Dipole Moments and Absorption Spectra of Heterocyclic Diketones

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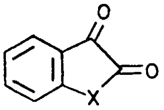
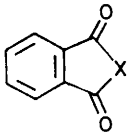
The electric dipole moments of isatin, benzo[*b*]furan-2,3-dione, benzo[*b*]thiophen-2,3-dione, and benzo[*c*]thiophen-1,3-dione in benzene solution at 25 °C have been measured and compared with those of their congeners related to indane-1,2- and -1,3-dione. The main features of the electronic spectra of all these diketones have been surveyed and interpreted with the aid of theoretical calculations performed at the INDO/S-CI level; in particular, the nature, location, and evolution of the $n \longrightarrow \pi^*$ transitions have been explained.

THE electronic structure and spectra of carbocyclic diketones have been the subject of a large number of experimental and theoretical studies. Less attention has been paid to the electronic properties of heterocyclic diketones. This paper reports some experimental measurements of electric dipole moments and an investigation of the electronic absorption spectra of heterocyclic diketones related to indane-1,2-dione (4) [compounds (1)—(3), series I] and to indane-1,3-dione (8) [compounds (5)—(7), series II]. Theoretical calculations at the INDO/S-CI level have been performed in order to rationalise the experimental data. Particular interest has been devoted to the $n \longrightarrow \pi^*$ transitions.



(1) X = O
(2) X = S
(3) X = NH
(4) X = CH$_2$



(5) X = O
(6) X = S
(7) X = NH
(8) X = CH$_2$

EXPERIMENTAL

Materials.—Isatin (3), phthalimide (7), and phthalic anhydride (5) were commercially available materials. Benzo[*b*]furan-2,3-dione (1), benzo[*b*]thiophen-2,3-dione (2), and benzo[*c*]thiophen-1,3-dione (6) were synthesized as described.[1] All compounds were purified by several crystallisations.

Physical Measurements.—Electric dipole moments of compounds (1)—(3) and (6) were determined in benzene solution at 25 ± 0.01 °C. Dielectric constants (ε_{12}), specific volumes (v_{12}), and refraction indices (n_{12}) of solutions at different weight fractions of solute (w_2) were measured using apparatus and techniques described earlier.[2] The total solute polarization has been obtained by extrapolation at infinite dilution ($P_{2\infty}$) using the Halverstadt–Kumler method.[3] The value of the experimental molar refraction (R_D) for the Na$_D$ line has been used as the electronic and atomic polarization ($P_e + P_a$) in calculating the dipole moments (μ) from Debye's formula. The estimated error in measured μ values is ± 0.01 D. The purity of each sample was $>99\%$ (g.l.c.). Benzene used as solvent was purified according to a literature method.[4]

U.v.–visible absorption spectra were recorded on a Perkin-Elmer 356 spectrophotometer.

Computations.—Since the INDO method with its original parametrisation is unable to account satisfactorily

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[3] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.

[4] A. Weissberger and E. Proskauer, 'Organic Solvents, Techniques of Organic Chemistry,' Interscience, New York, 1955, vol. VII.

for excited states, we used a variant (INDO/S-CI) in which the parametrisation and the integral evaluation follow the proposals of Ellis *et al.*[5] The orbital electronegativities and the Slater–Condon integrals were given the spectroscopic values provided by Hinze and Jaffé.[6,7] (The parametrisation adopted[8] is collected in Table 1.) The two-centre coulomb integrals were determined using the Mataga–Nishimoto formula. The resonance integrals were calculated from the Jaffé formula,[5] the *k* parameter being assumed to be 0.585 for the π-component of overlap.

TABLE 1

Atomic parametrisation (eV)

Atom	$\frac{1}{2}(I + A)_s$	$\frac{1}{2}(I + A)_p$	F^0	F^2	G^1	$-\beta^0$
H	7.175		12.85			12.0
C	14.960	5.805	10.93	4.51	6.90	17.5
N	20.485	8.480	11.88	6.46	8.96	26.0
O	27.255	10.965	15.13	6.90	11.81	45.0
S	15.810	8.415	9.82	4.54	3.07	16.0[a]

[a] Ref. 8.

The total electronic dipole moments were evaluated as the sum of the contributions from the formal atomic charges and atomic dipoles.

The transition energies were computed from the INDO wavefunctions which have been refined by a CI treatment restricted to the 30 lowest singly excited states. The oscillator strengths for the various transitions were determined with the dipole length operator.

