1,3-Dipolar Character of Six-membered Aromatic Rings. Part XXXII.[1] Derivatives of 1-Aryl-3-imidopyridiniums: Preparation and *X*-Ray Crystal Structure

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Various 3-imidopyridiniums have been prepared. The *X*-ray structure of 1-methyl-3-methylsulphonylimidopyridinium confirms the betaine structure.

HAVING previously studied extensively 1-substituted-3-oxidopyridiniums,[2] we have now investigated analogous 3-imido-derivatives (*a*) because superior crystallinity makes them more suitable for *X*-ray crystallographic study and (*b*) to investigate possible 1,3-dipolar reactivity.

1-Methyl-3-methylsulphonylaminopyridinium iodide (1) [readily prepared from 3-methylsulphonylaminopyridine [3] (4) and methyl iodide] when treated with Amberlite IRA 401 (OH) resin gives the betaine (7), m.p. 209—210 °C (*m*/*e* 186), with an n.m.r. spectrum (Table 1) showing upfield shifts of the pyridine ring protons characteristic for the conversion of a halide into a betaine.[4] The betaine (7) has previously been detected [3] in solution and isolated [3] as the perchlorate salt.

Similarly, 1-methyl-3-(2,4,6-trinitroanilino)pyridinium iodide (2) [prepared from 3-(2,4,6-trinitroanilino)pyridine [5] (5) and methyl iodide] furnished 1-methyl-3-(2,4,6-trinitrophenylimido)pyridinium (8), m.p. 258—259 °C (*m*/*e* 319). 3-(2-Nitroanilino)pyridine [6] (6) reacted with methyl iodide to yield the corresponding

TABLE 1

Proton n.m.r. spectra of betaines and halides [a]

	Compound			
Proton(s)	(1) [b]	(2) [c]	(7) [b]	(8) [c]
2	8.70d	8.69d	8.15d	8.35d
4	8.04dt *	8.22dt	7.94dt	7.64dt
5	8.34q	8.03q	7.70q	7.83q
6	8.59d	8.87d	8.06d	8.49d
NMe	4.41s	4.33s	4.23s	4.29s
SO_2Me	3.29s		2.99s	
Ph		9.12s		8.63s

[a] TMPSA as internal standard. [b] In D_2O. [c] In $(CD_3)_2SO$.
* dt = doublet of triplets.

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[2] N. Dennis, A. R. Katritzky, and Y. Takeuchi, *Angew Chem. Internat. Edn.*, 1976, **15**, 1.

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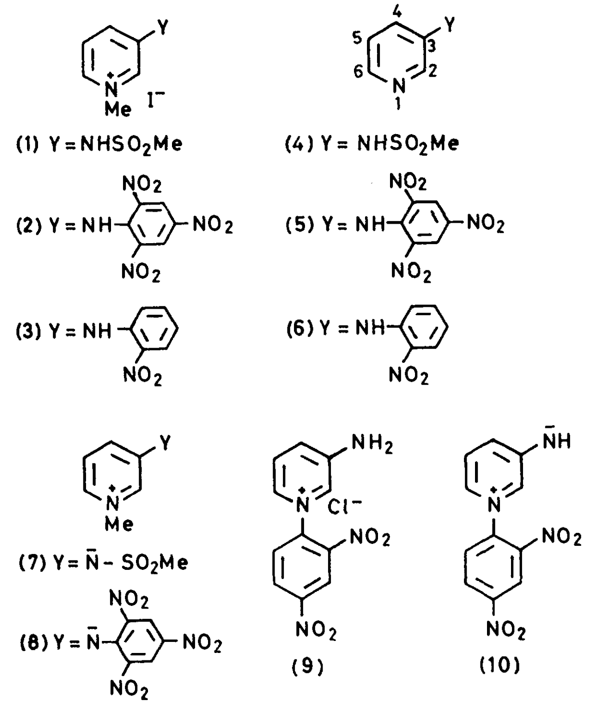
[5] M. D. Coburn and J. L. Singleton, *J. Heterocyclic Chem.*, 1972, **9**, 1039.

[6] T. V. Tsaranova, *Khim. geterotsikl. Soedinenii*, 1965, 909 (*Chem. Abs.*, 1966, **64**, 12637*d*).

quaternary salt (3), m.p. 155—156 °C. However, treatment of 3-amino-1-(2,4-dinitrophenyl)pyridinium chloride (9) (prepared from 3-aminopyridine and 2,4-dinitrochlorobenzene [7]) with triethylamine yielded 3-aminopyridine and 2,4-dinitrochlorobenzene rather than the corresponding betaine (10).



Betaines (7) and (8) were both recovered unchanged when heated with various olefinic electron-deficient and electron-rich dipolarophiles, with dimethyl acetylenedicarboxylate they gave resinous products.

We attribute the superior reactivity in 1,3-dipolar addition of 3-oxidopyridiniums compared to the present 3-imidopyridiniums to the fact that the former form αβ-unsaturated ketones whereas the latter would lead to αβ-unsaturated imines, a less stable class of compound.

X-Ray Crystal Structure of Betaine (7)

Well-shaped, colourless, monoclinic crystals were obtained by slow evaporation at 5 °C from methanol–ethanol.

