

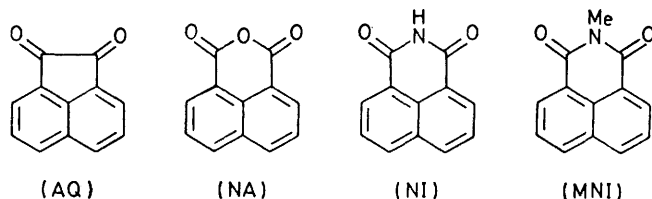
Photoelectron and Electronic Spectra of Acenaphthenequinone, Naphthalic Anhydride, and Naphthalimide

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The u.v. photoelectron spectra of acenaphthenequinone, naphthalic anhydride, naphthalimide, and *N*-methyl-naphthalimide are reported and interpreted employing correlative arguments assisted by results of semiempirical calculations. The core ionisation energies (I.E.s) of the atoms of the carbonyl groups are also reported. For a series of cyclic anhydrides and imides it is shown that there is a fair correlation between the average I.E.s of the carbonyl lone pair orbitals and the average C=O stretching frequencies, while there is no direct correlation between the average *n* I.E.s and the ¹³C carbonyl chemical shifts.

The main features of the u.v.-visible spectra of these compounds have been analysed theoretically by means of SCF-INDO/S-CI calculations and an elucidation of the electronic bands is given in terms of *n* → *π** carbonyl transitions and *π* → *π** transitions of specifically naphthalene origin.

In continuation of a systematic experimental and theoretical investigation of the photophysical properties of heterocyclic diketones,¹⁻⁵ we report here an interpretation of the main features of the u.v. photoelectron and u.v.-visible absorption spectra of naphthalic anhydride (NA), naphthalimide (NI), *N*-methyl-naphthalimide (MNI), and the related carbocyclic system acenaphthenequinone (AQ). A thorough knowledge of



their electronic structures is of current interest since NA and its derivatives form an important group of precursors for organic dyes and have also found applications as fluorescent dyes and in optical bleaching preparations. With this in mind, measurements of the core ionisation energies of the atoms of the carbonyl groups are also reported.

EXPERIMENTAL

All compounds were commercially available products except MNI which was prepared from NA according to general literature methods.⁶

The u.v. photoelectron spectra (Figure 1) were recorded on a Perkin-Elmer PS18 spectrometer. The He(I) resonance line at 584 Å (21.22 eV) served as the ionisation source and the spectra were calibrated against Ar and Xe lines. Reproducibility was ±0.05 and the accuracy of the ionisation energies (I.E.s) was estimated to be ±0.05 or ±0.1 eV depending upon the number of decimal points quoted in Table I. The X-ray photoelectron spectra were recorded on an A.E.I. ES200B spectrometer using Al K_{21,2} as the ionisation radiation. The samples were sublimed *in vacuo* and condensed on to a cooled copper surface before and during measurements. The main C_{1s} line from the samples (assumed to be 285.0 eV) was used for calibration purposes. The reproducibility of the I.E. values was ±0.1 eV.

U.v.-visible absorption spectra for ethanolic solutions were recorded with a Perkin-Elmer 356 spectrophotometer.

I.r. spectra were obtained with a Perkin-Elmer 225 spectrophotometer for Nujol mulls. ¹³C N.m.r. spectra for [2H₆]-dimethyl sulphoxide solutions were run on a Bruker WP80 spectrometer equipped for Fourier transform operation.

SCF-PPP calculations were carried out using parameters reported by Nishimoto and Forster,⁷ except that a value of -25.7 eV was used for the valence-state ionisation energy of >NMe, and the two-centre electron repulsion integrals were estimated by the Mataga-Nishimoto formula.⁸

The singlet-singlet transition energies were computed by a 'spectroscopic' variant of the INDO method, described previously,² referred to as INDO/S-CI, in which the parametrisation and integral evaluation follow the proposals of Ellis *et al.*⁹ The transition energies were computed 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. X-Ray geometries¹⁰ were used for all compounds.

