J.C.S. Perkin II

Electronic Structure and Photophysical Properties of Quinolinic Anhydride, Quinolinic Thioanhydride, and *N*-Methylquinolinimide

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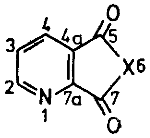
The photophysical properties of the title compounds have been investigated by the following methods: He^I photoelectron spectroscopy, u.v. absorption, ^1H and ^{13}C n.m.r. spectroscopy. The main features of these spectra (the ordering and splitting of the *n* CO and π_X ionizations, the location and nature of the $n\rightarrow\pi$ and $\pi\rightarrow\pi$ transitions, and the spread of the chemical shifts) have been surveyed and interpreted in terms of qualitative and correlative arguments and also with the aid of *ab initio* and semiempirical calculations. The electric dipole moments of quinolinic thioanhydride and *N*-methylquinolinimide have been also measured in benzene solution at 25 °C and compared with those of their benzene congeners.

IN previous papers[1-6] we have studied the electronic structure and various spectroscopic properties of heterocyclic 1,2- and 1,3-dicarbonyl compounds containing the benzene nucleus. We have now extended such investigations to some pyridine analogues, namely quinolinic anhydride (1), quinolinic thioanhydride (2), and *N*-methylquinolinimide (3), and in this paper we present and interpret the following photophysical properties: He^I photoelectron (p.e.) spectra, u.v. absorption, and ^1H and ^{13}C n.m.r. spectra. The discussion of the results is based on qualitative and correlative arguments and is also assisted by comparison with theoretical values calculated by the SCF-MO *ab initio* and semiempirical methods. This paper also reports measurements of the electric dipole moments of (2) and (3).



(1) X=O
(2) X=S
(3) X=NCH3

TABLE 1

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

Compound	α [a]	β [b]	$P_{2\infty}$/cm³	R_D/cm³	μ/D (obs.)	μ/D (MINDO/3)	μ/D (STO-3G)
(1)					5.54 [c]	5.91 (5.35) [d]	4.17
(2)	11.37	−0.337	392.43	48.1	4.13	7.09 (5.04)	
(3)	3.41	−0.554	187.9	45.8	2.84	3.65 (3.36)	2.56

[a] $d = \Sigma(\varepsilon_{12}-\varepsilon_{10})/\Sigma w_2$. [b] $\beta = \Sigma(v_{12}-v_{10})/\Sigma w_2$. [c] In dioxan at 20° (L. R. Caswell, L. Y. Soo, D. H. Lee, R. G. Fowler, and J. B. Campbell, *J. Org. Chem.*, 1974, **39**, 1527). [d] Values calculated from the atomic formal charges.

Since the chemistry of quinolinimide (3; X = NH) is complicated by the presence of an imidole form with O–H · · · N hydrogen bonding, as discussed elsewhere,[7] we have chosen the *N*-methyl derivative (3; X = NCH_3) as the congener of (1) and (2) in the present study.

EXPERIMENTAL

Materials.—Quinolinic anhydride (1), m.p. 137° (from toluene), and *N*-methylquinolinimide (3), m.p. 122—123° [from benzene–ligroin (1 : 1)], were synthesized by literature methods.[8] Quinolinic thioanhydride (2) was prepared from (1) (4 g) and sodium sulphide hydrate (8 g). After stirring of the powdered reagents, the melted mixture was poured into a 20% solution of hydrochloric acid (20 cm³) in crushed ice. The precipitate obtained was filtered, washed with water, and dried. The crude material was crystallized from ligroin, m.p. 91° (Found: C, 50.1; H, 1.8; N, 8.6; S, 19.3. Calc. for $C_7H_3NO_2S$: C, 50.9; H, 1.8; N, 8.5; S, 19.4%).

Physical Measurements.—The electric dipole moments of (2) and (3) were determined in benzene solution at 25 ± 0.01 °C, using apparatus and techniques described earlier.[9] The total solute polarization was obtained by extrapolation to infinite dilution ($P_{2\infty}$) using the Halverstadt–Kumler method.[10] The value of the experimental molar refraction

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[1] V. Galasso, G. Pellizer, A. Lisini, and A. Bigotto, *Org. Magnetic Resonance*, 1975, **7**, 591.

