239. *Absorption Spectra of Ketones. Part VI.*† *Intramolecular Charge-transfer Spectra, and Further Examples of Intensified n $\longrightarrow$ π* Transitions.*

By H. Birnbaum, R. C. Cookson, and N. Lewin.

The ultraviolet spectra of several benzo-homologues of bicyclo[2,2,2]octenone show that progressive reduction in the ionisation potential of the aromatic ring increases the intensity of the $n \longrightarrow \pi^*$ band of the ketone. The long-wavelength bands of α-diketones are affected in the same way. The α-diketone group is a good acceptor for intramolecular charge-transfer, and absorption apparently due to such transitions is shown where the donor is a double bond (VI) or two benzene rings (VII).

During the last few years, in seeking a suitable framework for systematic study of intramolecular charge-transfer spectra and the effects of perturbation on $n \longrightarrow \pi^*$ transitions,[1,2,3] we have made a variety of bicyclo[2,2,2]octanes with electron-donors (tetrasubstituted double bonds or aromatic rings) in one bridge and acceptors (carbonyl, diketone, or quinone groups) in another. This paper reports some of the more interesting spectra.

The increase in intensity of the $n \longrightarrow \pi^*$ band produced by supply of electrons to the phenyl group in non-planar α-phenyl ketones[1] is illustrated by the spectra (Table 1) of the ketones (I) and (II) obtainable from the dimer[4] of 2-acetoxy-2-methylcyclohexadienone. Changing the substituent in the benzene ring *para* to the CO group from OAc to OH (or OMe) to O^- causes a sharp increase in the intensity of the band at about 310 mμ, but hardly affects its position. For the spectra in neutral ethanol (Nos. 1—4) the tail of the absorption at shorter wavelengths contributes negligible intensity at 310 mμ; extrapolation suggests that in alkaline solution (No. 5) up to half the intensity of the longest-wavelength band may come from the tail of the shorter band, which is also responsible for at least some of the apparent shift in the $n \longrightarrow \pi^*$ band to longer wavelength. This increase in intensity without change in energy is consistent with all the long-wavelength bands' being $n \longrightarrow \pi^*$ transitions.[1,3]

Table 1. *Absorption maxima* (*m*μ) (ε *in parentheses*).

No.	Compound		Solvent
1	(I; R = R′ = Ac)	264 (480), 300 (310), 307 (310)	EtOH
2	(I; R = Me, R′ = H)	281 (1700), 309 (720)	EtOH
3	(I; R = R′ = H)	284 (2150), 309 (760)	EtOH
4	(II)	240—242[a] (4000), 283 (2100), 311 (800)	EtOH
5	(I; R = R′ = H)	271 (7000), *ca.* 300[a] (4300), 317—329 (3200)	0·1N-NaOEt–EtOH
6	(III)	238 (5000), 430—435 (130)	Dioxan
7	(IV; R = Ac)	252 (4100), 279 (3500), 438 (170)	Dioxan
8	(IV; R = H)	270 (7100), 299—304[a] (2400), 446 (760)	EtOH
9	(IV; R = H)	258—266[a] (6700), 450 (920)	0·1N-NaOEt–EtOH
10	(V)[c]	293 (15), 478,[b] 465,[b] 457,[b] 447[b]	Cyclohexane
11	(VI)	238 (2600), 271 (1750), 460 (150)	Cyclohexane

Inflexion. [b] ε 30—40. [c] Alder, Schäfer, Esser, Krieger, and Reubke, *Annalen*, 1955, **593**, 23.

Similar compounds containing an α-diketone group were obtained from the dimer[5,6] (III) of *o*-benzoquinone, and again the intensity of the band at longest wavelength increases in the order: OAc > OH > O^- (Nos. 6—9). [The band centred on 450 mμ in alkali

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† Part V, *J.*, 1956, 3675.

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

[2] Cookson and Lewin, *Chem. and Ind.*, 1956, 984.

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

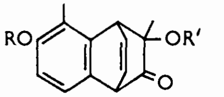
[4] Metlesics and Wessely, *Monatsh.*, 1957, **88**, 108.

[5] Patchett and Witkop, *J. Org. Chem.*, 1957, **22**, 1477.

