81. *Absorption Spectra of Ketones. Part VII.*† *The* n $\longrightarrow$ π^* *Band of Axial and Equatorial 2-Arylcyclohexanones.*

By R. C. Cookson and J. Hudec.

In a series of phenylcholestanones only those with an axial phenyl group on the carbon atom next to the carbonyl group have an abnormally intense $n \longrightarrow \pi^*$ band. Asymmetric ketones with a large Cotton effect associated with such an intensified $n \longrightarrow \pi^*$ transition have a positive Cotton curve when the right-hand *p*-orbital of the oxygen atom, viewed down the oxygen–carbon bond of the carbonyl group, overlaps the π-orbital of an aromatic ring or olefinic group below the carbonyl group.

Most α-phenyl ketones have a more intense $n \longrightarrow \pi^*$ band at about 300 mμ than their saturated analogues. A survey of the data showed that the intensity of the band was very sensitive to the stereochemistry of the phenyl and carbonyl groups and suggested that, in the particular case of 2-phenylcyclohexanones, the intensity would be enhanced when the phenyl group was axial, not when it was equatorial.[1] Partly to test further this dependence of intensity on conformation we synthesised some epimeric pairs of phenylcholestanones.[2]

Table 1 shows that in fact the axial phenyl ketones (Nos. 3, 5, 7, 8) do exhibit enhancement of the $n \longrightarrow \pi^*$ band, while the equatorial epimers (Nos. 4, 6, 9, 10) show only the

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† Part VI, *J.*, 1961, 1224.

[1] Cookson and Wariyar, *J.*, 1956, 2302, and references given there.

[2] Hudec, Ph.D. Thesis, London, 1958.

TABLE 1.

Absorption spectra of α-phenyl ketones in ethanol: wavelengths of maxima in mμ (ε in parentheses below wavelength).

No.	Compound	Conform. of Ph	$A_{1g} \longrightarrow B_{2u}$ benzene band						$n \longrightarrow \pi^*$ band		
1	2-Phenylcyclohexanone [c]	*eq*		247 (115)	252 (160)	258 (195)	264 (150)			291 (40)	
2	2,2-Diphenylcyclohexanone [d]	*eq*, *ax*				~258 (475)				298 (125)	
3	3α-Phenylcholestan-2-one (I; R = H)	*ax*		249 (238)	254 (267)	260 (287)	266 (243)		292	299 (220)	308 [a] (185)
4	3β-Phenylcholestan-2-one (II; R = H)	*eq*	242 (143)	247 (171)	252 (215)	258 (247)	264 (191)			278—286 (60)	
5	3α-*p*-Methoxyphenylcholestan-2-one	*ax*	230 (7700)	278 (1820)	284 (1550)					298 [a] (510)	309 [a] (350)
6	3β-*p*-Methoxyphenylcholestan-2-one	*eq*	224 (12500)	275 (1900)	282 (1600)					290 [b] (180)	
7	3β-Methyl-3α-phenylcholestan-2-one (I; R = Me)	*ax*		248 [a] (145)	254 (191)	260 (228)	266 (192)		291 (142)	297 (153)	306 [a] (130)
8	3β-Methoxy-3α-phenylcholestan-2-one (I; R = OMe)	*ax*			254 (292)	260 (358)	266 (349)	270 (262)		297·5 (227)	
9	3α-Methoxy-3β-phenylcholestan-2-one (II; R = OMe)	*eq*		247 (161)	252 (217)	258 (244)	265 (215)	269 (122)			306 (64)
10	2α-Phenylcholestan-3-one (III)	*eq*	243 (208)	247 (233)	252 (274)	258 (308)	264 (261)			276 [a] (119)	
11	3α-Methylcholestan-2-one	—								288 (40)	
12	3β-Methylcholestan-2-one	—								286—289 (40)	
13	2β-Formyl-2α-phenyl-A-norcholestane (IV; R = H)				255 (288)	261 (330)	267 (312)			295 (353)	
14	2β-Acetyl-2α-phenyl-A-norcholestane (IV; R = Me)				256 (305)	262 (352)	269 (350)			290 (380)	
15	2β-Formyl-2α-methyl-A-norcholestane									287 (32)	

[a] Inflexion. [b] ε at 290 mμ (no max.). [c] Wildman and Wildman, *J. Org. Chem.*, 1952, **17**, 581. [d] Bennet and Burger, *J. Amer. Chem. Soc.*, 1953, **75**, 84.

