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The Ultraviolet Absorption of Isolated Double Bonds[1]

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The apparent absorption, in the region 200–215 mμ, of some 40 acyclic and cyclic compounds containing isolated double bonds has been measured on a Beckman D. K. spectrophotometer. Substituents on the double bonds, strain effects in the rings, and the proximity of ionic groups increase the apparent absorption intensity. The results are compared with those previously reported by workers using a Unicam D. U. spectrophotometer.

Though ethylenic double bonds absorb in the vacuum ultraviolet region of the spectrum (160–190 mμ),[2] when the absorption is measured with standard photoelectric spectrometers "false energy" maxima appear in the region 200–215 mμ,[3] due to scattered light received by the photocell.[4] The results depend on the type of instrument used and even vary with different models.[3a] The effective lower wavelength limit of the Beckman D. U. spectrophotometer, without photomultiplier tube attachment, is about 208–210 mμ, and accordingly this instrument has been little used to detect isolated double bonds. However, the Beckman D. K. self-recording spectrophotometer has its scale graduated to 185 mμ, and can be used effectively to about 190 mμ. The absorption of a number of compounds containing ethylenic double bonds, both acyclic and cyclic, including many steroid and terpene derivatives, has been measured with this instrument, to determine the effect of the environment of the double bond on its absorption (see table).

EXPERIMENTAL

Non-denatured commercial 95% ethanol was purified by refluxing with zinc-dust and sodium hydroxide.[3a]

The liquid olefins were freshly distilled before use. The steroids and triterpenes were samples which had been recrystallized for analysis.

The ethanolic solutions were of such strength that they gave transmissions of 30–60% (E = 0.3–0.5). Departures from Beer's law were noted at wavelengths below 215 mμ[3b] but these were small (<15%), if readings were kept within these limits. The results are given in Table I.

Corrections can be applied for the scattered light,[3c,5] but these depend on the age of the hydrogen lamp and the setting of the instrument and are not practical for routine work. Accordingly no corrections were applied in the present work.

DISCUSSION

A monosubstituted ethylene shows an absorption maximum at about 180 mμ (*e.g.*, 1-pentene has $\lambda_{\text{max.}}$ 180 mμ, ε 15,500)[6] and substitution causes displacements to longer wavelength.[7] For 1-octene (see Table I) the "false energy" maximum occurs as a broad peak of low intensity at *ca.* 210 mμ, but in the di- and tri-substituted ethylenes (II and III) the shift in the real maximum due to substitution is manifested by steady increments in the intensity of the apparent maximum. Similarly, in the cyclohexene series (IV–VI), though cyclohexene has a maximum in the vacuum ultraviolet at 182 mμ (ε 6600)[8] its "false energy" maximum is at 207 mμ with very low intensity, and alkyl substitution, in (V) and (VI), while producing little change in wavelength, results in large increases in intensity. In the bridge-ring compounds (VII–IX) the strain in the double bond[9] produces further increases in intensity.[10]

The absorption of compounds IV, V, and VI has been measured with a small quartz spectrometer[11] (see Figure 1). In this instrument the light is dispersed by the prism after passing through the solution and the light scattering is greatly reduced. These results are compared with the present work on the Beckman D. K. spectrophotometer in Figure 1, and it is seen that due to the scattered light received by the latter instrument the results it gives are lower than the true absorption[12] and apparent displacements to longer wavelengths are produced.

Bladon, Henbest, and Wood[3a] noted that, for a series of steroids, in general compounds with tri-

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[9] *Cf.* O. H. Wheeler, *Chemistry & Industry*, 1020 (1954).

[10] [1,2,2]-Bicycloheptene has $\lambda_{\text{max.}}$ 196 mμ, in the vacuum ultraviolet; S. Stokes and L. W. Pickett, *J. Chem. Phys.*, **23**, 258 (1955).

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[12] *Cf.* Ref. 3c, 4a,b.