RESULTS AND DISCUSSION

Photoelectron Spectra.—The present molecules can be regarded as being formed by joining an *α*- or *β*-dicarbonyl fragment to a naphthalene nucleus. Based on this assumption and on qualitative perturbation MO arguments, four *π* and two *n* bands are expected to be present in the low I.E. region of the u.v. photoelectron spectrum of AQ and one more *π* band (of predominantly heteroatom character) in the spectra of NA, NI, and MNI. The actual number of bands observed in the spectra (Figure 1) is less, however, indicating that some overlap occurs. In particular, inspection of the relative intensities and full widths at half-maximum (F.W.H.M.) of the bands in the low I.E. region suggests clearly that the first band results from two photoprocesses for AQ and only one for the other compounds; in all cases it shows vibrational structure at 1350 ± 50 cm⁻¹, which may be identified as a skeletal ring stretch. Furthermore, the *π* bands of specifically naphthalene nature must be stabilised relative to those in naphthalene (NP) itself¹¹ by the primarily inductive influence of the dicarbonyl group.

In particular, the *π* band shifts to be noted are the following: (a) passing from NP to AQ results in a nearly

constant stabilisation of *ca.* 0.62 eV while with respect to the parent carbocyclic system acenaphthene¹² this effect amounts to 0.95 eV for all bands but the second, for which a value of 0.70 eV is observed; (b) upon change from an α - to a β -dicarbonyl system (AQ \rightarrow NA) the π I.E.s are raised by *ca.* 0.15 eV because of the greater inductive effect of the $-\text{CO}-\text{O}-\text{CO}-$ system; (c) the destabilisation of the π I.E.s by *ca.* 0.25 eV upon replacing the O atom in NA with NH to form NI reflects the change in the $-I$ power of the heteroatom. The assignment of the π bands of MNI follows readily from that of NI keeping in mind the destabilising effect of the methyl group, especially on π_N , as already observed on going from phthalimide to *N*-methylphthalimide.³

To confirm this assignment the measured vertical I.E.s were correlated with the orbital energies ϵ_j obtained from SCF-PPP calculations, assuming Koopmans' theorem to hold. The equation (1) for the regression line, obtained from a least-squares procedure

$$\text{I.E.}_{\text{obs.}} = -1.0755\epsilon_j - 1.7377 \text{ eV} \quad (1)$$

with 23 points, has a correlation coefficient (*R*) of 0.985 and a standard deviation (s.d.) of 0.18 eV. The values calculated according to equation (1) (Table I) are in fair agreement with the observed I.E.s and provide substantial corroboration to the assignment proposed for the π bands.

Having assigned the uppermost π I.E.s, we can then settle the assignment of the two *n* I.E.s, n_+ (CO in-phase combination) and n_- (CO out-of-phase combination). This is facilitated by the intensity (F.W.H.M.) and shape

