194. *Infrared Absorption of* 1 : 2-*Disubstituted* cis-*Ethylenic Centres.*

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The infrared spectra of further groups of compounds containing disubstituted *cis*-double bonds in different environments are reported, attention being concentrated on the olefinic C–H out-of-plane bending vibration.

In a previous study [1] the absorption of disubstituted *cis*-ethylenic centres at different positions in the steroid nucleus was investigated. It was found that the olefinic C–H out-of-plane bending absorption (800—650 cm.$^{-1}$) was the most useful in establishing the presence of this grouping, and that the results could be correlated with the degree of strain in the unsaturated bonds. The work has now been extended by the examination of simple mono- and bi-cyclic systems (Table 1) and compounds (largely steroids) in which the *cis*-double bond is conjugated with C=C or C=O groups (Table 2).

Tables.—The spectra were recorded on a Perkin-Elmer model 21 double-beam spectrometer fitted with a sodium chloride prism. The experimental conditions were as previously described,[1] except that carbon disulphide solutions were used in all regions. Intensity values, given in parentheses after the C–H out-of-plane bending frequencies, are in mole^{-1} l. cm.$^{-1}$ units.

TABLE 1. *Infrared frequencies* (*cm.*$^{-1}$) *of mono- and bi-cyclic compounds containing disubstituted* cis-*double bonds.*

No.		Olefinic C–H stretching	C=C stretching			Olefinic C–H out-of-plane bending *			
1	*cyclo*Pentene	3045		1612			695 (70)		
2	*cyclo*Hexene	3020		1650			718 (70)		
	cyclo*Hex-2-enyl compounds* (I)								
3	(I; R = OH)	3022	1689		1651		724 (115)		
4	(I; R = OAc)	3030	1688		1651		727 (80)		
5	(I; R = OMe)	3035	1688		1650	725 (65)		702 (60)	
6	(I; R = OEt)	3025	1683		1651		724 (75)		
7	(I; R = Br)	3028	1687		1641	731 (250)		723 (100)	
	cyclo*Hex-3-enyl compounds* (II)								
8	(II; R = OH)	3030		1649			733 (50)		655 (105)
9	(II; R = OAc)	3025		1662			741 (45)		654 (85)
10	(II; R = OMe)	3020		1654			730 (50)		†
11	(II; R = OEt)	3020		1654			735 (40)		655 (80)
12	*cyclo*Hex-1-en-4-one (III)...	3020		1651			731 (20)		660 (95)
	bicyclo[2 : 2 : 1]*Hept-5-en-2-yl compounds* (IV)								
13	(IV; R = CO_2H)						705 (140)		
14	(IV; R = CO_2Me)	3070					705 (190)		
15	(IV; R = $CH_2{\cdot}OH$)	3070				715 (170)		704 (70)	
16	(IV; R = OAc)	3075				718 (190)		710 (105)	
17	(IV; R = $CH_2{\cdot}OMe$)	3065				716 (140)		704 (75)	

* Intensities in parentheses. † Absorption rising steeply at 650 cm.$^{-1}$.

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[1] Henbest, Meakins, and Wood, *J.*, 1954, 800.

TABLE 2. *Compounds containing conjugated* cis-*double bonds, and, in square brackets, reference compounds without* cis-*double bonds. Prominent bands in the* 900—650 cm.$^{-1}$ *region, probably associated with olefinic* C–H *out-of-plane bending.*

		$>$C=CH–	–CH=CH–		
	Type (V)				
18	3β-Acetoxycholesta-6 : 8-diene			720 (130)	
19	3β-Methoxy-11α-methylergosta-6 : 8 : 22-triene			720 (105)	
	Type (VI)				
20	*cyclo*Hex-2-enone		752 (50)		730 (100)
21	*trans*-Δ^1-Octahydro-9-methyl-3-oxonaphthalene			782 (150)	
22	Cholest-1-en-3-one *			778 (170)	
23	Cholest-2-en-1-one		808 (75)		793 (55)
24	5α-Hydroxycholest-3-en-2-one			775 (145)	
	Type (VII)				
25	$\Delta^{1(11):9}$-Decahydro-1 : 12-dimethyl-6 : 7-*iso*propylidenedioxy-2-oxophenanthrene			776 (155)	
26	[$\Delta^{1(11)}$-Dodecahydro-1 : 12-dimethyl-6 : 7-*iso*propylidenedioxy-2-oxophenanthrene]			—	
27	Cholesta-4 : 6-dien-3-one (R = H) *	876 (265)	773 (45)		753 (65)
28	[Cholest-4-en-3-one *]	867 (140)		—	
29	[Ergosta-4 : 7 : 22-trien-3-one]	868 (140)		—	
30	Cholesta-3 : 5-diene-7-one (R = H)	884 (140)	778 (90)		733 (40)
31	[Cholest-5-en-7-one]	861 (60)		—	
32	[3β-Acetoxycholest-5-en-7-one *]	869 (75)		—	
	Type (VIII)				
33	Cholesta-1 : 4 : 6-trien-3-one	892 (330)	765 (120)		695 (80)
34	Androsta-1 : 4 : 6-trien-3-one	892 ($\sim$350)	767 (115)		696 (75)
	Type (IX)				
35	Cholesta-1 : 3 : 5-trien-7-one	875 (220)	723 (215)		678 (215)

* Frequencies agree closely with those given by R. N. Jones *et al.*[4]

The C=O frequencies of some of these compounds are : no. 21, 1690; no 22, 1684; no. 23, 1682; no. 24, 1681; no. 35, 1661 cm.$^{-1}$.