TABLE I

ULTRAVIOLET ABSORPTION OF DOUBLE BONDS

		$\lambda_{max.}$, mμ	$\epsilon_{max.}$	ϵ_{210}	ϵ_{215}
I	1-Octene	*ca.* 210	400	—	300
II	2,4,4-Trimethylpentene-1	206	820	570	400
III	2,4,4-Trimethylpentene-2	207	2,500	2,200	1,700
IV	Cyclohexene	207	450	300	100
V	1-Methylcyclohexene	208	1,400	1,300	650
VI	1,2-Dimethylcyclohexene	208	2,500	2,300	1,400
VII	α-Pinene	210	4,400	—	3,400
VIII	β-Pinene	208	5,200	4,600	2,300
IX	Camphene	206	5,500	4,000	1,700
X	Cholestene-2	205	5,600	3,800	2,900
XI	Cholestene-4	206	5,500	4,300	2,800
XII	Cholestene-5	206	2,100	1,300	400
XIII	Δ^2-Pregnenolone-20	205	2,500	1,900	1,500
XIV	Δ^5-Pregnenolone	205	3,300	1,700	450
XV	β-Sitosterol	206	4,200	3,000	2,200
XVI	Ergostene-7	209	10,400	10,200	7,700
XVII	Ergostene-7-3β-ol	208	6,300	6,200	5,300
XVIII	Stigmasterol	205	5,500	2,900	1,400
XIX	Fucosterol	207	4,200	3,500	1,700
XX	Zymosterol	209	3,500	3,450	3,100
XXI	Cholesterol	206	3,400	2,000	750
XXII	Allocholesterol	207	6,500	4,900	1,900
XXIII	Cholesteryl acetate	206	2,800	700	200
XXIV	Cholesteryl chloride	207	3,300	2,800	900
XXV	Cholesteryl bromide	209	5,300	5,200	4,500
XXVI	Cholestanone enolacetate	208	1,400	1,300	980
XXVII	Diosgenin	206	4,900	3,600	2,200
XXVIII	Criptogenin	207	4,700	3,600	1,900
XXIX	γ-Hecogenin	*ca.* 212	6,100	6,000	600
XXX	Lanostenol acetate	207	7,300	6,600	4,500
XXXI	Lanosterol acetate	207	9,200	7,800	4,900
XXXII	β-Amyrin	207	6,600	5,500	3,200
XXXIII	Lupeol	206	2,500	2,000	1,500
XXXIV	Oleanic acid	207	4,700	3,600	1,900
XXXV	Oleanic acid acetate methyl ester	207	6,200	5,300	3,800
XXXVI	Maniladiol	206	6,200	4,900	3,400
XXXVII	Longispinogenin	206	6,700	5,300	2,700
XXXVIII	Estrone methyl ether	207	16,100	11,000	8,000
XXXIX	Lupeol benzoate	206	16,700	13,400	11,000

substituted double bonds absorbed at *ca.* 203 mμ (ϵ *ca.* 3,000) and those with tetrasubstituted double bonds at *ca.* 207 mμ ($\epsilon \geqslant 5{,}000$). In the present work the results are very similar although the wavelength differences are not so great (at 205 and 208 mμ). These workers noted the stronger absorption of Δ^7-compounds as compared to Δ^5-compounds (*cf.* XVI and XVII and also XII and XIV) and interpreted the results as due to the influence of the neighboring positions which can give tetra-substituted double bonds (Δ^8 and $\Delta^{8(14)}$). However, the increase in absorption is probably a strain effect (see above), since the double bonds at the junction of rings B and C will be more strained than those at the more flexible ring A-B junction.

Since the absorption of an acyclic double bond is small (*cf.* I), those compounds (XVIII-XX) which contain both cyclic (Δ^5) and acyclic (side-chain) double bonds show only a small increase in absorption over those with only a single cyclic double bond. The effect of neighboring ionic groups is to increase the intensity of absorption (*cf.* XXI–XXV) and this is large when the group is strongly ionic, as in cholesteryl bromide (XXV), or is in an allylic position as in allocholesterol (XXII). However, the vinylic derivative cholestanone enol acetate (XXVI) does not show this effect, presumably due to the absence of hyperconjugation in this case. A saturated cyclic ether side-chain, as in diosgenin (XXVII) or criptogenin (XXVIII) does not contribute to the absorption, but a cyclic vinylic ether, as in hecogenin acetate (XXIX), results in a bathochromic shift and intensity increase, since dihydropyran derivatives themselves have high absorption in this region.[3c]

The previously published work on the absorption of triterpenes using a Unicam spectrophotometer[3b] did not include measurements below 210 mμ. In the present work the absorption of a series of triterpenes has been measured to 200 mμ (XXX–XXXVII). As in the case of the steroids those compounds (XXXII, XXXIV, XXXVII) with trisubstituted double bonds show an absorption maxima at 207 mμ, and those (XXX and XXXI) with tetrasubstituted double bonds absorb at the same wavelength, but with higher intensity. An acyclic

