with LAH; the acetate of this alcohol was prepared by the method described by Bailey *et al.*[18] b.p. 78°/10 mm.

endo - 2 - Bicyclo[2.2.2]octylcarbinol was prepared by LAH reduction of the Diels-Alder adduct of 1,3-cyclohexadiene with acrolein;[23] the unsaturated alcohol, b.p. 104°/20 mm, was hydrogenated with a 5% Pd/C catalyst at 20°. Again the acetate of the reduced alcohol was prepared as described by Bailey *et al.*[18] b.p. 116°/20 mm.

5 - Bromomethylbicyclo[2.2.2]octene - 2 and 5 - bromomethylbicyclo[2.2.1]heptene - 2 were prepared as described by Alder and Windemuth.[24]

5,6 - Bicyclo[2.2.2]octene - 2 - dicarbinol was obtained by LAH reduction of the Diels-Alder adduct of 1,3-cyclohexadiene with maleic anhydride.[27] Tosylation of the dialcohol (m.p. 96°) by standard methods[28] yields a white crystalline product: m.p. 57°.

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