The experimental geometries[9] were used for compounds (3), (6), and (7), while idealised geometries have been calculated for the other compounds from structural data on similar compounds.[10]

RESULTS AND DISCUSSION

Dipole Moments.—The experimental results are collected in Table 2 together with the other observed values[11-13] and the theoretical estimates.

The measured dipole moments of the 1,2-diketones of series I vary in the order O < S < NH but are in more markedly the reverse sense for series II. These opposite trends can be qualitatively rationalised in terms of two-way charge transfer involving the heteroatom, which displays a σ-electron acceptor property as well as a π-electron donor property, and of the specific site occupied by the heteroatom in the molecule.

In series II the molecular symmetry causes the heteroatom properties to act in the opposite sense to series I in determining the value of μ. The marked differences in electronegativity and electron-releasing power of the heteroatoms are responsible for the net change of μ along this series. As regards the indane-1,3-dione (8) its μ value is somewhat higher than phthalimide (7) in view of the minor importance of the hyperconjugative effect of the $>CH_2$ group relative to the conjugative ability of the $>NH$ group.

In series I the heteroatom X can interact directly with the nearer carbonyl group and with the benzenoid nucleus. In addition to electron drift from X to the O atom of the nearer carbonyl group, a mesomeric transfer from X to the distant CO group can occur across the aromatic π-framework. Unlike the related symmetric 1,3-diketones, in these asymmetric systems both the heteroatom properties enhance μ. The overall charge distribution turns out, therefore, to be critically dependent on the electron-donating power of the heteroatom, and, as a consequence, the dipole moment increases with electron-donating power. These arguments account for the opposite behaviour and different degree of variation shown by the dipole moments in series I and II.

TABLE 2

Polarization data and dipole moments (in benzene at 25°)

Compound	α[a]	ε_{10}[b]	β[c]	v_{10}[d]	γ[e]	$P_{2\infty}/cm^3$	R_D/cm^3	μ/D obs.	μ/D calc.
(1)	18.41	2.2732	−0.421	1.149 54	0.315	546.82	40.5	4.97	7.39
(2)	17.40	2.2739	−0.269	1.149 54	0.201	582.12	48.5	5.10	7.26
(3)	24.43	2.2730	−0.607	1.149 64	0.887	702.34	48.2	5.65	8.11
(6)	9.91	2.2736	−0.243	1.149 39	0.173	351.34	48.9	3.84	6.78
(5)								5.24[f]	6.77
(7)								2.12[g]	4.18
(8)								2.73[h]	3.71
(4)									7.57

[a] $\alpha = \Sigma(\varepsilon_{12} - \varepsilon_{10})/\Sigma w_2$. [b] $\varepsilon_{10} = \lim_{w_2 \to 0} \varepsilon_{12}$. [c] $\beta = \Sigma(v_{12} - v_{10})/\Sigma w_2$. [d] $v_{10} = \lim_{w_2 \to 0} v_{12}$. [e] $\gamma = \Sigma(n^2_{12} - n^2_{10})/\Sigma w_2$. [f] Ref. 11. [g] Ref. 12. [h] Ref. 13.

As can be seen from the last column in Table 2, the agreement between theoretical and experimental values is not satisfactory. Clearly, theory overemphasizes the charge separation in the five-membered ring and, in particular, the shift of electrons towards the O atoms of the two carbonyl groups.

Electronic Spectra.—*Spectral survey.* The u.v.–visible spectra of the 1,2-diones (1)—(3) are dominated by four absorption bands which are well separated and can therefore be confidently attributed to different electronic

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transitions. The first, broad and low intensity band lies in the visible region ($\lambda > 340$ nm) and is responsible for the yellow-orange colours of the compounds; the second medium intensity band occurs in the range 280—300 nm; the third high intensity band appears in the interval 225—250 nm; and the fourth high-intensity band lies below 225 nm.

On the basis of experimental study of substituent and solvent effects on the spectrum of isatin (3), Mangini and Passerini [14] concluded that the band in the visible region is due to an $n \longrightarrow \pi^*$ transition involving primarily the 1,2-dione, or more properly, the oxoamide NH-CO-CO; the two bands in the near u.v. region are identified as $\pi \longrightarrow \pi^*$ benzoyl bands (chromophore C_6H_4CO), from modification of the B_{1u} and E_{2g} bands of benzene; and the fourth band is presumably correlated with a $\pi \longrightarrow \pi^*$ transition of type E_{1u}. The thorough investigation of the absorption, emission, and c.d. spectra of indane-1,2-diones (4) ($X = CR^1R^2$) performed by Arnett *et al.*[15] provides substantial corroboration for the assignments suggested by Mangini and Passerini for isatin and, in addition, convincing evidence that a second $n \longrightarrow \pi^*$ carbonyl transition is obscured beneath the long wavelength tail of the first observed $\pi \longrightarrow \pi^*$ absorption band. Our observations of solvent effects for the two other compounds, (1) and (2), agree with the evidence [14] for isatin. The assignment of the spectra of all compounds in series I is established as that for isatin.

