Evidence from the Ultraviolet Photoelectron and *X*-Ray Photoelectron Spectra of Phthalimide, Quinolinimide, and their *N*-Methyl Derivatives regarding the Prevailing Tautomeric Form of Quinolinimide

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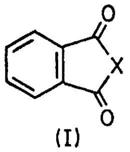
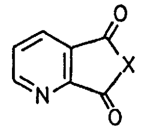
The presence of an anomalous band at 12.1 eV in the u.v. photoelectron spectrum of quinolinimide when compared with those of *N*-methylquinolinimide, phthalimide, and *N*-methylphthalimide is explained as being due to a tautomeric form of quinolinimide different from that in the other compounds. This conclusion is supported by results obtained from *X*-ray photoelectron measurements. I.r. and ^{1}H n.m.r. evidence also confirms the existence of a form with strong hydrogen bonding

We have recently analysed the photoelectron (He^{I}) spectra of heterocyclic 1,3-dicarbonyl compounds containing both the benzene (I)[1] and pyridine nuclei (II).[2] In the course of these investigations we found that the u.v. photoelectron spectrum of quinolinimide (IIc) exhibits some features indicative of a structure different from that of its congeners. In order to elucidate the structural properties of quinolinimide we undertook a comparative analysis of the u.v. photoelectron and *X*-ray photoelectron results of phthalimide (Ic), *N*-methylphthalimide (Id), quinolinimide (IIc), and *N*-methylquinolinimide (IId). To obtain further structural information, i.r. and n.m.r. measurements were also carried out. The assignments of the u.v. photoelectron spectra were made on a correlative basis and were also assisted by the results of semi-empirical calculations.



(I)



(II)

a; X = O
b; X = S
c; X = NH
d; X = NCH_3

EXPERIMENTAL AND CALCULATIONS

Compounds (Ic) and (IId) were available from previous studies.[1,2] Compound (Id) was prepared from (Ia) according to Vogel[3] and compound (IIc) was synthesised as described in the literature.[4]

The u.v. photoelectron spectra were recorded on a Perkin-Elmer PS18 photoelectron spectrometer. The He^{I} resonance line at 58.4 nm (21.22 eV) served as the ionisation source. The spectra were calibrated against Ar and Xe lines. The accuracy of the ionisation energies is estimated to be ±0.05 or ±0.1 eV.

The *X*-ray spectra were recorded by means of an A.E.I. ES200B photoelectron spectrometer using Al $K_{\alpha_{1,2}}$ as the ionising radiation. The samples were sublimed *in vacuo* and condensed onto a cooled gold surface before and during measurements. The $\text{Au}_{4f_{7/2}}$ line (binding energy 83.8 eV)

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[1] V. Galasso, F. P. Colonna, and G. Distefano, *J. Electron Spectroscopy*, 1977, **10**, 227.

[2] A. Bigotto, V. Galasso, F. P. Colonna, G. Distefano, G. C. Pappalardo, and G. Scarlata, *J.C.S. Perkin II*, in the press.

[3] A. I. Vogel, 'Practical Organic Chemistry,' Longman, Green and Co., London, 1962.

[4] E. Suchard, *Ber.*, 1925, **58**, 1727.

from this surface was obtained, together with the signals from the samples, and used for calibration purposes. When calibrating, very thin layers of sample were used so that the signal from the gold was in all cases much more intense than that of the sample to minimise charging effects. Due to the uncertainty involved in the calibration procedures the absolute values of the ionisation energy of the C_{1s}, N_{1s}, and O_{1s} lines may be in error by as much as 1 eV. However, the reproducibility was better than ±0.2 eV for successive sublimations, so that the relative error between corresponding lines of two samples will be of that order.

To assist the spectral analysis we have correlated the measured ionisation energies with the orbital energies obtained from EHT and PPP calculations, assuming Koopmans' theorem to hold.