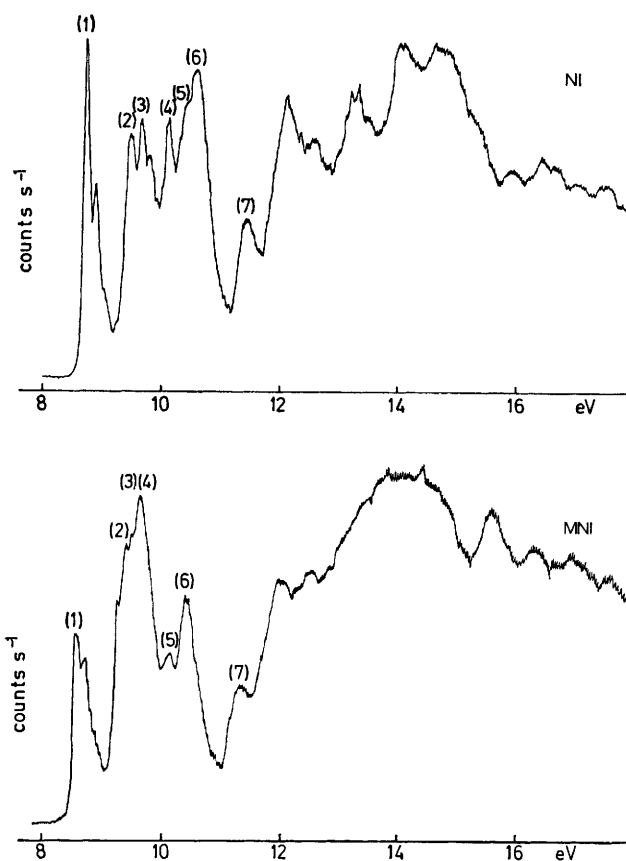
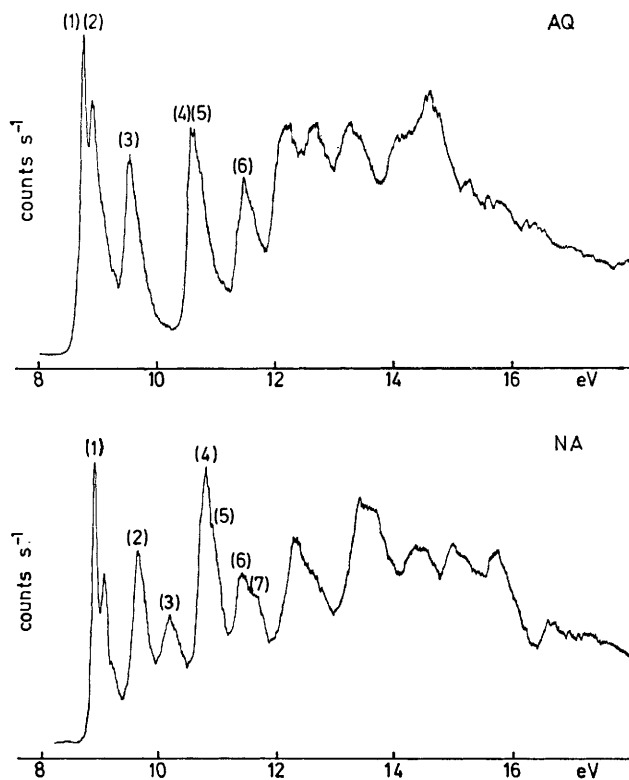


FIGURE 1 He(I) photoelectron spectra of acenaphthenequinone (AQ), naphthalic anhydride (NA), naphthalimide (NI), and *N*-methylnaphthalimide (MNI)

of the bands and by reference to the results for the related compounds phthalic anhydride and phthalimide³ and for carbocyclic 1,2- and 1,3-dicarbonyl compounds.^{13,14}

TABLE I

Measured vertical I.E.s and calculated π I.E.s (in eV)				
Compound	Band	I.E. _{obs.}	Assignment	I.E. _{calc.}
AQ	(1)	{ 8.77 }	$\pi(a_2)$	8.69
	(2)		n_+	
	(3)	9.53	$\pi(b_1)$	9.48
	(4)	{ 10.60 }	$\pi(b_1)$	10.44
	(5)		n_-	
	(6)	11.48	$\pi(a_2)$	11.40
NA	(1)	8.92	$\pi(a_2)$	8.68
	(2)	9.66	$\pi(b_1)$	9.53
	(3)	10.23	n_-	
	(4)	10.78	$\pi(b_1)$	10.37
	(5)	10.95	n_+	
	(6)	11.40	$\pi_O(b_1)$	11.14
	(7)	11.65	$\pi(a_2)$	11.46
NI	(1)	8.68	$\pi(a_2)$	8.68
	(2)	9.43	$\pi(b_1)$	9.51
	(3)	9.63	n_-	
	(4)	10.07	$\pi_N(b_1)$	10.03
	(5)	10.34	n_+	
MNI	(6)	10.54	$\pi(b_1)$	10.64
	(7)	11.40	$\pi(a_2)$	11.45
	(1)	8.57	$\pi(a_2)$	8.67
	(2)	9.40	$\pi(b_1)$	9.50
	(3)	{ 9.63 }	n_-	
	(4)		$\pi_N(b_1)$	9.96
	(5)	10.1	n_+	
(6)	10.40	$\pi(b_1)$	10.61	
(7)	11.35	$\pi(a_2)$	11.43	

The complete assignments and the correlation diagram derived therefrom are in Table 1 and Figure 2.