[2] V. Galasso and G. C. Pappalardo, *J.C.S. Perkin II*, 1976, 574.

[3] V. Galasso, G. Pellizer, H. LeBail, and G. C. Pappalardo, *Org. Magnetic Resonance*, 1976, **8**, 457.

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

[5] V. Galasso, G. Pellizer, and G. C. Pappalardo, *Org. Magnetic Resonance*, 1977, **9**, 401.

[6] A. Bigotto and V. Galasso, *Spectrochim. Acta*, in the press.

[7] G. Distefano, D. Jones, F. P. Colonna, A. Bigotto, V. Galasso, G. C. Pappalardo, and G. Scarlata, *J.C.S. Perkin II*, 1978, 441.

[8] A. W. Dox, *J. Amer. Chem. Soc.*, 1915, **37**, 1948; P. Hemmerich and S. Fallab, *Helv. Chim. Acta*, 1958, **41**, 498.

[9] G. C. Pappalardo and S. Pistarà, *J. Chem. Eng. Data*, 1972, **17**, 2.

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

(R_D) for the Na_D line was used as the electronic and atomic polarization ($P_e + P_a$) in calculating the dipole moment (μ) from Debye's formula. The μ values obtained (accuracy ± 0.02 D) and the relevant polarization data are reported in Table 1.

P.e. spectra were recorded on a Perkin-Elmer PS18 photoelectron spectrometer. The He^I resonance line at 584 Å (21.21 eV) served as the ionization source. The spectra were calibrated against Ar and Xe lines. Reproducibility was ± 0.05 eV and the accuracy of the ionization energies (I.E.) is estimated to be ± 0.05 or ± 0.1 eV depending upon the number of decimals quoted in Table 2.

TABLE 2

Experimental and computed I.E. values (eV) and corresponding MO assignments[a]

Compound	Band	I.E. (exp.)	Assignment	I.E. (MINDO/3)	I.E. (STO-3G)
(1)	(1)	10.5_5	n_N	9.33	9.41
	(2)	10.87	$\pi(a_2)$	10.29	8.71
	(3)		n_-	10.31	9.93
	(4)	11.55	$\pi(b_1)$	10.58	9.41
	(5)	11.88	n_+	10.91	10.98
	(6)	12.03	π_X	12.03	10.09
				11.79 σ	13.22 π
(2)	(1)	10.05	n_N	9.61	
	(2)		n_-	9.09	
	(3)		$\pi(a_2)$	9.79	
	(4)	10.67	π_X	10.30	
	(5)	10.99	n_+	9.25	
	(6)	11.2_3	$\pi(b_1)$	10.74	
				11.78 σ	
(3)	(1)	9.8_5	n_N	9.13	9.19
	(2)	10.0	n_-	9.67	9.28
	(3)	10.0	$\pi(a_2)$	9.95	8.19
	(4)	10.43	π_X	10.47	9.03
	(5)	11.10	n_+	10.89	10.83
	(6)	11.2_5	$\pi(b_1)$	10.35	8.96
				11.48 σ	12.72 π

[a] Compounds (1)—(3) have no C_{2v} symmetry, however the $\pi(a_2)$–$\pi(b_1)$ MO labelling serves a useful purpose in identification.

U.v. absorption spectra in ether were recorded on a Perkin-Elmer 356 spectrophotometer.

^1H N.m.r. spectra were measured on a Varian Associates A-60A spectrometer operating at 60 MHz for $CDCl_3$ solutions with tetramethylsilane as internal reference. Natural abundance proton decoupled ^{13}C n.m.r. spectra were obtained using a Bruker HX-90 spectrometer operating at 22.63 MHz in the pulsed Fourier transform mode. Spectral widths of 5 000 Hz and pulse widths of 6 and 10 μs were used. All the spectra were run at ambient probe temperature for a saturated solution of (1) in [^2H]DMF–$CDCl_3$ and for 0.8M solutions of (2) and (3) in $CDCl_3$ with tetramethylsilane as internal reference.