The parametrisation adopted in the PPP calculations was taken from Fabian *et al.*[5] [with the exception of using the value -22.18 for $W(NCH_3)$ [6] and -2.10 eV for β of ' single ' C–C bonds], and the two-centre repulsion integrals were estimated by the Mataga–Nishimoto formula.

The EHT calculations were performed by taking the values of the valence state ionisation potentials from Hoffmann and Imamura [7] and the values of the orbitals exponents from Clementi and Raimondi,[8] except the one for hydrogen, where 1.30 was preferred [9] to the usual value of 1.00.

TABLE 1

Experimental and theoretical u.v. photoelectron ionization energies (IE) (eV) and corresponding MO assignments

Compound	IE_{exp}	Assignment [a]	IE_{th} (EHT) [b,d]	IE_{th} (PPP) [d]
(Ic) [c]	9.78	π (b_1)	10.74	10.84
	9.90	n_-	10.49	
	9.90	π (a_2)	10.95	11.01
	10.56	π_X	11.92	11.36
	10.68	n_+	10.76	
	12.5	σ	11.47	
(Id) [d]	9.55	π (b_1)	10.64	10.71
	9.9	n_-	10.46	
	9.9	π (a_2)	10.95	10.99
	10.1_5	π_X	11.65	11.15
	10.5	n_+	10.72	
	12.5	σ	11.36	
(IIc) [d]	10.0	n_N	10.00	
	10.0	n_{CO}	10.72	
	10.0	π (a_2)	10.78	10.32
	10.8_5	σ_{CN}	11.18	
	10.8_5	π (b_1)	11.54	10.90
	12.1	π (CO–N–COH)	12.09	11.58
	13.0	σ	12.14	
(IId) [e]	9.8_5	n_N	10.15	
	10.0	π (a_2)	10.64	10.74
	10.0	n_-	10.72	
	10.43	π_X	11.75	11.16
	11.10	n_+	11.34	
	11.2_5	π (b_1)	11.51	11.52
	13.2	σ	12.07	

[a] The standard π (a_2) and π (b_1) MO labelling refers to local symmetry of the six-membered ring. [b] EHT values minus a 3 eV empirical scale factor. [c] Ref. 1. [d] This work. [e] Ref. 2,

DISCUSSION

The experimental u.v. photoelectron results are summarised in Table 1. The valence regions of the spectra of (Ic) and (IId) have been assigned [1,2] on correlative grounds from simple related molecules and *ab-initio* GTO and semi-empirical calculations. The assignment of (Id) follows readily from that of (Ic) keeping in mind the destabilising effect of the methyl group on the π-MOs, especially π_x.

The u.v. photoelectron spectrum of (IIc) (Figure 1) shows two broad intense bands followed by a third band with vibrational fine structure not present in the spectra of (IId) and (Ic and d). This band (ionisation energy 12.1 eV) has an intensity of *ca.* 40% for each of the first two bands. This ratio did not change after several sublimations nor when the spectrum was recorded at different temperatures (80—120°). It is therefore a characteristic feature of the spectrum of (IIc) and must be ascribed to an MO which does not have counterpart in the other derivatives (I) and (II). The peculiar electronic structure of (IIc) could be rationalised if one assumes that this compound exists in a tautomeric form different from that of its congeners.