In the spectra of the symmetric 1,3-diketones (5)—(8) at least three distinct absorptions are discernible: a broad band of medium intensity appears in the long wavelength region (280—310 nm) and two bands of moderate-to-high intensity lie at shorter wavelengths (255—235 and at <225 nm). In the case of phthalic anhydride (5) and phthalimide (6) the long wavelength band exhibits two maxima, which probably represent the vibrational fine structure of one electronic transition.[16] Unlike the related colourless heterocyclic compounds, indane-1,3-dione (8) exhibits a pale yellow colour caused by a fourth structured band of moderate intensity lying in the low energy part of the spectrum. This band can be classified as $n \longrightarrow \pi^*$ since its position shifts to higher energy and its vibrational structure becomes increasingly blurred with increasing polarity of the solvent; this attribution agrees with the results by Belaits and Nurmukhametov [17] who have detected some evidence for $n \longrightarrow \pi^*$ transitions in the low-frequency regions of the electron absorption and luminescence spectra of indane-1,3-dione.

All the reported experimental investigations on the heterocyclic 1,3-diketones (see *e.g.* refs. 16—20) agree in assigning the bands observed in the u.v. region to $\pi \longrightarrow \pi^*$ transitions; these assignments have also been assumed in theoretical studies which take into account only the π-framework.[21] It is worth mentioning, however, that Lutskii *et al.*[20] have attributed the long wavelength band of phthalic anhydride to a $\pi_{\text{ring}} \longrightarrow \pi_{\text{CO}}^*$ transition with some addition of $\pi_{\text{ring}} \longrightarrow \pi_{\text{ring}}^*$ and $n_{\text{CO}} \longrightarrow \pi^*_{\text{CO}}$ transitions.

Quantum-mechanical results. Tables 3 and 4 present the calculated results for the lower excitation energies and related oscillator strengths.

In order to give a standard classification to the excited electronic states we have adopted the labelling of the highest occupied and lowest empty MOs localized primarily on the dicarbonyl group proposed by Arnett *et al.*[15] for 1,2-diketones: n_+, n_-, π^*_+, and π^*_-.† The n MO of higher binding energy is calculated to be n_- in series I and n_+ in series II; in both series it exhibits the heteroatom order: $O > NH > S > CH_2$. The energy separation between the two n MOs is predicted to be of the order of 2.1—2.8 eV in series I and <0.5 eV in series II. The calculated n_-/n_+ splitting for indane-1,2-dione is 2.4 eV which compares satisfactorily with the photoelectronic spectrum result of 2.1 eV.[15]

As shown by the results reported in Table 3, the observed spectra of indane-1,2-dione and its hetero-analogues are fairly well reproduced by the calculations. In particular, the INDO/S-CI results predict the first two singlet-singlet transitions to be of the $n \longrightarrow \pi^*$ type, well spaced and weakly allowed in electric dipole radiation, localized essentially on the CO-CO-X fragment. The lower estimated transition can be described as a nearly pure $n_+ \longrightarrow \pi^*_+$ excitation; the second excited state is composed by an admixture of $n_+ \longrightarrow \pi^*_-$ and $n_- \longrightarrow \pi^*_+$ configurations. The energy computations suggest that this second transition, not observed in the absorption spectra, is probably buried below the cut-off of the next allowed band of medium intensity, in agreement with the conclusions by Arnett *et al.*[15] for indane-1,2-dione. The third excited state arises essentially from the configuration $\pi \longrightarrow \pi^*_+$: the corresponding observed band can therefore be recognised as a 'benzoyl' band, consistent with the classification of Mangini and Passerini [14] for isatin. The fourth and fifth excited states originate from scrambled combinations of several $\pi \longrightarrow \pi^*$ configurations involving the entire π-electron framework. In conclusion, it can be said that the present theoretical results corroborate, on a quantitative basis, the previous empirical assignments.