Compounds : 9, 11, and 17, Henbest and Nicholls, unpublished work. 19, E. R. H. Jones, Meakins, and Stephenson, unpublished work. 35, Henbest and Wilson, *Chem. and Ind.*, 1956, 86. Compounds 21, 25, and 26, kindly supplied by Professor R. B. Woodward; no. 24 by Dr. W. Bergmann; nos. 33 and 34 by Dr. G. Rosenkranz and Dr. F. Sondheimer. The remainder were prepared by published methods.

In the *cyclo*hexene derivatives (I) and (II) the presence of substituents α or β to the double bond does not cause any marked change in the olefinic C–H stretching frequencies relatively to the value for *cyclo*hexene itself (3020 cm.$^{-1}$). The increase observed when comparing the *bicyclo*heptenes (IV) with *cyclo*pentene is probably associated with increased rigidity and/or strain in the *cis*-double bond in the bridged nucleus rather than with substitution at the β-position. Dissymmetry in the groups attached to the *cis*-double bonds increased in the sequence (IV)–(II)–(I), and this leads to clear distinctions between the three groups in the 1700—1600 cm.$^{-1}$ (C=C stretching) region. While no bands are observed for the *bicyclo*heptene derivatives, both *cyclo*hexene types give the expected (weak) 1650 cm.$^{-1}$ band, and the allylic systems (I) have a second (very weak) component near 1685 cm.$^{-1}$. A more marked case of unsymmetrical substitution leading to splitting of C=C absorption is found with vinyl ethers (CH_2=CH·OR), where a heteroatom is directly linked to the olefinic bond,[2] and in enol esters (unpublished observations).

cis-Double bonds in acyclic systems generally give one band associated with the olefinic C–H out-of-plane bending motion. But compounds with cyclic *cis*-bonds often give several bands which can be related equally to the olefinic centre, and it is not feasible to single out any particular component as the out-of-plane bending band.[1] In groups (I) and (IV) a change of substituent may cause a single peak to become a closely separated

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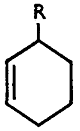
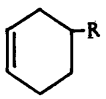
[2] Meakins, *J.*, 1953, 4170.

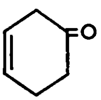
doublet, but despite this, general positions for the absorptions of systems (I), (II), and (IV) can be discerned. Group (I) has band(s) at ~725 cm.$^{-1}$ (ε 50—120). [3-Bromo*cyclo*hexene (no. 7) is exceptional in the intensity of its 731 cm.$^{-1}$ band. This effect is probably connected with the presence of halogen in a cyclic system : equatorial C–Br in bromosteroids and in bromo*cyclo*hexanes gives bands in the 750—700 cm.$^{-1}$ region.[3]] Compounds with β-substitution (II) have two bands, the weaker near 735 cm.$^{-1}$ and the stronger around 655 cm.$^{-1}$. The proximity of the latter to the end of the sodium chloride range introduces some uncertainty into the frequency and intensity figures : it also emphasises the fact that certain types of *cis*-bonds have at least some of their bending bands below 650 cm.$^{-1}$ (cf. cholesta-3 : 5-diene discussed below). The increased intensities of the *bicyclo*heptene peaks are in line with our previous findings that increasing the degree of alkylation at the carbon atoms adjacent to a cyclic *cis*-bond enhances the intensity of absorption.



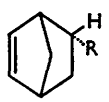
(I)



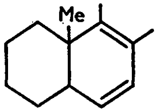
(II)



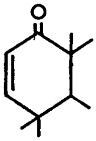
(III)



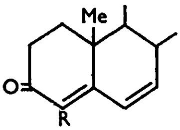
(IV)



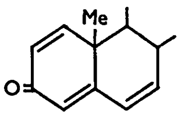
(V)



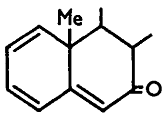
(VI)



(VII)



(VIII)



(IX)

In a series of *cyclo*hexene derivatives the bending bands move to higher frequency as the strain of the system increases.[1] However, it appears that comparisons between *different* series cannot be made on this basis, since the more strained *cyclo*pentene and the *bicyclo*heptene compounds have frequencies (695 and ~710 cm.$^{-1}$) lower than that for the less strained *cyclo*hexene (718 cm.$^{-1}$).