usual low intensity. [The $n \longrightarrow \pi^*$ band of the 3β-*p*-methoxyphenyl ketone (as II; R = H) (No. 6) is entirely submerged under the tail of the *p*-methoxyphenyl chromophore.] That lowering the ionisation potential of the adjacent benzene ring raises the intensity of the $n \longrightarrow \pi^*$ band has already been observed empirically[1,3] and interpreted theoretically,[4] and it is substantiated by the increase in ε produced by introduction of a *p*-methoxy-group into the axial ketone (I; R = H) (compare Nos. 3 and 5). As might have been expected,[5] an axial methoxy-group shifts the $n \longrightarrow \pi^*$ maximum to substantially longer wavelengths (*ca.* 24 mμ; compare Nos. 4 and 9), whereas an equatorial one moves it very slightly the other way (*ca.* —2 mμ: compare Nos. 3 and 8). Saturated alkyl groups on the α-carbon atom of a ketone, of course, cause little change in the $n \longrightarrow \pi^*$ band: cholestan-2-one and its axial and equatorial 3-methyl derivatives (Nos. 11 and 12) have almost identical absorption in this region. As usual,[1] introduction of an α-phenyl group that increases the intensity also moves the maximum about 10 mμ to the red (compare Nos. 11 and 3; 15 and 13).

In α-bromo-ketones (V) only the conformation around the 1,2-bond needs to be considered. In α-phenyl ketones (VI) the conformation around the $C_{(2)}$–phenyl bond is also involved. Accordingly, whereas axial α-bromocyclohexanones always show an enhanced $n \longrightarrow \pi^*$ band,[6] axial α-phenylcyclohexanones may not always do so. An example of the importance of conformation around the $C_{(2)}$–phenyl bond is provided by

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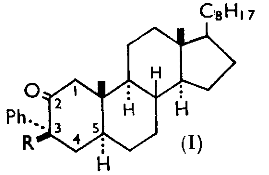
[3] Birnbaum, Cookson, and Lewin, *J.*, 1961, 1224.

[4] Labhart and Wagnière, *Helv. Chim. Acta*, 1959, **42**, 2219,

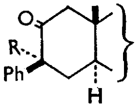
[5] Cookson and Dandegaonker, *J.*, 1955, 352.

[6] Cookson, *J.*, 1954, 282.

the axial phenyl ketones (I; R = H, OMe, and Me). Substitution of methyl (No. 7) for hydrogen (No. 3) reduces the intensity, although methoxyl (No. 8) has no effect. This is understandable if in the conformation for greatest interaction the plane of the benzene ring makes a large angle with the plane containing the $C_{(3)}$–Ph and $C_{(3)}$–$C_{(2)}$ bonds in formula (I). Repulsion between an equatorial 3β-substituent and the *o*-hydrogen atom will tend to rotate the benzene ring out of the favourable conformation (see IX), a CH_3 group being more effective than an oxygen atom. 2β-Phenylcholestan-3-one, the missing member of the four phenylcholestan-2- and -3-ones, differs from (I; R = H) in the environment of the chromophore only in having the phenyl group in its favourable conformation opposed to an axial 10-methyl group instead of only to an axial 5-hydrogen atom. It would thus be an interesting test case, predicted to show little enhancement of intensity because the repulsion would rotate the phenyl group away from the conformation favourable to spectroscopic interaction; attempts to synthesize it, though, failed.



(I)



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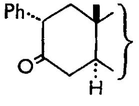

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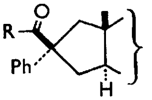

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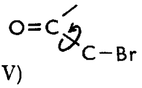

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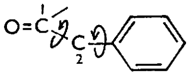

(VI)

The aldehyde (IV; R = H) (No. 13) and ketone (IV; R = Me) (No. 14) have the most intense $n \longrightarrow \pi^*$ bands of any reported derivative of phenylacetaldehyde or phenylacetone. Progressive alkylation on the α-carbon atom increases the intensity (see Tables 2 and 3 in ref. 1) by restricting rotation so that the carbonyl and the phenyl group face one another. The extreme is reached in structures (IV), where the cyclopentane ring jams the molecule largely in the favourable conformation in which the benzene ring and the plane of the COR group make a large angle with the plane containing the CO–C and C–Ph bonds.