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† The n,π labelling is incorrect, in a strict sense, for (4) and (8) because the two methylene hydrogen atoms destroy planarity. However, the resultant n,π orbital mixing, while real, is quite negligible and the n,π labelling retains general validity even in these cases.

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For the symmetric 1,3-diketones the INDO/S-CI treatment (Table 4) predicts two low energy, closely spaced $n \longrightarrow \pi^*$ transitions involving primarily the CO–X–CO group. The weakly allowed state of symmetry ${}^1B_2$ is a combination of the configurations $n_- \longrightarrow \pi^*{}_-$ and $n_+ \longrightarrow \pi^*{}_+$, with the first configuration making the dominant contribution. The transition ${}^1A_1 \rightarrow {}^1A_2$, electric dipole forbidden, arises instead from a mixture of excitations $n_+ \longrightarrow \pi^*{}_-$ and $n_- \longrightarrow \pi^*{}_+$, the first being more important. The fact that these two ' quinonoid ' electron-transfer transitions are not discernible in the spectra of the heterocyclic 1,3-diketones can be taken as experimental evidence in favour of very low or null intensity; their

TABLE 3

Experimental and calculated energies (in eV) for the low lying singlet excited states of indane-1,2-dione and related heterocyclic compounds

Compound	Experiment E (log ε)	Theory E	Theory f	Theory State	Main components of CI wavefunctions (in %) [d]
(1)	3.59 (3.24) [a]	3.01	0.0002	${}^1A''$	86 ($n_+ \longrightarrow \pi^*{}_+$)
		4.34	0.0021	${}^1A''$	26 ($\sigma \longrightarrow \pi^*{}_+$); 24 ($n_+ \longrightarrow \pi^*{}_-$); 19 ($n_- \longrightarrow \pi^*{}_+$)
	4.41 (3.77)	4.35	0.0625	${}^1A'$	70 ($\pi \longrightarrow \pi^*{}_+$)
	5.48 (3.89)	4.99	0.1998	${}^1A'$	55 ($\pi \longrightarrow \pi^*{}_+$); 19 ($\pi \longrightarrow \pi^*{}_+$)
	5.90 (3.93)	5.59	0.2506	${}^1A'$	38 ($\pi \longrightarrow \pi^*{}_-$); 21 ($\pi \longrightarrow \pi^*$); 13 ($\pi \longrightarrow \pi^*$)
		6.25	0.2737	${}^1A'$	45 ($\pi \longrightarrow \pi^*$); 34 ($\pi \longrightarrow \pi^*$)
(2)	3.05 (2.70) [a]	2.98	0.0002	${}^1A''$	85 ($n_+ \longrightarrow \pi^*{}_+$)
		3.90	0.0002	${}^1A''$	40 ($n_- \longrightarrow \pi^*{}_+$); 28 ($n_+ \longrightarrow \pi^*{}_-$)
	4.09 (3.41)	4.43	0.0591	${}^1A'$	69 ($\pi \longrightarrow \pi^*{}_+$)
	4.90 (4.12)	4.94	0.1236	${}^1A'$	35 ($\pi \longrightarrow \pi^*{}_+$); 27 ($\pi \longrightarrow \pi^*$); 26 ($\pi \longrightarrow \pi^*{}_+$)
	5.51 (4.24)	5.75	0.2677	${}^1A'$	48 ($\pi \longrightarrow \pi^*{}_+$); 25 ($\pi \longrightarrow \pi^*$); 17 ($\pi \longrightarrow \pi^*$)
		6.08	0.3532	${}^1A'$	83 ($\pi \longrightarrow \pi^*$)
(3)	2.98 (2.85) [b]	2.65	0.0002	${}^1A''$	85 ($n_+ \longrightarrow \pi^*{}_+$)
		4.13	0.0016	${}^1A''$	31 ($n_+ \longrightarrow \pi^*{}_-$); 24 ($n_- \longrightarrow \pi^*{}_+$); 14 ($\sigma \longrightarrow \pi^*{}_+$)
	4.17 (3.53)	4.16	0.0890	${}^1A'$	88 ($\pi_n \longrightarrow \pi^*{}_+$)
	5.12 (4.37)	4.89	0.0287	${}^1A'$	37 ($\pi \longrightarrow \pi^*$); 35 ($\pi \longrightarrow \pi^*{}_+$)
	5.90 (4.13)	5.80	0.5900	${}^1A'$	60 ($\pi \longrightarrow \pi^*{}_+$); 15 ($\pi \longrightarrow \pi^*$)
		5.87	0.0003	${}^1A''$	41 ($n_+ \longrightarrow \pi^*$); 19 ($\sigma \longrightarrow \pi^*{}_+$)
(4)	2.39 (1.5_0) [c]	2.31	2×10^{-6}	${}^1A''$	81 ($n_+ \longrightarrow \pi^*{}_+$)
	(3.57)	3.68	2×10^{-7}	${}^1A''$	29 ($n_+ \longrightarrow \pi^*{}_-$); 26 ($n_- \longrightarrow \pi^*{}_+$)
	3.97 (3.5_0)	4.42	0.0431	${}^1A'$	63 ($\pi \longrightarrow \pi^*{}_+$); 20 ($\pi \longrightarrow \pi^*$)
	4.56 (3.9_5)	5.16	0.3326	${}^1A'$	69 ($\pi \longrightarrow \pi^*{}_+$); 18 ($\pi \longrightarrow \pi^*{}_+$)
		5.66	0.1145	${}^1A'$	34 ($\pi \longrightarrow \pi^*$); 24 ($\pi \longrightarrow \pi^*{}_+$); 20 ($\pi \longrightarrow \pi^*$)
		5.75	0.0001	${}^1A''$	53 ($n_+ \longrightarrow \pi^*$)