The main features of the n I.E.s (absolute values, ordering, and splitting) are consistent with the typical patterns established for other cyclic 1,2- and 1,3-dicarbonyl compounds.^{13,14} In particular, the n_- and n_+ I.E.s (9.60 and 10.04 eV) of the monocyclic compound cyclohexane-1,3-dione¹³ are quite close to those observed for NI and lower by 0.6–0.9 eV relative to those for NA. This behaviour implies that in NI the annelation (destabilising) effect is virtually compensated for by the σ -withdrawing (stabilising) power of the N atom and in NA the large electronegativity of the O atom is

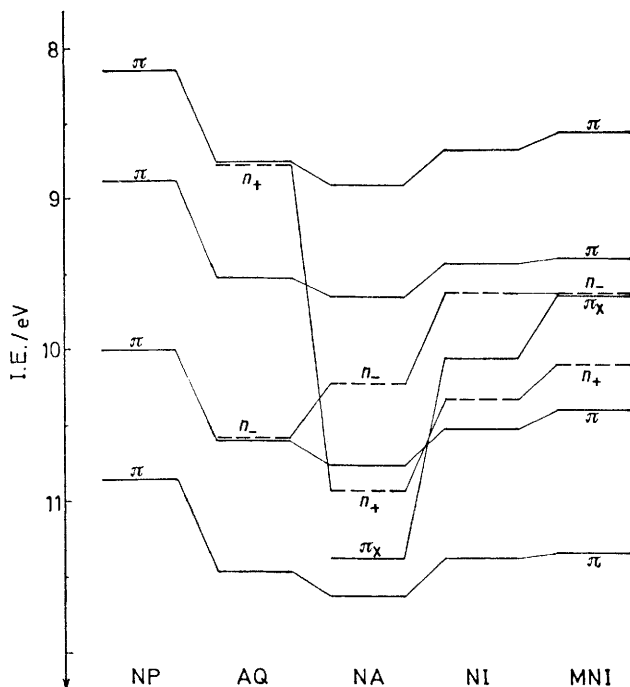


FIGURE 2 Partial correlation diagrams of the I.E.s of naphthalene (NP), acenaphthenequinone (AQ), naphthalic anhydride (NA), naphthalimide (NI), and *N*-methylnaphthalimide (MNI)

the dominant factor. Comparison of the n_{\pm} and π_0 I.E.s of NA with those of the corresponding benzene compound phthalic anhydride³ shows a small destabilisation by 0.3–0.4 eV in NA as a result of larger MO delocalisation and the $+I$ effect of the naphthalene nucleus relative to benzene. A similar effect is apparent also for the related pairs of compounds NI and phthalimide and MNI and *N*-methylphthalimide.³

The n I.E. values are mainly determined by the electron distribution in the CO groups. It is of interest, therefore, to attempt to correlate the n I.E. values (influenced by the charge on the O atom) with the carbonyl chemical shifts in the ¹³C n.m.r. spectra (influenced by the charge on the C atom) and with the C=O stretching frequencies (influenced by the C⁺-O⁻ bond polarity). For a representative sample of cyclic imides and anhydrides, Table 2 includes the average n I.E. values together with the average $\nu(\text{C=O})$ stretching

TABLE 2

Average n ionisation energies,* average C=O stretching frequencies, and carbonyl ¹³C n.m.r. chemical shifts † of some cyclic anhydrides and imides

Compound	I.E./eV	$\nu(\text{cm}^{-1})$	$\delta/\text{p.p.m.}$
Naphthalic anhydride	10.59 ^a (10.54)	1 755 ^a	156.9 ^a
Naphthalimide	9.85 ^a (9.82)	1 686 ^a	164.1 ^a
Phthalic anhydride	10.97 ^b (11.08)	1 806 ^d	162.6 ^k
Phthalimide	10.35 ^b (10.46)	1 747 ^c	167.6 ^k
Succinic anhydride	11.20 ^c (11.21)	1 819 ^f	173.9 ^a
Succinimide	10.44 ^c (10.47)	1 748 ^g	180.4 ^a
Maleic anhydride	11.48 ^b (11.34)	1 831 ^h	165.0 ^l
Maleimide	10.64 ^c	1 765 ^h	173.0 ^m
Glutaric anhydride	10.87 ^c (10.90)	1 789 ⁱ	168.5 ⁿ
Glutarimide	10.27 ^c (10.21)	1 723 ^j	173.8 ⁿ

* Values in parentheses are those calculated according to equation (2). † Downfield of tetramethylsilane.