Labhart and Wagnière, who considered the coupling of olefin and carbonyl groups in conjugated and unconjugated ketones,[4] attributed intensified $n \longrightarrow \pi^*$ absorption to mixing of the non-bonding *p*-orbital on oxygen with the olefinic π-orbital of nearly the same energy. The guess[1] that maximum intensification in a ketone $\overset{4}{C}{=}\overset{3}{C}{-}\overset{2}{C}{-}\overset{1}{C}{=}O$ would occur when the *p*-orbitals of $C_{(1)}$ and $C_{(3)}$ are in the same plane as $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$ was therefore not quite right: the overlap then would be appropriate rather to maximum charge-transfer absorption ($\pi \longrightarrow \pi^*$). Why the earlier description serves fairly well in many cases (*e.g.*, the discussion above) is because the increased $n \longrightarrow \pi^*$ intensity comes from the $\pi \longrightarrow \pi^*$ absorption: if there is no $\pi \longrightarrow \pi^*$ absorption, obviously the $n \longrightarrow \pi^*$ band cannot appropriate its intensity.

The intensity borrowed by the $n \longrightarrow \pi^*$ transition from the charge-transfer transition (CT) is given by the approximate expression:[7]

$$f'_{n \rightarrow \pi^*} = f_{\mathrm{CT}} \frac{(S \times P)^2}{(E_{\mathrm{CT}} - E_{n \rightarrow \pi^*})^2}, \qquad (1)$$

where *f* is the oscillator strength of the transition denoted by the subscript, *S* is the overlap integral between the oxygen non-bonding orbital and the $2p_\pi$-orbital of the adjacent olefinic carbon atom, and *P* is the resonance energy between these orbitals for unit

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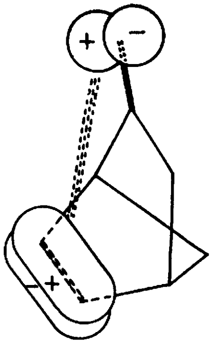
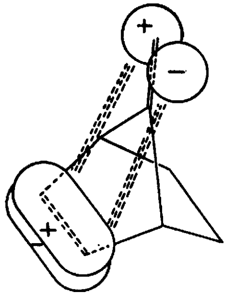
[7] Herzberg and Teller, *Z. phys. Chem.*, 1933, *B*, **21**, 410.

overlap.† [A *p*-methoxy-group (No. 5), for example, increases the intensity by bringing the energies (*E*) of the two transitions closer together.] Accordingly, two extreme situations can be foreseen in which unsaturated ketones will not show intensified $n \longrightarrow \pi^*$ absorption. The first is when the overlap integral between the appropriate *p*- and π-orbitals is zero; the second when there is no charge-transfer.



(VII)

(Net bonding overlap)



(VIII)

(Bonding overlap = antibonding overlap)

Examples are now known [8] where carbonyl and olefin groups face one another and thus show the charge-transfer band, but do not show intensified $n \longrightarrow \pi^*$ absorption, because of lack of overlap. The two isomeric bicyclo[2,2,1]heptenones provide an instructive comparison. Both show the charge-transfer band (VII [4] has $\lambda_{\text{max.}}$ 215 mμ, ε 2800 in cyclohexane; VIII [9] has 225 mμ, ε 1200 in iso-octane), but only (VII) has an intense $n \longrightarrow \pi^*$ transition ($\lambda_{\text{max.}}$ 304 mμ, ε 290): the band in the symmetrical isomer (VIII) is as weak ($\lambda_{\text{max.}}$ 275 mμ, ε 33) as in its dihydro-derivative (ε 32). The diagrams illustrate the situation: in the unsymmetrical isomer, even more than in bicyclo[2,2,2]octenone analysed by Labhart and Wagnière, there is overlap between the *p*-orbital of the oxygen and the olefinic π-orbital; in the symmetrical isomer (VIII), however, the nodal planes of the oxygen *p*-orbital and the olefinic π-orbital are orthogonal to one another, so that the overlap integral is zero.