[a] In Et$_2$O, present work. [b] Ref. 14. [c] Ref. 15. [d] MOs labelled simply as π refer to generic π-MOs.

TABLE 4

Experimental and calculated energies (in eV) for the low lying singlet excited states of indane-1,3-dione and related heterocyclic compounds

Compound	Experiment E (log ε)	Theory E	Theory f	Theory State	Main components of CI wavefunctions (in %) [f]
(5)		4.17	0	${}^1A_2$	59 ($n_+ \longrightarrow \pi^*{}_-$); 15 ($n_- \longrightarrow \pi^*{}_+$)
		4.25	0.0036	${}^1B_2$	59 ($n_- \longrightarrow \pi^*{}_-$); 14 ($n_+ \longrightarrow \pi^*{}_+$)
	4.20 (3.44) [a]	4.64	0.0270	${}^1A_1$	60 ($\pi \longrightarrow \pi^*{}_-$); 34 ($\pi \longrightarrow \pi^*$)
	5.06 (3.74)	5.43	0.2643	${}^1B_1$	90 ($\pi \longrightarrow \pi^*$)
	5.89 (4.58)	6.11	0.9433	${}^1A_1$	50 ($\pi \longrightarrow \pi^*$); 38 ($\pi \longrightarrow \pi^*$)
		6.12	0	${}^1A_2$	32 ($n_+ \longrightarrow \pi^*{}_-$); 28 ($\sigma \longrightarrow \pi^*{}_-$); 16 ($n_+ \longrightarrow \pi^*$)
(6)		3.66	0.0006	${}^1B_2$	56 ($n_- \longrightarrow \pi^*{}_-$); 15 ($n_+ \longrightarrow \pi^*{}_+$)
		3.74	0	${}^1A_2$	49 ($n_+ \longrightarrow \pi^*{}_-$); 19 ($n_- \longrightarrow \pi^*{}_+$); 18 ($n_- \longrightarrow \pi^*$)
	4.10 (3.23) [b]	4.57	0.0115	${}^1A_1$	56 ($\pi \longrightarrow \pi^*{}_-$(; 38 ($\pi \longrightarrow \pi^*$)
	4.96 (3.99)	5.05	0.3165	${}^1B_1$	91 ($\pi \longrightarrow \pi^*{}_-$)
	5.39 (4.46)	6.10	1.1843	${}^1A_1$	54 ($\pi \longrightarrow \pi^*$); 39 ($\pi \longrightarrow \pi^*{}_-$)
		6.51	0.0044	${}^1B_1$	46 ($\pi \longrightarrow \pi^*{}_-$); 45 ($\pi \longrightarrow \pi^*$)
(7)		3.86	0.0027	${}^1B_2$	66 ($n_- \longrightarrow \pi^*{}_-$); 12 ($n_+ \longrightarrow \pi^*{}_+$)
		4.07	0	${}^1A_2$	56 ($n_+ \longrightarrow \pi^*{}_-$); 18 ($n_- \longrightarrow \pi^*{}_+$)
	4.16 (3.27) [c]	4.63	0.0237	${}^1A_1$	59 ($\pi \longrightarrow \pi^*{}_-$); 35 ($\pi \longrightarrow \pi^*$)
	5.21 (4.03)	5.15	0.0776	${}^1B_1$	84 ($\pi \longrightarrow \pi^*{}_-$)
		6.12	0	${}^1A_2$	36 ($n_- \longrightarrow \pi^*$); 30 ($n_+ \longrightarrow \pi^*{}_-$); 23 ($\sigma \longrightarrow \pi^*{}_-$)
	5.71 (4.61)	6.13	0.9641	${}^1A_1$	49 ($\pi \longrightarrow \pi^*$); 39 ($\pi \longrightarrow \pi^*$)
(8)	3.52 (2.28) [d]	3.26	0.0000_2	${}^1B_2$	56 ($n_- \longrightarrow \pi^*{}_-$); 15 ($n_+ \longrightarrow \pi^*{}_+$)
		3.40	0	${}^1A_2$	47 ($n_+ \longrightarrow \pi^*{}_-$); 21 ($n_- \longrightarrow \pi^*{}_+$)
	4.13 (3.05) [e]	4.56	0.0266	${}^1A_1$	61 ($\pi \longrightarrow \pi^*{}_-$); 34 ($\pi \longrightarrow \pi^*$)
	4.86 (3.97)	5.49	0.2812	${}^1B_1$	86 ($\pi \longrightarrow \pi^*{}_-$)
		5.69	0	${}^1A_2$	42 ($n_+ \longrightarrow \pi^*{}_-$); 21 ($\sigma \longrightarrow \pi^*$); 18 ($n_- \longrightarrow \pi^*$)
		5.76	0.0016	${}^1B_2$	42 ($n_- \longrightarrow \pi^*{}_-$); 16 ($n_+ \longrightarrow \pi^*$)
	5.46 (4.59)	6.13	1.0927	${}^1A_1$	54 ($\pi \longrightarrow \pi^*$); 28 ($\pi \longrightarrow \pi^*{}_-$)