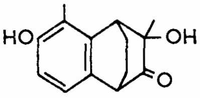
[6] Harley-Mason and Laird, *J.*, 1958, 1718.

(No. 9) is very broad, so that, if it is due to the α-diketone perturbed by the catechol anion, the ε value underestimates its relative strength. The dimer (III) and especially its enol (IV; R = H) were unstable in solution.] All these compounds show great intensification of the longest-wavelength band compared with the parent bicyclo[2,2,2]octanedione [7] (V) (No. 10).

The strong absorption (No. 8) of the compound (IV; R = H) at 270 mμ, where catechol has ε about 2500, and at shorter wavelengths is remarkable. While much of the strength of the 270 mμ band might have come from intensification of the forbidden *B*-band of benzene, it was tempting to consider that a contribution might come from separate charge-transfer from the catechol group (of low ionisation potential) to the α-diketone group (of high electron-affinity). The diketone [8] (VI) was therefore particularly interesting, because the absorption of the isolated chromophores it contains is so weak. In fact it did show (No. 11) a fairly strong band at 238 mμ, assigned to the charge-transfer transition.† The next step was to put a benzene ring on each side of the α-diketone: the spectrum of the appropriate compound (VII) showed in a spectacular degree all the effects that have been mentioned.



(I)



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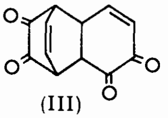

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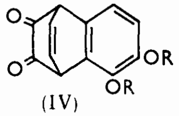

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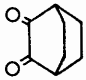
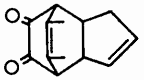
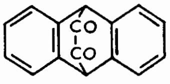


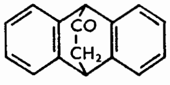
(V)



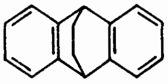
(VI)

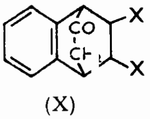


(VII)

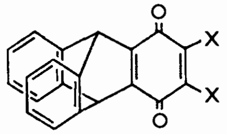


(VIII)

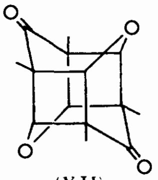

(IX)



(X)



(XI)



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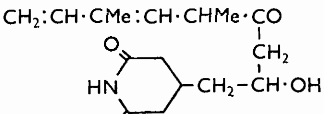

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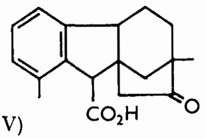

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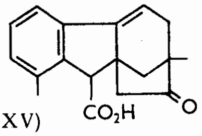
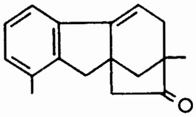
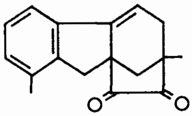


(XV)



(XVI)



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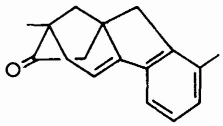

(XVIII)

The monoketone (VIII) (No. 13; Table 2) showed an intense $n \longrightarrow \pi^*$ band, about twice as strong as that of the analogous ketones [1] with only one benzene ring (X). In ethanol the fine structure of the $n \longrightarrow \pi^*$ band evident in hexane was not resolved: it appeared as a broad band with a maximum at 296 mμ (ε 730) and a shoulder at 302—306 mμ (ε 675), the expected slight shift to shorter wavelength. The spectrum of the oxime followed that of the ketone (VIII) very closely, but the $n \longrightarrow \pi^*$ band was, of course,

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† We are most grateful to Professor L. Horner for his kindness in providing a sample of compound (VI).

[7] Alder, Schäfer, Esser, Krieger, and Reubke, *Annalen*, 1955, **593**, 23.

[8] Horner and Spietschka, *Annalen*, 1953, **579**, 159.

missing. Mutual perturbation of the transitions of both the α-diketone and the benzene chromophores, and the superposition of an extraordinarily intense charge-transfer band make the spectrum (No. 14) of the diketone (VII) dramatically different from the sum of the spectra of the two isolated systems present in the diketone (V) (No. 10) and the dihydroanthracene (IX) (No. 12). The longest-wavelength band of the α-diketone is even more intense than that of the catechol derivative (IV; R = H) (No. 8), and the band with its peak at 290 mμ also is remarkably strong for an $n \longrightarrow \pi^*$ transition. [Unlike the 300 mμ band of the monoketone (VIII) this band shows no detectable fine structure even in cyclohexane]. The band at 272 mμ probably represents enhancement of the forbidden aromatic band at about the same wavelength in the monoketone (VIII) and hydrocarbon (IX). But the spectrum is dominated by the very intense intramolecular charge-transfer band with maxima at 246 and 253 mμ.†

TABLE 2. *Absorption bands* (mμ) (ε *in parentheses*).