The other possible cause of lack of intensification of the $n \longrightarrow \pi^*$ absorption is exemplified by the equatorial α-phenylcyclohexanones: here, in the favoured conformation in which the benzene ring is at right angles to the plane of the carbonyl group, the overlap of the oxygen *p*- and the phenyl π-orbital is nearly at a maximum, but it is the very conformation that makes charge-transfer impossible (because the nodal planes of the π- and π^*-orbitals are then orthogonal). The geometry for maximum intensity of the $n \longrightarrow \pi^*$ band in a particular system must, then, strike a balance by obtaining good p–π overlap without loss of too much intensity from the charge-transfer band ($\pi \longrightarrow \pi^*$), for it is by borrowing some of the latter that the $n \longrightarrow \pi^*$ transition gains intensity.‡

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† We thank Dr. S. F. Mason for drawing our attention to this equation, the exact form of which is

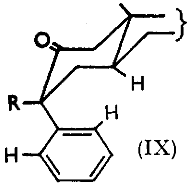
$$\frac{f'_{n \rightarrow \pi^*}}{f_{\text{CT}}} = \frac{E_{n \rightarrow \pi^*}}{E_{\text{CT}}}\left(\frac{S \times P}{E_{\text{CT}} - E_{n \rightarrow \pi^*}}\right)^2.$$

‡ The abnormal bands at 290 and 300 mμ in the spectra of dehydrogibberic acid and its derivatives, are not, as suggested,[3] due to charge-transfer, but merely to the styrene chromophore, enhanced by the rigidity of the system.

[8] Cookson, Hill, and Hudec, *Chem. and Ind.*, 1961, 589; Winstein, de Vriess, and Orloski, *J. Amer. Chem. Soc.*, 1961, **83**, 2020.

[9] Norton, Ph.D. Thesis, Harvard, 1955; see also Cookson, Hudec, and Williams, *Tetrahedron Letters*, 1960, No. 22, 29.

The aromatic *B*-band was also affected in the steroid ketones that showed enhanced $n \longrightarrow \pi^*$ absorption. Usually only three vibrational maxima, shifted about 2 mμ to longer wavelengths, could be seen, whereas the ketones with the normal weak $n \longrightarrow \pi^*$ band retained the fine structure of the *B*-band in full detail. The presence of a charge-transfer band at shorter wavelength in the spectra of the ketones with high $n \longrightarrow \pi^*$ absorption was indicated by the fact that the minima on the short-wavelength side of the *B*-band were about 10 mμ to longer wavelength than those of the ketones with low $n \longrightarrow \pi^*$absorption.



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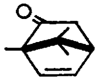
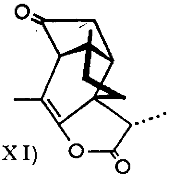


(X)



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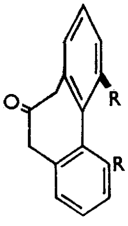

(XII)

TABLE 2.

Rotatory dispersion in methanol: molecular rotations (wavelengths in mμ in parentheses below rotation).

No.	Peak	Trough	Amplitude (peak − trough)/100	No.	Peak	Trough	Amplitude (peak − trough)/100
3	+14,600°	−15,700°	+303	9	+5170	−4550 [a]	+97 [b]
	(317)	(280)			(330)	(275)	
4	+2350	−2960 [a]	+53 [b]	11	+6580	−4400	+110
	(317)	(270)			(315)	(275)	
5	+15,900	*c*		12	+4900	−5350	+103
	(320)				(308)	(280)	
7	+18,100	−21,700	+398				
	(315)	(272)				Cholestan-2-one [d]	
8	+18,650	−19,600 [a]	+383 [b]		+6300	−5850	+122
	(315)	(270)			(310)	(267)	

[a] Trough not reached: rotation given for shortest wavelength measured. [b] Amplitude may, therefore, be greater than this. [c] Could not be read. [d] Djerassi, Closson, and Lippman, *J. Amer. Chem. Soc.*, 1956, **78**, 3163.

Asymmetric ketones with an intense $n \longrightarrow \pi^*$ band usually have a very large amplitude of the Cotton curve centred on the same wavelength.[1] The rotatory dispersion of the phenylcholestanones in Table 2 (kindly measured by Professor W. Klyne and Miss J. Jackson of Westfield College, London, to whom we offer our best thanks) confirms the finding that the axial α-phenyl ketones, with high ultraviolet absorption, have large amplitudes, while the equatorial ketones, with low absorption, have lower amplitudes. The peak of the curve for the ketone with an axial methoxy-group (No. 9) is shifted to longer wavelengths, in accord with its ultraviolet spectrum.

The four axial 3α-arylcholestan-2-ones (IX) (Nos. 3, 5, 7, and 8), dehydrocamphor (X) and its derivatives,[10] santonide and parasantonide[11] (XI), and Mislow's ketones[12] (XII) all have an exceptionally intense $n \longrightarrow \pi^*$ band associated with a strong Cotton effect. The formulæ illustrating the absolute configurations of the molecules show that the intensification of the $n \longrightarrow \pi^*$ absorption is due in all cases to the mixing of the right-hand *p*-orbital of the oxygen atom, viewed down the O=C bond, with a π-orbital below the

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[10] Asahina, Ishidate, and Tukamoto, *Ber.*, 1936, **69**, 355; S. MacKenzie, unpublished work.