[a] Ref. 16. [b] In Et$_2$O, present work. [c] Ref. 17. [d] In Bz, this work. [e] Ref. 14. [f] MOs labelled simply as π refer to generic π-MOs.

computed locations suggest, however, that these excitations are probably masked in the long wavelength tail of the $\pi \longrightarrow \pi^*$ of lower energy. In the case of indane-1,3-dione these bands are predicted to lie at shorter frequencies in agreement with experimental evidence. As regards instead the bands appearing in the u.v. region, these are ascribed to $\pi \longrightarrow \pi^*$ transitions involving strongly the phthaloyl fragment CO–C_6H_4–CO.

Focusing attention on the important $n \longrightarrow \pi^*$ transitions, the spectral features of the two examined series of diketones permit at least the following observations. (i) Both the computed and observed energy of the first $n \longrightarrow \pi^*$ band of the 1,2-diketones is strongly dependent on the heteroatom: the band undergoes a considerable hypsochromic displacement in the order: $CH_2 < NH < S < O$; its intensity also increases markedly upon substitution of CH_2 with X. These effects demonstrate therefore that the responsible chromophore is essentially the group CO–CO–X. (ii) The theoretical results for the 1,3-diketones anticipate a similar but minor blue shift of the first $n \longrightarrow \pi^*$ band on passing from indane-1,3-dione to phthalic anhydride, that is diagnostic of an operative chromophore of the type CO–X–CO. (iii) For both series theory predicts the first two transitions to be of the type $n \longrightarrow \pi^*$, their splitting being of the order of 1—1.5 eV in the 1,2-diketones and <0.2 eV in the 1,3-diketones. These results are consistent with experimental evidence on indane-1,2-dione [15] and naphtho-1,4-quinone,[22] which can be considered as a carbocyclic system related to the present 1,3-diketones. (iv) The $n \longrightarrow \pi^*$ bands of the 1,2-dicarbonyls are found to be red-shifted with respect to those of the 1,3-dicarbonyls, in the same way as shown by the related carbocyclic compounds, naphtho-1,2- and -1,4-quinone.[22-24]

All of these properties can be readily accounted for in terms of two main factors: (*a*) the involvement of the heteroatom orbitals in the *n* MOs, which depends both on the nature and the site occupied by the heteroatom; and (*b*) the n_-/n_+ splitting, which in series I arises both from direct through-space and indirect through-bond interactions of the two carbonyl groups while in series II only from an indirect through-bond mechanism transmitted *via* the heteroatom.

Support by the Consiglio Nazionale delle Ricerche of Italy is gratefully acknowledged.

[5/1330 *Received, 7th July,* 1975]

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