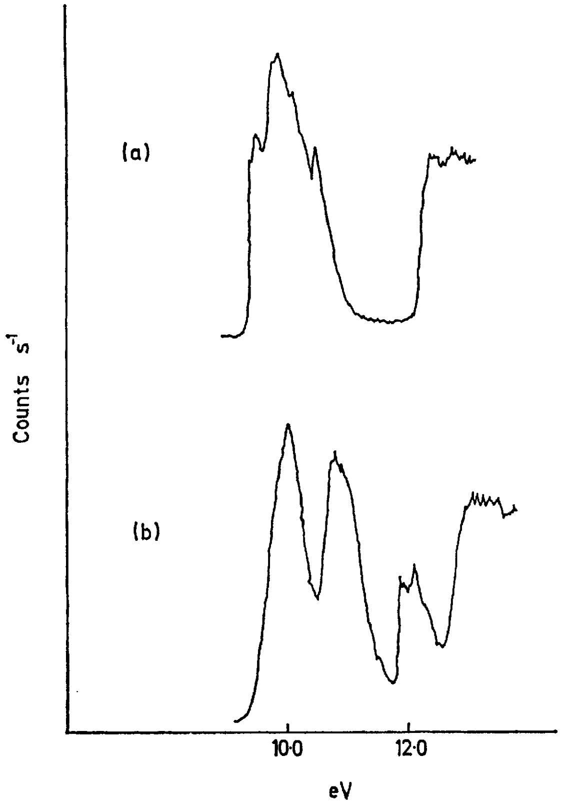

FIGURE 1 U.v. photoelectron spectra of (a) *N*-methylphthalimide and (b) quinolinimide in the gas phase

The same conclusion can be drawn from analysis of the *X*-ray spectra. In fact, the spectra of the benzene derivatives are very similar to each other [(Ic and d)] both in energy and full width at half maximum (FWHM) of the N_{1s}, O_{1s}, and $C_{1s}(CO)$ and $C_{1s}(CH)$ lines and in the energy and intensity of the satellite peaks, probably

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[5] J. Fabian, A. Mehlhorn, and R. Zaradnic, *Theor. Chim. Acta*, 1968, **12**, 247.

[6] J. S. Kwiatkowski, *Theor. Chim. Acta*, 1968, **10**, 47.

[7] R. Hoffmann and A. Imamura, *Biopolymers*, 1969, **7**, 207.

[8] E. Clementi and A. Raimondi, *J. Chem. Phys.*, 1963, **38**, 2626.

[9] R. Hoffmann and J. R. Swenson, *J. Phys. Chem.*, 1970, **74**, 415.

deriving from shake-up phenomena,[10] in the N_{1s}, C_{1s}, and O_{1s} regions of the spectra (Table 2). However, in the case of the pyridine derivatives (IIc and d) (Figure 2) * several differences were observed on going from (IId) to (IIc) for all the observed peaks confirming a peculiar electronic structure for (IIc). The largest differences were observed in the C_{1s}(CO) and O_{1s} energy regions suggesting that the carbonyl group is mainly involved in the different tautomeric form of this compound. Both photoelectron spectral data, however, do not provide conclusive evidence on the nature of the prevailing tautomeric form.