^a Present work. ^b Ref. 3a. ^c Ref. 13. ^d Y. Hase, C. U. Davanzo, K. Kawai, and O. Sala, *J. Mol. Structure*, 1976, **30**, 37. ^e Ref. 5. ^f S. A. A. Zaidi and Z. A. Siddiqi, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1404. ^g T. Wolbæk, P. Klåboe, and D. H. Christensen, *Acta Chem. Scand.*, 1976, **30A**, 531. ^h A. J. Barnes, L. LeGall, G. Madec, and J. Lauransan, *J. Mol. Structure*, 1977, **38**, 109. ⁱ G. Borgen, *Acta Chem. Scand.*, 1974, **28B**, 13. ^j J. W. Thompson, jun., G. E. Leroi, and A. I. Popov, *Spectrochim. Acta*, 1975, **31A**, 1553. ^k Ref. 1b. ^l C. A. Tolman, A. D. English, and L. E. Manzer, *Inorg. Chem.*, 1975, **14**, 2353. ^m M. T. Chenon, R. J. Pugmire, D. M. Grant, R. P. Panzica, and L. B. Townsend, *J. Heterocyclic Chem.*, 1973, **10**, 427. ⁿ F. J. Koer, A. J. deHoog, and C. Altona, *Rec. Trav. chim.*, 1975, **94**, 75.

frequencies and the $\delta(^{13}\text{C})$ carbonyl chemical shifts of the neutral molecules. The correlation between I.E. and $\nu(\text{C=O})$ obeys equation (2), with $R = 0.987$ and s.d. =

$$\text{I.E.} = 0.010 5\nu - 7.9010 \text{ eV} \quad (2)$$

0.08 eV, which demonstrates the parallel between structural and electronic effects upon these two properties. Some deviations from linearity [values calculated according to equation (2) are in Table 2] may arise from the slightly different nature of the normal modes* and/or from uncertainties in the photoelectron assignments due to band overlapping. On the other hand, it is clear from Table 2 that there is no direct correlation between the n I.E. and $\delta(^{13}\text{C})$ values. This is not unexpected, however, since the chemical shifts are determined by a subtle interplay of charge and magnetic anisotropy effects, which vary significantly not only with the different $-I$ and $+R$ powers of the O and N atoms but also with the molecular size, conformation, and conjugation.

Information on the charge borne by the atoms of the carbonyl groups can also be obtained from the following core I.E. values for O_{1s} and C_{1s}: NA: O_{1s}, 532.8; C_{1s}, 289.1 eV; NI and MNI: O_{1s}, 532.2; C_{1s}, 288.4 eV. The

* For instance, in the imides H-bonding perturbation is operative in the solid state.

X-ray photoelectron data* for NI and MNI are equal as are their average n I.E. values. On going from NI to NA the larger electronegativity of the bridgehead atom decreases the charge density of the carbonyl carbon atoms which, in turn, withdraw negative charge from the carbonyl oxygen atoms; as a consequence the polarity of the carbonyl bond is reduced. These effects are reflected by the increase in the O_{1s} I.E., the average n I.E., and the average C=O stretching frequency.

Electronic Spectra.—There is a close correspondence of bands in the absorption spectra of NA and NI: two partly overlapping bands of medium intensity and with a tail extending towards the visible range appear in the long-wavelength region with maxima at *ca.* 340 and 330 nm and two bands of high intensity lie at shorter wavelengths with maxima at *ca.* 230 and 213 nm. AQ displays some spectral resemblance to NA and NI in the u.v. region with the bands shifted to lower wavelengths and a further weak absorption at *ca.* 500 nm.