No.	Compound	Charge-transfer band	Benzene band	Carbonyl band	Diketone band	Solvent
12	(IX)	—	253^a (500), 259^a (745), 265 (1350), 272 (1770)	—	—	Cyclohexane
13	(VIII)	—	253 (820), 261^a (740), 266·5 (975), 273·5 (970)	287 (530), 296·5 (710), 307·5 (735), 319 (442)	—	Hexane
14	(VII)	245 (28,000) 253 (46,000)	272 (3430)	290 (2890)	339 (210), 357 (270), 377 (420), 458 (980)	Cyclohexane

[a] Inflexion.

In ethanol the diketone (VII) gave a solution that was only very pale yellow, and the spectrum resembled that of the monoketone (VIII), no doubt through addition of ethanol to one of the carbonyl groups. The structure of the diketone (VII), important to prove because of its unusual spectrum, was confirmed [9] by formation of a quinoxaline, hydrolysis to 9,10-dihydroanthracene and oxalic acid, and conversion with alkaline hydrogen peroxide into 9,10-dihydroanthracene-*cis*-9,10-dicarboxylic acid.

TABLE 3. *Absorption maxima* (mμ) (ε *in parentheses*).

No.	Compound		Solvent
15	2,3-Dimethylbenzoquinone [b]	250 (18,000), 257 (16,000), 337 (1100), 425 (35)	Chloroform
16	(XI; X = H)	243—247 (20,000), 300 (820), 415 (320)	Chloroform
17	(XI; X = Cl)	275 (17,000), 321—322 (950), 433—434 (250)	Chloroform
18	(XIV) [c]	265 (360), 274 (300), 300 (31)	Ethanol
19	(XV) [c]	260 (14,000), 269 (12,000), 290 (3200), 300 (2750)	Ethanol
20	(XVI) [c]	259·5 (13,000), 269 (12,000), 290 (4200), 301·5 (4200)	Ethanol
21	(XVII) [c]	*ca.* 250 (14,000), 257 (16,000), 267 (13,000), 290 (4500), 301 (4500)	Ethanol

[a] Inflection. [b] Flaig and Salfeld, *Annalen*, 1958, **618**, 117. Cross, Grove, MacMillan, and Mulholland, *J.*, 1958, 2520.

Quinones are good acceptors in intermolecular charge-transfer (where the donor and acceptor in the complex presumably occupy parallel planes) so that it is interesting that the quinones [10,11] (XI; X = H or Cl) (Nos. 16—17; Table 3) gave no clear evidence of intramolecular charge-transfer, although the intensity of the longest-wavelength band was

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† The spectrum of the α-methylene derivative of the ketone (VIII) (*i.e.* VII, with one :O replaced by :CH_2), which has just been reported (Snyder and Clement, *J. Amer. Chem. Soc.*, 1960, **82**, 1424), also shows strong interaction: $\lambda_{max.}$ 247^a (5400), 274^a (3200), 285 (3800) and 343 mμ (730).

[9] Cf. Vaughan and Yoshimine, *J. Org. Chem.*, 1957, **22**, 528.

[10] Clar, *Ber.*, 1931, **64**, 1676.

[11] Bartlett, Ryan, and Cohen, *J. Amer. Chem. Soc.*, 1942, **64**, 2649.

again enhanced compared with those for simple quinones[12] (*e.g.* No. 15). One obvious difference between the dihydroanthracenes with α-diketone (VII) and *p*-quinone (XI) as acceptor groups is the less favourable orientation of the transition moment of the latter.

Yates and Jorgenson[13] recently reported that the photodimer (XII) of 2,6-dimethyl-4-pyrone shows an unusual spectrum for a compound saturated but for the carbonyl groups: presumably the maximum at 233 mμ (ε 6600) arises from charge-transfer from the oxygen atoms to the carbonyl groups.