Computations.—The I.E. values were calculated using both the *ab initio* Gaussian-70 package of Hehre *et al.*[11] with the STO-3G basis set and the MINDO/3 semiempirical procedure.[12] The missing parameters $B_{S.O(N)}$ and $\alpha_{S.O(N)}$, required for MINDO/3, were chosen as the geometric mean of the parameters for bonds between like atoms. Unfortunately, convergence difficulties were encountered in the *ab initio* treatment for compound (2) which could not be circumvented either by changing the geometrical model or by using a different basis set.

The singlet–singlet transition energies were computed by a variant of the INDO method, described previously [2] and referred to as INDO/S-CI, in which the parametrization and integral evaluation follow the proposals of Ellis *et al.*[13] 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.

The ring current contributions to the ^1H shielding constants and the magnetic susceptibility normal to the molecular plane were evaluated by the CHF perturbation theory.[14] The MO set used as zero-order function to solve the perturbation problem was obtained by the SCF-MO-VI/1 version of the PPP method proposed by Yoshida and Kobayashi.[15] Using the formal atomic charges yielded by the MINDO/3 treatment, the electric field effect on the proton resonance shifts was estimated by expression (1) derived from the dependence of shielding on electric fields proposed by Buckingham,[16] taking the electric fields as arising from point charges. In equation (1) constants A and

$$\sigma_E = -A \sum_i q_i \cos \theta_i r_i^{-2} - B \sum_i q_i^2 r_i^{-4} \qquad (1)$$

B were given the values adopted by Emsley [17] in a similar calculation for pyridine. The contribution to ^1H shielding from local diamagnetic currents was evaluated from the Ramsey approximate equation (2) where q_{1s} is the total electron density on the hydrogen atom.

$$\sigma_{dia} = (e^2/3mc^2) q_{1s} \langle r^{-1} \rangle_{1s} \qquad (2)$$

For the sake of simplicity calculations were not made on compound (3) but on the parent compound quinolinimide; the N-methyl substituent may be regarded as a minor perturbation to the electronic structure and related properties of the unsubstituted compound.

Idealized geometries were calculated for all compounds from structural data on similar compounds.[18]

RESULTS AND DISCUSSION

P.e. Spectra.—On the basis of qualitative MO models six bands are expected in the low I.E. region of the p.e. spectra of compounds (1)—(3) (Figure 1). These bands derive from ionizations from two pyridine-like π MOs, two CO lone-pairs, one N lone-pair, and one π MO localized mainly on the heteroatom X. Hereafter these MOs are referred to as $\pi(a_2)$, $\pi(b_1)$, n_+ (CO in-phase combination), n_- (CO out-of-phase combination), n_N, and π_X according to the standard designations; as a matter of fact, the atomic orbital composition of these MOs is somewhat more complex due to the lack of symmetry. The actual number of bands observed in the spectra of (1)—(3) is, however, less than expected, but

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[11] W. J. Hehre, W. A. Lathan, M. D. Newton, and J. A. Pople, Quantum Chemistry Program Exchange, Bloomington, Indiana, Program no. 236.

[12] R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, 1975, **97**, 1285.

[13] R. L. Ellis, G. Kuehnlenz, and H. H. Jaffé, *Theor. Chim. Acta*, 1972, **26**, 131.

[14] G. G. Hall and A. Hardisson, *Proc. Roy. Soc.*, 1962, **A268**, 328.

[15] Z. Yoshida and T. Kobayashi, *Theor. Chim. Acta*, 1970, **19**, 377.

[16] A. D. Buckingham, *Canad. J. Chem.*, 1960, **38**, 300.

[17] J. W. Emsley, *J. Chem. Soc. (A)*, 1968, 1387.

[18] P. J. Wheatley, in 'Physical Methods in Heterocyclic Chemistry,' ed. A. R. Katritzky, Academic Press, New York, 1972, vol. 5.

the intensity and shape of some bands indicate that some I.E.s are degenerate or almost so.