Four of the conjugated compounds (nos. 22, 27, 28, and 32) shown in Table 2 have been studied previously by R. N. Jones and his collaborators in an important survey of the spectra of oxo-steroids.[4] They showed that a particular system (such as the $\Delta^{4:6}$-3-oxo-grouping) is asociated with a number of bands which persist unchanged throughout a series of steroids containing that system. To make specific assignments of these bands to different bonds and atoms within these systems is difficult : indeed, in complex cases, it may be impossible to make a satisfactory assignment in terms of localised vibrations. Nevertheless an attempt is made here to pick out certain peaks as being associated mainly with the *cis*-bond. It must be stressed that we do not imply that the bands shown in Table 2 are the only ones in which the C–H bending of the *cis*-bond is concerned, merely that they are the ones having a high " contribution " from the *cis*-bond.

Previous knowledge of the effect of C=C conjugation on the *cis*-double bond frequencies is largely confined to polyenes. In type (X), where the *cis*-bond is part of a homoannular system, the out-of-plane bending frequency is relatively constant at ~725 cm.$^{-1}$ for a variety of end groups (X; R = CH$_2$·OH, COMe, CO$_2$Me, etc.).[5] The dienes of type (V) (nos. 18 and 19) with values of 720 cm.$^{-1}$ are in agreement with this. With acyclic *cis*-bonds (XI) the position of the band is more variable. The frequency appears to increase

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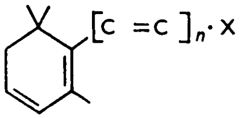
[3] Barton, Page, and Shoppee, *J.*, 1956, 331.

[4] R. N. Jones, Herling, and Katzenellenbogen, *J. Amer. Chem. Soc.*, 1955, **77**, 651.

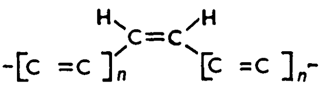
[5] Farrar, Hamlet, Henbest, and E. R. H. Jones, *J.*, 1952, 2657.

as conjugation is extended, reaching a value of ~780 cm.$^{-1}$ in cases such as 9 : 9′-*cis*-β-carotene.[6] (It should be noted that most of the " conjugating " double bonds in polyenes are trisubstituted: the same effects may not apply with other types of olefinic bonds; cf. the effect of conjugation with different types of double bonds on the bending frequency of *trans*-double bonds.[7, 8]) With the heteroannular cholesta-3 : 5-diene (XII) only weak bands occurred between 900 and 650 cm.$^{-1}$. Examination with a potassium bromide prism (kindly made by Dr. J. E. Page, of the Glaxo Laboratories) showed the main *cis*-band to be at 616 cm.$^{-1}$ (ε 150), the mono-olefin cholest-3-ene giving bands at 773 (ε 110) and 671 cm.$^{-1}$ (ε 125).

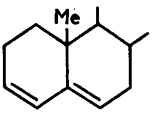
Conjugation of alicyclic *cis*-bonds with acid, ester, and amide groups [8] (XIII; X = OH, OR, NHR) moves the bending band from ~700 to 820 cm.$^{-1}$. From the spectra published by Schinz and his co-workers [9] it appears that this correlation is not applicable to conjugated ketones (XIII; X = alkyl). (It is difficult to find the bending bands in these cases; peaks around 750 cm.$^{-1}$ appear to be the most probable.) With the simplest cyclic example, *cyclo*hex-2-enone (no. 22) the main band appears at 730 cm.$^{-1}$, which represents a small increase with respect to *cyclo*hexene (718 cm.$^{-1}$), but in the more complex compounds (nos. 22—24), where the bi- or poly-cyclic skeleton reduces the flexibility of the *cyclo*hexenone ring, a larger increase occurs.



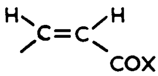
(X)



(XI)



(XII)



(XIII)

The assignments shown for type (VII) are supported by comparisons between compounds containing a *cis*-bond and reference substances of similar structures (given in Table 2) lacking this function. In the remaining types, (VIII) and (IX), there are insufficient examples for general proposals. The main conclusion to be drawn is that conjugation of a cyclic *cis*-double bond with an oxo-group again moves the bending band(s) to higher frequency.

Compounds 27—35 all contain a $>C=CH\cdot CO-$ grouping which gives rise to strong peaks between 895 and 860 cm.$^{-1}$ attributable to the C–H bending band of the trisubstituted double bond, shifted from its normal position (~815 cm.$^{-1}$) by conjugation. The effect, which again involves frequency increase of an olefinic bending band by ketonic conjugation, has been noted previously for the Δ^4-3-oxo-system,[4, 10] as has the fact that 3β-acetoxy-Δ^5-7-ketones absorb [4] near 904 and 867 cm.$^{-1}$. The absence of the higher-frequency band in the Δ^5-7-ketone (no. 31) indicates that this band is associated with the acetate group, and that of lower frequency with the olefinic bond.

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[6] Oroshnik and Mebane, *J. Amer. Chem. Soc.*, 1954, **76**, 5719.

[7] Chapman and Taylor, *Nature*, 1954, **174**, 1011.

[8] Allan, Meakins, and Whiting, *J.*, 1955, 1874.

[9] Theus, Surber, Colombi, and Schinz, *Helv. Chim. Acta*, 1955, **38**, 239; Gamboni, Theus, and Schinz, *ibid.*, p. 255.

[10] Elks, *J.*, 1954, 468.