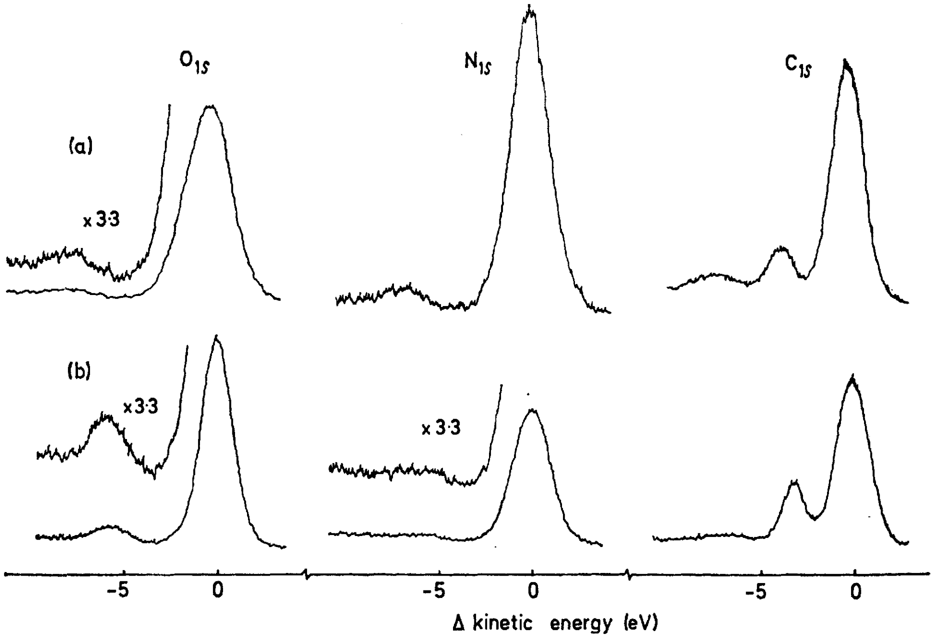

FIGURE 2 O_{1s}, N_{1s}, and C_{1s} regions of the *X*-ray photoelectron spectra of (a) quinolinimide and (b) *N*-methylquinolinimide

TABLE 2

Ionisation energies and FWHM (in parentheses) values in eV from the *X*-ray photoelectron spectra

Compound	O_{1s}	N_{1s}	C_{1s}(CO)	C_{1s}(CH)
(Ic)	534.0	401.3	289.0	285.2
	(1.7)	(1.6)	(1.5)	(1.5)
(Id)	534.1	401.4	288.9	285.3
	(1.7)	(1.7)	(1.5)	(1.7)
(IIc)	534.7	401.1	289.6	286.1
	(2.6)	(1.9)	(1.7)	(2.0)
(IId)	534.3	401.1	289.1	285.9
	(1.6)	(2.3)	(1.4)	(2.1)

In order to gain information about the structure, i.r. and ^{1}H n.m.r. measurements were carried out on the compound. The i.r. spectrum demonstrates the singularity of (IIc) with respect to the other derivatives. In particular, comparison with the spectrum of (Ic) suggests that the difference is mainly in the C(O)–N(H)–C(O) fragment. In fact, whereas the solid state spectrum of phthalimide (Ic) clearly shows the NH stretching band at 3 200 cm^{-1}, no such band may be detected in the range 3 500—3 000 cm^{-1} for quinolinimide (IIc). The Nujol spectrum of (IIc) shows a complex absorption pattern below 3 000 cm^{-1} from which two broad and rather strong bands at 2 440 and 1 900 cm^{-1} and a weaker broad maximum at 2 800 cm^{-1} can be singled out. This pattern is similar to that described for systems with strong hydrogen bonds of the type O–H · · · Base [11,12] rather than to that usually found for N–H · · · X systems, thus suggesting the existence of a strong inter- or intra-molecular interaction of the types in structures (2) and (3), between a proton bound to one of the oxygen atoms and an electron donor atom. Unfortunately, lack of solution i.r. data, due to the low solubility of (IIc) in suitable solvents, does not permit us to draw more precise conclusions.

The ^{1}H n.m.r. spectrum ([$^2H_7$]DMF; 60 MHz) provides evidence for the existence of two structures in solution. The chemical shift difference between the pyridine 2-H in the two forms was found to be extremely large (19 Hz), whereas no more than 1 Hz difference was found for the centre of the multiplets of 3- and 4-H. This suggests the involvement of the pyridine nitrogen atom in hydrogen bonding in one of the structures to account for the different shielding effects on 2-H. Confirmation of very strong hydrogen bonding is provided by the low rate of exchange with heavy water. On the basis of the n.m.r. results, the dimer (3) seems the most likely structure to occur in the solution state.

Thus, the i.r. and n.m.r. evidence indicates structures (2) and (3) stabilised by hydrogen bonding, and excludes

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* The broadening of the N_{1s} and C_{1s}(CH) lines on going from compounds (I) to (II) derives from the substitution of the benzene by the pyridine nucleus. Also the increase of the C_{1s}(CH) ionisation energy has the same origin.

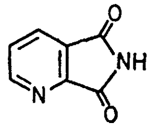
[10] M. A. Brisk and A. D. Baker, *J. Electron Spectroscopy*, 1975, **7**, 197.