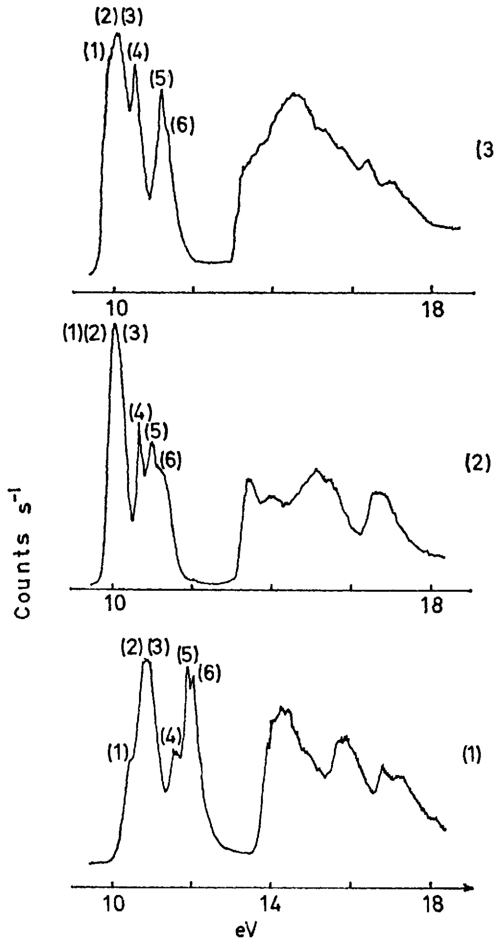

FIGURE 1 Photoelectron He^{I} spectra of quinolinic anhydride (1), quinolinic thioanhydride (2), and *N*-methylquinolinimide (3)

To settle the specific assignments of the bands reference was made to the results obtained for the benzene congeners phthalic anhydride, phthalic thioanhydride, and phthalimide [4] and for small related compounds such as pyridine,[19] maleic and succinic anhydride,[20] and succinimide.[21] Further, it was considered that, if compounds (1)—(3) are regarded as formed by welding pyridine to a CO–X–CO molecule, the following effects should be expected: (1) energy stabilization of the pyridine-like MOs relative to the originals in pyridine caused by the primarily inductive influence of the –CO–X–CO– system, and (2) some destabilization of the n_-, n_+, and π_X MOs of the –CO–X–CO– group due to the larger MO delocalization and inductive effect of pyridine relative to the –CH=CH– subunit. As for the methyl group effect in (3; X = NCH$_3$) compared with (3; X = NH), it can be anticipated that the π_X ionization is lowered by *ca.* 0.4 eV whereas the other ionizations are essentially unaffected. The assignments based on this reasoning and the correlation diagram derived therefrom are presented in Table 2 and Figure 2,

The lone-pair splitting n_-–n_+, arising from through-bond interaction between the two semilocalized *n* CO orbitals, ranges from *ca.* 0.9 to *ca.* 1.2 eV, *i.e.* of the order reported in the literature for other cyclic 1,3-dicarbonyl compounds. It is somewhat larger than that found for the corresponding benzene compounds [4] as a result of the greater inductive power exerted on the –CO–X–CO– fragment by the pyridine nucleus relative to benzene. In fact, both n_- and n_+ are stabilized relative to the benzene congeners, n_+ to a greater extent than n_- because n_+ has greater amplitude at the carbon atom directly linked to the pyridine nitrogen. The higher $n_\pm$ I.E. values of (1) relative to (2) and (3) reflect the greater $-I$ effect of the O atom relative to S and NCH$_3$.

Regarding the correlation of the empirical assignments with quantum mechanical calculations, the MINDO/3 results reproduce qualitatively the general tendencies of the I.E.s in (1) (with the exception of one spurious σ MO intermingled between the correct *n* and π MOs) and in (3) [with only one inversion between $\pi(b_1)$ and π_X] but exaggerate the mixing (and so alter the ordering) of the n_N and $n_\pm$ ionizations in (2) perhaps because of inadequate choice of the $B_{S,O(N)}$ and $\alpha_{S,O(N)}$ parameters. The orbital sequence provided by the *ab initio* treatment of (1) and (3) is unsatisfactory. When doing such a correlation between theory and experiment one must however bear in mind that the reorganization and relaxation energies (neglected by calculation) accom-