The present molecules can be regarded as systems in which a naphthalene unit is tightly conjugated with a strongly localised -CO-CO- or -CO-X-CO- unit. The Platt classification¹⁵ may therefore be a useful scheme for correlating some of their electronic transitions with those of the subsystem naphthalene. Furthermore, the $n \rightarrow \pi^*$ electronic transitions may be described using the nomenclature of the highest occupied and lowest unoccupied MOs localised primarily on the dicarbonyl group as proposed by Arnett *et al.*¹⁶ for 1,2-diketones: n_- , n_+ , π_-^* , and π_+^* . This classification, of course, serves only as a useful tool for interpretation and has no absolute significance since all the MOs are delocalised over all the molecule and considerable mixing of locally excited states of both subsystems occurs in some transitions. On this basis, the INDO/S-CI treatment (Table 3) provides the following interpretation of the spectra.†

For NA and NI the two highest-wavelength bands should be composed of the two lowest theoretical transitions of 1L_b and 1L_a type, respectively, the first being longitudinally and the second transversely polarised.‡ The longitudinally polarised transition predicted at *ca.* 5.50 eV is strongly allowed and of the classical 1B_b -type; it can thus be assigned to the intense band observed at *ca.* 5.38 eV. Two almost degenerate, oppositely polarised transitions calculated at *ca.* 5.98 eV could be thought of as responsible for the shortest-wavelength band; the more intense component is generated by an electronic excitation mechanism similar to that governing the 5.63 eV band of naphthalene. Therefore, according to the present results, the bands of NA and NI of specifically naphthalene nature show a bathochromic shift with respect to the original bands in

* For AQ: O_{1s} , 532.0 eV; C_{1s} , 287.8 eV.

† The theoretical f values are compared in Table 3 with the experimental $\log \epsilon$ values and not with the experimental f values since the complex absorption band envelope of the present compounds places strong doubts on the ability of deconvolution procedures to yield physically meaningful results and to generate a unique solution for the experimental f values.

TABLE 3
Experimental and calculated energies (in eV) for the low-lying singlet excited states

Compound	Experimental	Theory				
	E (log ϵ)	E	f	State	Type	
AQ	<i>ca.</i> 2.48	2.39	6×10^{-5}	1B_1	$n \rightarrow \pi^*$	
	(1.30) ^a					
	(3.39) sh	3.68	0	1A_2	$n \rightarrow \pi^*$	
	3.96	4.14	0.0089	1B_2	$\pi \rightarrow \pi^*$	
	(3.80)	4.30	0.0066	1B_2	$\pi \rightarrow \pi^*$	
	4.09	4.66	0.2441	1A_1	$\pi \rightarrow \pi^*$	
	(3.86)	4.84	0.0079	1A_1	$\pi \rightarrow \pi^*$	
		5.29	0	1A_2	$n \rightarrow \pi^*$	
		5.47	6×10^{-5}	1B_1	$n \rightarrow \pi^*$	
		5.69	1.8143	1B_2	$\pi \rightarrow \pi^*$	
		(4.65) ^b	5.86	0.0001	1B_1	$\sigma \rightarrow \pi^*$
		6.05	6.02	0.6701	1A_1	$\pi \rightarrow \pi^*$
		(4.57)	6.20	6×10^{-5}	1A_1	$\pi \rightarrow \pi^*$
	NA	3.68	4.01	0.0160	1B_2	$\pi \rightarrow \pi^*$
		(3.96) ^b				
		3.80	4.17	0.4403	1A_1	$\pi \rightarrow \pi^*$
		(4.00)	4.80	0	1A_2	$n \rightarrow \pi^*$
			4.89	0.0014	1B_1	$n \rightarrow \pi^*$
			5.03	0.1738	1B_2	$\pi \rightarrow \pi^*$
			5.37	0.0167	1A_1	$\pi \rightarrow \pi^*$
		5.39	5.48	1.4629	1B_2	$\pi \rightarrow \pi^*$
		(4.44)	5.49	5×10^{-5}	1B_1	$n \rightarrow \pi^*$
		5.85	5.97	0.4078	1A_1	$\pi \rightarrow \pi^*$
		(4.39)	5.99	0.0360	1B_2	$\pi \rightarrow \pi^*$
			6.29	0.2373	1A_1	$\pi \rightarrow \pi^*$
			6.30	0	1A_2	$n \rightarrow \pi^*$
NI		3.63	4.06	0.0213	1B_2	$\pi \rightarrow \pi^*$
		(3.97) ^b				
		3.75	4.28	0.4299	1A_1	$\pi \rightarrow \pi^*$
		(3.99)	4.47	0.0013	1B_1	$n \rightarrow \pi^*$
			4.60	0	1A_2	$n \rightarrow \pi^*$
		5.24	0.2662	1B_2	$\pi \rightarrow \pi^*$	
		5.46	0.0228	1A_1	$\pi \rightarrow \pi^*$	
		5.38	5.54	1.0738	1B_2	$\pi \rightarrow \pi^*$
		(4.60)	5.76	2×10^{-5}	1B_1	$n \rightarrow \pi^*$
		5.85	5.98	0.1970	1B_2	$\pi \rightarrow \pi^*$
		(4.33)	5.99	0.5647	1A_1	$\pi \rightarrow \pi^*$
			6.03	0	1A_2	$n \rightarrow \pi^*$
			6.32	0.1315	1A_1	$\pi \rightarrow \pi^*$