[11] Woodward and Kovach, *J. Amer. Chem. Soc.*, 1950, **72**, 1009; Woodward and Yates, *Chem. and Ind.*, 1954, 1391; Bruderer, Arigoni, and Jeger, *Helv. Chim. Acta*, 1956, **39**, 858; Mitchell and Schwarzwald, *J.*, 1939, 889.

[12] Mislow, *Angew. Chem.*, 1958, **70**, 683; Mislow, Glass, O'Brien, Rutkin, Steinberg, and Djerassi, *J. Amer. Chem. Soc.*, 1960, **82**, 4740; Mislow and Djerassi, *ibid.*, p. 5247.

plane of the carbonyl group. If the Cotton effect is associated with the asymmetric $n \longrightarrow \pi^*$ transition, then all the ketones should have the same sign of the Cotton effect. In fact, it is positive. Symmetry requires that, if the effect is positive when the π-orbital is in the lower right quadrant, it should be positive also in the upper left, and negative in the other two far quadrants.† This constitutes, of course, a special case of the octant rule,[14] but because of the ability of the π-electrons greatly to increase the intensity of the transition it will usually overpower other factors in deciding the sign of the Cotton effect.

Obviously, if the absolute configuration of a flexible, unsaturated ketone is known, the sign and size of its Cotton effect may reveal its conformation. For example, the positive Cotton curve of the aldehyde (IV; R = H) ($A = +95$) indicates that conformations with the carbonyl-oxygen atom near $C_{(4)}$ are more highly populated than those with the oxygen near $C_{(1)}$. This and other examples will be discussed in a later paper.

Finally, the more general implications of the phenomenon are worth noting. The borrowing of intensity from the charge-transfer transition by the $n \longrightarrow \pi^*$ transition, which confers asymmetry on the mixed transition and occurs to such an extreme in the santonides [1,11] and dehydrocamphors,[10] is probably also responsible for the enhanced absorption [6] and optical activity [14] of axial (but not equatorial) α-bromo-ketones, and of ketones with other suitably disposed atoms with unshared electrons, and even alkyl groups and ring-residues.‡ As required by equation (1), the wider the gap between the energies of the two transitions, the less is the enhancement of intensity and (for a similar asymmetric geometrical arrangement) the lower the rotatory power of the mixed transition, until in the limit it reaches the unperturbed $n \longrightarrow \pi^*$ of formaldehyde (ε 5).[15] This point of view gives a clearer physical significance ¶ to the octant rule, which becomes general, applying to asymmetric ketones of all structures. Similar generalisations may be expected to apply to other $n \longrightarrow \pi^*$ transitions made asymmetric by mixing with $\pi \longrightarrow \pi^*$.

Experimental.—Ultraviolet spectra of ethanol solutions were measured on a Unicam SP. 500 or SP. 700 spectrophotometer (for the loan of which we are indebted to the Royal Society). Rotatory dispersion of methanol solutions was measured on a Rudolph spectropolarimeter.

Birkbeck College, London, W.C.1.
The University, Southampton.

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† The biphenyl derivatives (XII) have a dyad axis of symmetry through the carbonyl group, so that each phenyl group contributes equally to the absorption and rotation. The similar geometry of the seven-membered ring in cyclohepta-1,3-dien-6-one itself also results [13] in a very intense $n \longrightarrow \pi^*$ band (ε 560).

‡ This idea has been put forward independently by Dr. S. F. Mason, who has measured the circular dichroism of the ketone (I; R = H).

¶ This is not to deny that electrostatic fields from the complete screening of atomic nuclei may also play a part. Interaction of charges, dipoles, and multipoles will obviously not be the same function of geometry and distance as will orbital-overlap.

[13] Meinwald, Emerman, Yang, and Büchi, *J. Amer. Chem. Soc.*, 1955, **77**, 4401.

[14] Quoted by Djerassi, " Optical Rotatory Dispersion," McGraw-Hill, New York, 1960, p. 178, and by Klyne, " Advances in Organic Chemistry: Methods and Results," Interscience Publ. Inc., New York, Vol. I, 1959, p. 239.

[15] Cohen and Reid, *J. Chem. Phys.*, 1956, **24**, 85.