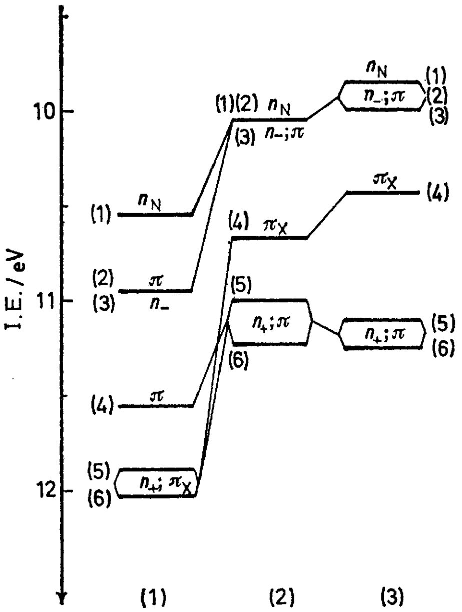

FIGURE 2 Partial energy level diagrams for the outer molecular orbitals of compounds (1)—(3)

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[19] E. Heilbronner, V. Hornung, F. H. Pinkerton, and S. F. Thames, *Helv. Chim. Acta*, 1972, **55**, 289.

[20] M. Almemark, J. E. Bäckvall, C. Moberg, B. Åkermark, L. Åsbrink, and B. Roos, *Tetrahedron*, 1974, **30**, 2503.

[21] W. Schäfer and A. Schweig as quoted by G. Lauer, W. Schäfer, and A. Schweig, *Tetrahedron Letters*, 1975, 3939.

panying n ionizations are greater than those for π ionizations.

U.v. Spectra.—The u.v. spectra of compounds (1)—(3) are dominated by three absorption bands. A broad band of medium intensity appears in the long wavelength region (260—290 nm) and two bands of moderate-to-high intensity lie at shorter wavelengths (260—225 nm) and at *ca.* 215 nm. In (1) and (2) the first band largely overlaps with the second while in (3) the second and third bands are mixed; in compounds (1)—(3) the first band exhibits some inflections which probably represent the vibrational fine structure of one electronic transition associated with the pyridine nucleus.

As shown by the results reported in Table 3 the observed spectra are fairly well reproduced by the INDO/S-CI calculations. In particular, the bands appearing in the u.v. region are correlated with $\pi \rightarrow \pi$ transitions involving the –CO–Py–CO– chromophore. The calculations indicate that the first and third bands are polarized approximately along the long molecular axis with the second band along the short axis. In all cases theory predicts the first four singlet transitions to be of $n \rightarrow \pi$ type, polarized perpendicular to the molecular plane and very weakly allowed in electric dipole radiation. These transitions are composed of scrambled admixtures of $n \rightarrow \pi$ excitations involving both the pyridine nucleus and the –CO–X–CO– group. [In this connection it should be pointed out that some bathochromic displacement of the 'pyridine' $n \rightarrow \pi$ transitions when referenced against pyridine should be expected as a result of the stabilisation undergone by the n_N orbital in (1)—(3) as demonstrated by the p.e. spectra.] The fact that these transitions are not discernible in the spectra can be taken as experimental evidence in favour of very low intensity: their computed locations suggest, however, that these transitions are, at least in part, probably obscured beneath the long wavelength tail of the first observed $\pi \rightarrow \pi$ absorption.