^a In cyclohexane, from ref. 20. ^b In ethanol, this work.

naphthalene, 1L_a shifting to a greater extent than 1L_b . This prediction is consistent with the stabilisation of the π occupied MOs, demonstrated by the u.v. photoelectron spectra, and with well established evidence that substituents capable of conjugating at positions 1 and 8 of naphthalene extend conjugation in a transverse direction and cause bathochromic and hyperchromic effects especially in the 1L_a band.¹⁷

For NA and NI the INDO/S-CI treatment predicts also two low-energy closely spaced $n \rightarrow \pi^*$ transitions involving primarily the -CO-X-CO- unit. The electric dipole-forbidden transition ${}^1A_1 \rightarrow {}^1A_2$ arises from a mixture of excitations $n_+ \rightarrow \pi_-^*$ and $n_- \rightarrow \pi_+^*$, the first being more important. The weakly allowed transition ${}^1A_1 \rightarrow {}^1B_1$, polarised perpendicular to the molecular plane, is a combination of the configurations $n_+ \rightarrow \pi_+^*$ and $n_- \rightarrow \pi_-^*$. The fact that these two 'quinonoid' electron-transfer bands are not discernible in the spectra¹⁸ can be taken as experimental evidence

‡ The longitudinal (transverse) direction is parallel (perpendicular) to the long axis of the naphthalene nucleus. The molecules are assumed to lie in the yz plane with the z axis as the C_2 axis.

in favour of very small or null intensity; their computed locations suggest, however, that these excitations are probably obscured beneath the overlapping tails of the intense second and third observed bands. It is satisfying that the theoretical relative positions of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions agree with conclusions from adsorption, fluorescence, phosphorescence, and solvent-effect measurements.¹⁸

For AQ the INDO/S-CI results indicate the first two singlet-singlet transitions to be of the $n \rightarrow \pi^*$ type, well spaced and localised essentially in the -CO-CO-unit. The lower estimated transition, polarised perpendicular to the molecular plane and very weakly allowed in electric dipole radiation, can be described as a nearly pure $n_+ \rightarrow \pi_+^*$ electron promotion and assigned to the weak band observed at *ca.* 2.48 eV. This assignment is consistent with the conclusion of Kuboyama¹⁹ based on an experimental study of the solvent effect on this band. The second, symmetry-forbidden transition is composed of an admixture of $n_+ \rightarrow \pi_-^*$ and $n_- \rightarrow \pi_+^*$ configurations; the energy computations suggest that it is probably buried below the cut-off of the lower allowed $\pi \rightarrow \pi^*$ transition, in agreement with the *ca.* 3.39 eV proposal by Fang and Singer²⁰ based upon the wavelength dependence of several photoprocesses involving AQ. The classification of the other observed bands of AQ parallels closely that proposed here for NA and NI. However, unlike these compounds, AQ is predicted to have also two $\pi \rightarrow \pi_{CO}^*$ transitions involving an electron redistribution between the naphthalene and dicarbonyl subsystems, obscured below the short-wavelength side of the 1L_b and 1L_a bands.