The spectrum of streptimidone[14] (XIII) clearly shows the effect of lowering the ionisation potential of the double bond in heightening the intensity of the $n \longrightarrow \pi^*$ transition of βγ-unsaturated ketones. Where acetone has ε 16 and analogous βγ-unsaturated ketones[1] have ε up to 300, streptimidone has a maximum at 291 mμ (ε 790). What seem to be even more extreme examples of the same effect are provided by the γδ-unsaturated ketone, dehydrogibberic acid (XV) and its derivatives.[15] If the maxima at 290 and 300 mμ (No. 19—21) really do come from the $n \longrightarrow \pi^*$ transition of the carbonyl perturbed by the styrene group, they represent the most intense carbonyl absorption yet recorded. Labhart and Wagnière[3] have attributed the increased strength of the $n \longrightarrow \pi^*$ transitions of βγ-unsaturated ketones to the overlap of the *p*-orbital of the oxygen atom with the π-orbital of the double bond in the ground state, which happens to have nearly the same energy. A model (XVIII) of " gebberone " (XVI) shows that the overlap of these orbitals, even allowing for the lower ionisation potential of the styrene double bond, can be only slight. The intensity here may come from the charge-transfer transition, which should have about the same energy.

EXPERIMENTAL

Ultraviolet spectra were measured on a Unicam S.P. 500 spectrometer and positions of maxima were determined graphically.

The diacetate (I; R = R′ = Ac) was made by boiling the dimer of 2-methylquinol diacetate with sodium acetate in acetic anhydride according to Wessely's directions.[4] After recrystallisation from ether it had m. p. 158°. The diol (I; R = R′ = H), crystallised from ethyl acetate, had m. p. 181°. The monomethyl ether (I; R = Me; R′ = H) (from methanol) had m. p. 151°. The dihydro-compound (II) (from methanol) had m. p. 183—184°.

The dimer (III) of *o*-benzoquinone, made by oxidation of catechol with silver oxide in acetone[6] in the dark, formed yellow crystals, double m. p. 125—130°, then 194—195°. The enolic tautomer (IV; R = H) crystallised from ethyl acetate–light petroleum (b. p. 40—60°) in orange-yellow plates, m. p. 193—194°, and the diacetate (IV; R = Ac) separated from the same solvent in yellow crystals, m. p. 141—142°.

9,10-Dihydro-11-oxo-9,10-ethanoanthracene[9,16] (VIII), got by oxidation of the alcohol with chromic oxide in pyridine, or cyclohexanone and aluminium t-butoxide in toluene, or benzoquinone and aluminium t-butoxide in benzene, had m. p. 152—153° after crystallisation from alcohol or light petroleum (b. p. 60—80°).

The monoketone (VIII) was oxidised with an equal weight of selenium dioxide in boiling acetic acid for 6 days or in dioxan at 165° for 2 hr. Recrystallisation from benzene or ethyl acetate yielded the yellow diketone (VII), m. p. 202—203° (Found: C, 82·0; H, 4·3. Calc. for $C_{16}H_{10}O_2$: C, 82·05; H, 4·4%).

The hydrazone of the monoketone (VIII) with sodium ethoxide in ethanol at 160° for 20 hr. formed the hydrocarbon (IX), m. p. 145—146° (from water-methanol).

Oxidation of dihydroxytriptycene with potassium bromate in acetic acid[11] gave the quinone (XI; X = H), m. p. 304° (from acetic acid). The dichloro-derivative[10] (XI; X = Cl) was made directly from the adduct of anthracene and benzoquinone by passing chlorine through

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[12] Flaig and Salfeld, *Annalen*, 1958, **618**, 117.
[13] Yates and Jorgenson, *J. Amer. Chem. Soc.*, 1958, **80**, 6150.
[14] van Tamelen and Haarstad, *J. Amer. Chem. Soc.*, 1960, **82**, 2974.
[15] Cross, Grove, MacMillan, and Mulholland, *J.*, 1958, 2520.
[16] Noland, Baker, and Freeman, *J. Amer. Chem. Soc.*, 1956, **78**, 2233.

a solution in boiling acetic acid. After crystallisation from acetic acid the dichloroquinone had m. p. 291° (decomp.).

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