TABLE 3

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

	Experiment	Theory			
Compound	E (log ε)	E	f	State	Type
(1)		3.04	0.0047	$^1A''$	$n \rightarrow \pi$
		3.87	0.0001	$^1A''$	$n \rightarrow \pi$
		4.12	0.0022	$^1A''$	$n \rightarrow \pi$
		4.67	0.0001	$^1A''$	$n \rightarrow \pi$
	4.61 (3.04)	4.68	0.0346	$^1A'$	$\pi \rightarrow \pi$
	5.10 (3.36)	5.43	0.2528	$^1A'$	$\pi \rightarrow \pi$
	5.77 (3.54)	6.21	1.0665	$^1A'$	$\pi \rightarrow \pi$
		6.38	0.0007	$^1A''$	$n \rightarrow \pi$
(2)		3.14	0.0033	$^1A''$	$n \rightarrow \pi$
		3.46	0.0004	$^1A''$	$n \rightarrow \pi$
		3.57	0.0006	$^1A''$	$n \rightarrow \pi$
		4.21	0.0001	$^1A''$	$n \rightarrow \pi$
	4.63 (3.41)	4.56	0.0556	$^1A'$	$\pi \rightarrow \pi$
	5.27 (4.05)	5.04	0.2814	$^1A'$	$\pi \rightarrow \pi$
		5.88	0.0000_2	$^1A''$	$n \rightarrow \pi$
	5.74 (4.29)	6.16	1.0978	$^1A'$	$\pi \rightarrow \pi$
		6.20	0.0006	$^1A''$	$n \rightarrow \pi$
(3)		3.06	0.0048	$^1A''$	$n \rightarrow \pi$
		3.76	0.0003	$^1A''$	$n \rightarrow \pi$
		3.86	0.0018	$^1A''$	$n \rightarrow \pi$
		4.55	0.0000_2	$^1A''$	$n \rightarrow \pi$
	4.54 (3.31)	4.65	0.0347	$^1A'$	$\pi \rightarrow \pi$
	5.46 (4.12)	5.20	0.0690	$^1A'$	$\pi \rightarrow \pi$
		6.14	0.0000_4	$^1A''$	$n \rightarrow \pi$
	5.82 (4.17)	6.21	0.9162	$^1A'$	$\pi \rightarrow \pi$
		6.42	0.2791	$^1A'$	$\pi \rightarrow \pi$

Dipole Moments.—The experimental dipole moments are collected in Table 1 together with the theoretical estimates. The measured μ values vary in the order $NCH_3 < S < O$; this can be rationalized in terms of the marked differences in electronegativity and mesomeric ability of the X atoms. Comparison with the benzene analogues[2] reveals a constant increase of 0.3 D for (1) and (2) and of 0.85 D for (3) which can be expected as a result of replacement of a carbon atom with the electron-withdrawing pyridine nitrogen atom. Indeed, the competing attractive forces for electrons of the anhydride, thioanhydride, and imide functions and of the pyridine nucleus cause larger asymmetry in the electronic charge distribution and thus an increase in μ.

The correlation between experiment and calculation is fairly satisfactory for (1) and (3). The MINDO/3 treatment gives an exaggerated value for (2) as a consequence of overemphasizing the contribution of the atomic dipole on the sulphur atom: the observed trend is correctly reproduced when only the contributions from formal atomic charges are taken into account.

N.m.r. Spectra.—The ^{1}H n.m.r. spectra were analysed using, in the iterative mode, the program LAME[22] coupled to the plotting routine NMRSIM until the computed spectra closely resembled the experimental ones. The r.m.s. error and the standard deviations in the derived parameters were in all cases better than 0.03 Hz. The appreciable broadening observed for the downfield resonance, clearly due to the proton α to the pyridine nitrogen atom, makes specific assignment of the resonances quite easy. As expected, both the range of the resonances and the coupling constants (Table 4) are quite similar to those found for the related pyridinecarbaldehydes.[23]

TABLE 4

^{1}H Chemical shifts[a] and coupling constants (Hz)

Compound	δ_2	δ_3	δ_4	J_{23}	J_{34}	J_{24}
(1)[b]	9.154	7.776	8.355	4.707	8.123	1.669
(2)[b]	9.147	7.815	8.402	4.757	8.048	1.695
(3)[c]	8.975	7.642	8.184	4.966	7.684	1.525

[a] At 60 MHz relative to Me_4Si as internal standard. [b] In CD_3Cl solution. [c] In $CDCl_3$ solution. CH_3 resonance at δ 3.268.

According to current thinking the magnitude of the chemical shifts of protons bound to aromatic systems are determined mainly by relative values of ring currents, magnetic anisotropy, local diamagnetic currents, and charges on other atoms. An insight, even though

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[22] C. W. Haigh, in 'Annual Reports on N.M.R. Spectroscopy,' ed. E. F. Mooney, Academic Press, London, 1971, vol. 4.