In addition to the good agreement between the experimental and theoretical transitions, good corroboration in favour of the spectral interpretation for NA, NI, and AQ given here is provided by the fact that the INDO/S-CI method leads to an excellent reproduction of the spectrum of naphthalene: theory, 4.03, 4.45, 5.73, and 6.34 eV; observed, 3.97, 4.29, 5.63, and 6.52 eV.²¹

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REFERENCES

- ¹ (a) V. Galasso, G. Pellizer, A. Lisini, and A. Bigotto, *Org. Magnetic Resonance*, 1975, **7**, 591; (b) V. Galasso, G. Pellizer, H. LeBail, and G. C. Pappalardo, *ibid.*, 1976, **8**, 457.
- ² V. Galasso and G. C. Pappalardo, *J.C.S. Perkin II*, 1976, 574.
- ³ (a) V. Galasso, F. P. Colonna, and G. Distefano, *J. Electron Spectroscopy*, 1977, **10**, 227; (b) G. Distefano, D. Jones, F. P. Colonna, A. Bigotto, V. Galasso, G. C. Pappalardo, and G. Scarlata, *J.C.S. Perkin II*, 1978, 441; (c) A. Bigotto, V. Galasso, F. P. Colonna, G. Distefano, G. C. Pappalardo, and G. Scarlata, *ibid.*, p. 1194.
- ⁴ A. Bigotto and V. Galasso, *Spectrochim. Acta*, 1978, **34A**, 923.
- ⁵ A. Bigotto and V. Galasso, *Spectrochim. Acta*, in the press.
- ⁶ A. I. Vogel, 'Practical Organic Chemistry,' Longman, London, 1962.
- ⁷ K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, 1966, **4**, 155.
- ⁸ N. Mataga and K. Nishimoto, *Z. physik. Chem. (Frankfurt)*, 1957, **13**, 140.
- ⁹ R. L. Ellis, G. Kuehnlenz, and H. H. Jaffé, *Theor. Chim. Acta*, 1972, **26**, 131.
- ¹⁰ T. C. W. Mak and J. Trotter, *Acta Cryst.*, 1963, **16**, 811; L. Nguyen Shok, L. A. Chetkina, M. G. Neigauz, G. A. Gol'der, E. M. Smelyanskaya, and Yu. G. Fedorov, *Kristallografiya*, 1971, **16**, 500; A. N. Sobolev, L. A. Chetkina, G. A. Gol'der, Yu. G. Fedorov, and V. E. Zavodnik, *ibid.*, 1973, **18**, 1157.
- ¹¹ F. Brogli, E. Heilbronner, and T. Kobayashi, *Helv. Chim. Acta*, 1972, **55**, 274.
- ¹² R. Boschi, E. Clar, and W. Schmidt, *J. Chem. Phys.*, 1974, **60**, 4406.
- ¹³ D. Dougherty, P. Brint, and S. P. McGlynn, *J. Amer. Chem. Soc.*, 1978, **100**, 5597.
- ¹⁴ R. Gleiter, P. Schang, and G. Seitz, *Chem. Phys. Letters*, 1978, **55**, 144.
- ¹⁵ J. R. Platt, *J. Chem. Phys.*, 1949, **17**, 484.
- ¹⁶ J. F. Arnett, G. Newkome, W. L. Mattice, and S. P. McGlynn, *J. Amer. Chem. Soc.*, 1974, **96**, 4385.
- ¹⁷ H. H. Jaffé and M. Orchin, 'Theory and Applications of Ultraviolet Spectroscopy,' Wiley, New York, 1962, pp. 305-307.
- ¹⁸ I. L. Belaits, R. N. Nurmukhametov, and D. N. Shigorin, *Zhur. fiz. Khim.*, 1969, **43**, 869.
- ¹⁹ A. Kuboyama, *Bull. Chem. Soc. Japan*, 1962, **33**, 1027.
- ²⁰ T. S. Fang and L. A. Singer, *J. Amer. Chem. Soc.*, 1978, **100**, 6276.
- ²¹ H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, 1949, **17**, 470.