[11] D. Hadzi, *J. Pure Appl. Chem.*, 1965, **11**, 435.

[12] A. R. Katritzky and P. J. Taylor, in ' Physical Methods in Heterocyclic Chemistry, ed. A. R. Katritzky, Academic Press, New York, 1974, vol. 4.

structures of type (4) which does not involve the pyridine nitrogen in hydrogen bonding.

If hydroxy-imide form of (IIc) also exists in the gas phase (u.v. photoelectron measurements; *ca.* 100°),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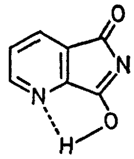
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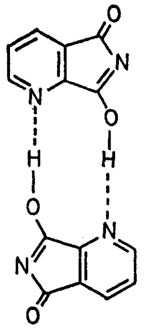
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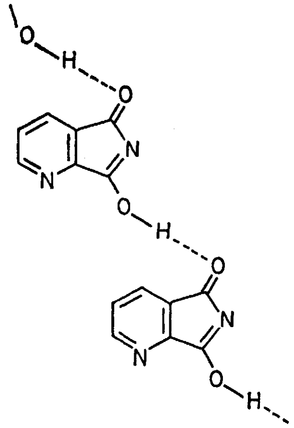
(4)

it can be stabilised only by intramolecular hydrogen bonding, *i.e.* structure (2) should prevail. Assuming that this is the case, it is possible to rationalise the u.v. photoelectron spectrum of (IIc). On the basis of qualitative MO models six bands are expected in the low ionisation energy region. These bands derive from ionisations from two pyridine-like π-MOs (π_{a2} and π_{b1}), one CO lone pair (n_{CO}), two σ-MOs mainly localised on the nitrogen atoms (n_N and $\sigma_{C=N}$), and one π-MO from the hydroxy-imide part of the molecule. The atomic orbital composition is somewhat more complex due to lack of symmetry and intimate mixing among the various group orbitals. The actual number of bands observed in the spectrum is three, but the intensity of the first two indicates that they are formed by two or three ionisation processes. The assignment reported in Table 1 is based on those for (IId), (Ic and d), and for small related compounds such as pyridine,[13] *trans-N*-ethylidenemethylamine,[14,15] simple ketones,[16-18] and alcohols.[19-21]

The EHT calculations reproduce well the ordering of the valence MOs of compounds (IIa, b, and d) [except π_x, see Table 1 for (IId)], but the agreement is unsatisfactory for (IIc) when calculations are carried out on form (1). On the contrary, the orbital sequence for the uppermost occupied MOs calculated for form (2) of (IIc) agrees with that based on the empirical assignment. This agreement confirms the prevalence of form (2) in the gas phase.

On the basis of the spectrum of (IId) and the shifts of the valence MOs deduced from the comparison of (Id) with (Ic), it is possible to reconstruct the virtual spectrum of the dicarbonyl tautomer (1) of quinolinimide. In particular, (1) should have two bands derived from ionisations from π_{b1} and n_+ MOs at *ca.* 11.2—11.3 eV, that is on the high ionisation energy tail of the second band in the spectrum of form (2). The absence of a shoulder at this energy indicates also that in the gas phase form (1), if present, is not more than a few per cent of form (2) in agreement with the solid-phase i.r. results.

In conclusion the present results indicate that quinolinimide (IIc), at variance with phthalimide (Ic), prefers a hydroxy-imide structure stabilised by O–H · · · N hydrogen bonding. In solution (n.m.r. measurements) two forms are present; in the solid phase one structure largely prevails, but the techniques used (*X*-ray photoelectron and i.r. spectroscopy) cannot distinguish between forms (2) and (3); in the gas phase (u.v. photoelectron measurements) only the intramolecularly hydrogen-bonded form (2) is present.

The absence of any evidence for structures such as (2) and (3) for (Ic) confirms the role played by the pyridine nitrogen in stabilising such structures in the case of (IIc).

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