[23] W. Danchura, T. Schaefer, J. B. Rowbotham, and D. J. Wood, *Canad. J. Chem.*, 1974, **52**, 3986.

approximate, into the relative importance of some of these factors in compounds (1)—(3) can be obtained from Table 5. Inspection of these theoretical results prompts the following observations. (1) A lower π current effect is operative in the present heterocycles than in benzene (the same conclusion can be inferred by examining the calculated contributions to the magnetic susceptibility normal to the molecular plane). (2) The downfield shifts of the protons *ortho* and *para* to the pyridine nitrogen with respect to benzene arise mainly from the electric field effect and, to a lesser extent, from local diamagnetic currents: the magnetic anisotropy should not play a major role in determining the absolute value of these shifts. (3) For the *meta*-proton the $\Delta\sigma_{\mathrm{E}}$ and $\Delta\sigma_{\mathrm{dia}}$ contributions are practically cancelled by the $\Delta\sigma_{\mathrm{ring}}$ contribution: it can then be argued that the moderate shift of this proton relative to benzene should be determined predominantly by magnetic anisotropy effects.

TABLE 5

Magnitude of different contributions to ^{1}H shielding constants relative to benzene

Compound	Proton	$\Delta\sigma_{\mathrm{ring}}$	$\Delta\sigma_{\mathrm{E}}$	$\Delta\sigma_{\mathrm{dia}}$	$\Delta\sigma_{\mathrm{obs}}$	$\Delta\chi$ [a]
(1)	2	0.439	-1.223	-0.587	-1.89	7.76
	3	0.439	-0.134	-0.335	-0.52	
	4	0.492	-1.607	-0.350	-1.09	
(2)	2	0.453	-1.145	-0.707	-1.89	9.34
	3	0.453	-0.050	-0.457	-0.55	
	4	0.573	-1.599	-0.335	-1.14	
(3)	2	0.528	-1.121	-0.499	-1.71	10.56
	3	0.528	-0.061	-0.247	-0.38	
	4	0.613	-1.408	-0.346	-0.92	

[a] χ = magnetic susceptibility normal to the molecular plane in 10^{-6} c.g.s. e.m.u. units.

The two signals at lowest field in the ^{13}C n.m.r. spectra were in each case readily assigned to the carbonyl carbons. The quaternary ring junction carbons were distinguished by means of off-resonance ^{1}H decoupled spectra. Specific assignments (Table 6) were made on qualitative arguments and by correlation with benzene congeners [3,5] and pyridinecarbaldehydes.[24]

TABLE 6

^{13}C Chemical shifts [a] of (1) in [^{2}H]DMF–$CDCl_3$ saturated solution and of (2) and (3) in $CDCl_3$ solution

Compound	C-2	C-3	C-4	C-4a	C-5	C-7	C-7a
(1)	153.9	126.7	128.8	137.3	158.3	192.5	143.9
(2)	156.8	128.5	132.1	134.0	186.9	187.8	156.4
(3) [b]	155.6	127.3	131.3	119.6	166.9	196.7	152.8

[a] In p.p.m. relative to Me_4Si as internal standard. [b] CH_3 resonance at δ 23.73 p.p.m.

The most striking aspect of the carbon resonances in these compounds concerns the spread of the carbonyl chemical shifts. The current interpretation of a downfield shift of carbonyl resonances invokes the polarity of the carbonyl π-bond,[25] while the scatter of chemical shift values is accounted for in terms of the bond polarity.[26] On these grounds, the present findings can be rationalized by considering that both the C(5)=O and C(7)=O bonds are affected by the inductive and mesomeric effects of the X atoms but the C(7)=O bond is more influenced by the electron withdrawal power of the pyridine nitrogen. Therefore, the C(5)=O shift should be expected to increase with decreasing electron acceptor power of the X atom, since withdrawal of electron charge from the carbonyl oxygen to the X atom is expected to decrease the carbonyl π-bond polarity. This argument implies a large spread of resonances and a trend just as shown by the measured shifts. On the other hand, the C(7)=O resonances should occur downfield relative to C(5)=O and within a more restricted range. This behaviour is shown by the signals assigned to C(7)=O.

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[7/1819 *Received*, 17*th October*, 1977]

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[24] H. L. Retcofsky and R. A. Friedel, *J. Phys. Chem.*, 1968, **72**, 2619.

[25] J. B. Stothers, in 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972.

[26] G. E. Maciel, *J. Chem. Phys.*, 1965, **42**, 2746; K. S. Dhami and J. B. Stothers, *Canad. J. Chem.*, 1965, **43**, 479, 498.