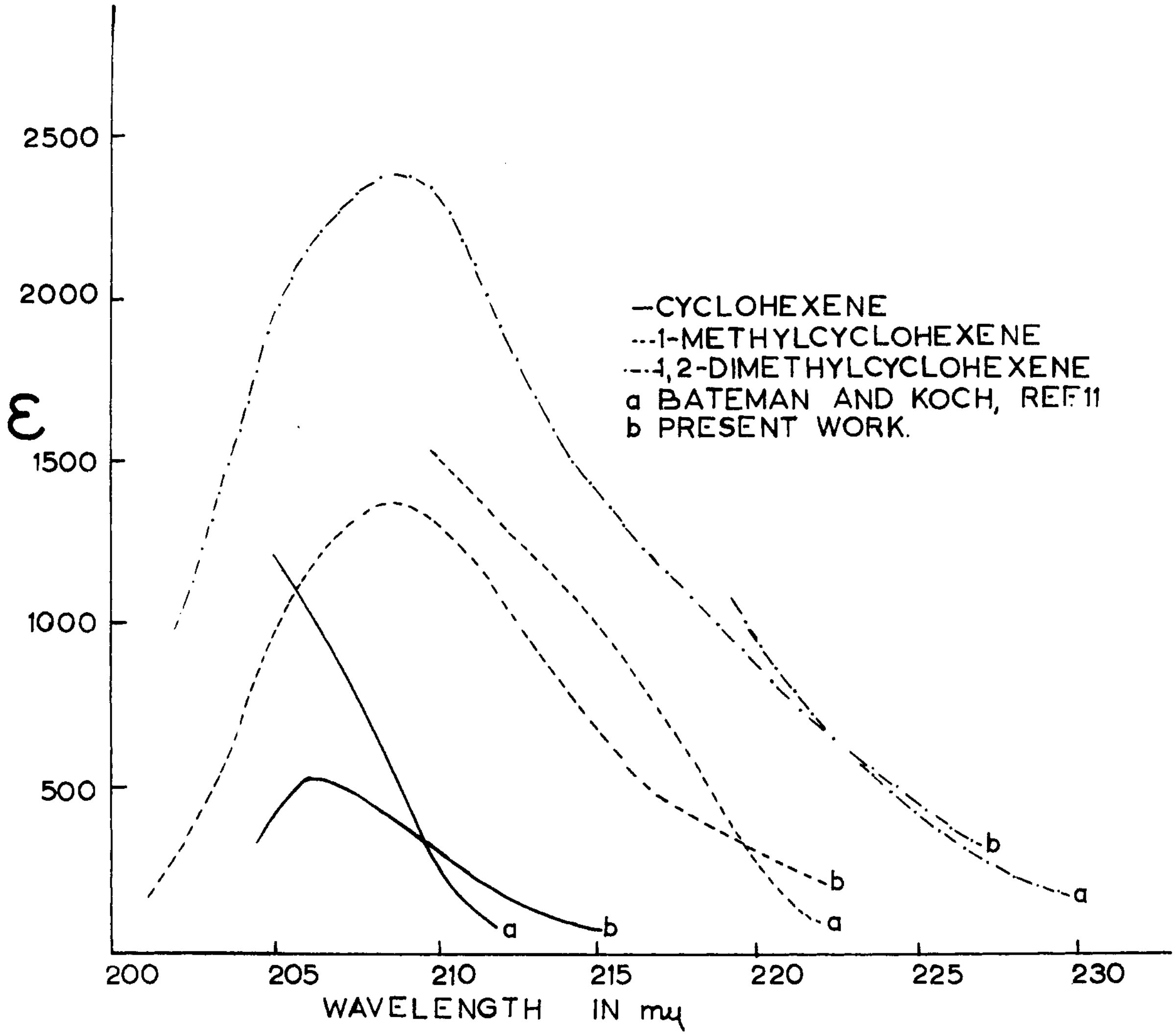

FIG. 1.—ULTRAVIOLET ABSORPTION SPECTRA OF CYCLOHEXENES IN RANGE 200–230 mμ.

double bond leads to low absorption intensity in lupeol (XXXIII) and to slightly increased intensity of absorption in lanosterol acetate (XXXI) as compared to lanostenol acetate (XXX).

The apparent absorption of two aromatic derivatives of different types (XXXVIII) and (XXXIX), was measured, and both exhibited high intensity absorption at 206–207 mμ. This may be the band of benzene at 183.5 mμ (ε 46,000)[13] displaced by substitution; Moser and Kohlenberg,[14] detected absorption at 201–208 mμ in a series of substituted benzoic acids and assigned the band to a displaced benzene band. However, in both cases the absorption is probably a "false energy" maximum arising from this benzene band which has been displaced by substitution to a wavelength just below the range of the instruments used.

Since the above results may vary slightly with the instrument, before measuring the absorption of a substance of unknown structure, it would be advisable to calibrate the instrument with substances of known structure.

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