Crystal Data.—$C_7H_{10}N_2O_2S$, $M = 186.2$. Monoclinic, $a = 9.964 \pm 0.003$, $b = 7.438 \pm 0.001$, $c = 11.366 \pm 0.002$ Å, $\beta = 96.46 \pm 0.02°$, $U = 837.1$ Å^3, $D_m = 1.475$ (by flotation), $Z = 4$, $D_c = 1.47$ g cm^{-3}. Space group $P2_1/c$ (C_{2h}^5) from systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). Mo-K_α radiation, $\lambda = 0.710$ 69 Å; μ(Mo-K_α) = 3.41 cm^{-1}. Cell parameters were derived from oscillation and Weissenberg photographs and refined by a least-square fit to the measured θ angles for 12 accurately centred reflections.

Three-dimensional *X*-ray diffraction intensity data from a crystal *ca.* 1.0 × 0.9 × 0.4 mm were collected on a computer-controlled Syntex P2$_1$ four-circle diffractometer by the θ—2θ scan technique, by use of graphite-monochromated Mo-K_α radiation. In the range $2 \leqslant 2\theta \leqslant 60°$, 2 289 reflections with $I \geqslant 3\sigma(I)$ were selected from the 3 342 reflections collected. The intensities of three standard reflections, chosen in different regions of the reciprocal space and measured every 50 reflections, remained essentially constant throughout. Data were corrected for Lorentz and polarization effects, but not for absorption or extinction.

The position of the sulphur atom in the asymmetric unit was found from an unsharpened Patterson synthesis. A Fourier synthesis phased on the sulphur atom produced a satisfactory trial structure. After a first block-diagonal (4 × 4) least-squares refinement of the positions of the atoms, to which sulphur and carbon form-factors and an overall isotropic temperature factor were assigned, the R value was 0.15. The chemical species were assigned from chemical evidence and by inspection of the peaks found in a Fourier synthesis. Three further cycles of least-squares refinement were then calculated with individual form-factors and individual thermal isotropic parameters, leading to $R = 0.08$.

A difference-Fourier synthesis computed at this stage showed residual electron density in all the positions expected for hydrogen atoms. A final refinement, in which all the non-hydrogen atoms were assumed to vibrate anisotropically and the hydrogen atoms isotropically, lowered R to 0.038. During the refinement the matrix was diagonalized in two blocks only, one containing all the positional terms and the other the thermal and scale parameters, and the weighting scheme was [8] $w = [a + |F_o| + c|F_o|^2]^{-1}$. A final difference-Fourier synthesis showed no significant residual electron density [$\sigma(\rho) = 0.09$ eÅ^{-3}]. A few peaks at the 3σ level could possibly be interpreted as ' bond ' electron density.

TABLE 2

Final positional parameters (× 10^4) with their estimated standard deviations in parentheses

	x	*y*	*z*
N(1)	2 340(12)	−2 027(10)	4 864(10)
C(2)	2 145(12)	−836(12)	3 968(11)
C(3)	3 192(11)	−368(11)	3 300(11)
C(4)	4 427(13)	−1 265(15)	3 602(15)
C(5)	4 592(15)	−2 474(16)	4 524(17)
C(6)	3 533(16)	−2 843(12)	5 170(15)
C(7)	1 191(17)	−2 420(17)	5 539(16)
N(2)	3 130(10)	840(10)	2 383(10)
S	1 921(3)	2 217(3)	2 144(2)
O(1)	2 118(12)	3 169(12)	1 066(10)
O(2)	588(10)	1 427(11)	2 167(11)
C(8)	2 110(15)	3 809(15)	3 302(14)
H(2)	13(2)	−4(2)	38(2)
H(4)	51(3)	−10(3)	32(3)
H(5)	55(3)	−30(3)	48(3)
H(6)	35(3)	−35(3)	59(3)
H(71)	4(3)	−23(3)	51(3)
H(72)	12(3)	−18(3)	61(3)
H(73)	13(3)	−36(3)	58(3)
H(81)	29(2)	45(3)	32(3)
H(82)	21(3)	32(3)	40(3)
H(83)	13(2)	47(3)	32(3)

Atomic scattering factors for sulphur, oxygen, nitrogen, and carbon were taken from ref. 9 and for hydrogen from ref. 10, and the calculations were carried out on a UNIVAC 1110 computer at Rome University, using the program library of the Laboratorio di Strutturistica Chimica ' Giordano Giacomello.' Atomic co-ordinates are given in

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[7] Von W. König, M. Coenen, W. Lorenz, F. Bahr, and A. Bassl, *J. prakt. Chem.*, 1965, **30**, 96.

[8] D. W. J. Cruickshank, in ' Computing Methods in Crystallography,' ed. J. S. Rollett, Pergamon Press, Oxford, 1965, p. 114.

[9] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[10] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

Table 2, whilst all other relevant data regarding molecular geometry and packing, and the observed structure amplitudes and calculated structure factors, are published in Supplementary Publication SUP 22019 (11 pp., 1 microfiche),* which includes final anisotropic temperature factors for non-hydrogen atoms, isotropic temperature factors for hydrogen atoms, observed structure amplitudes and calculated structure factors, bond lengths and angles, the least-squares plane of the pyridinium ring with distances of atoms from this plane, and internal rotation angles of the side-chain of the molecule.

Intramolecular bond lengths and angles are shown in Figures 1 and 2, together with the crystallographic numbering used. The estimated standard deviations are in general 0.002 Å and 0.1° for bond lengths and angles not involving hydrogen atoms.

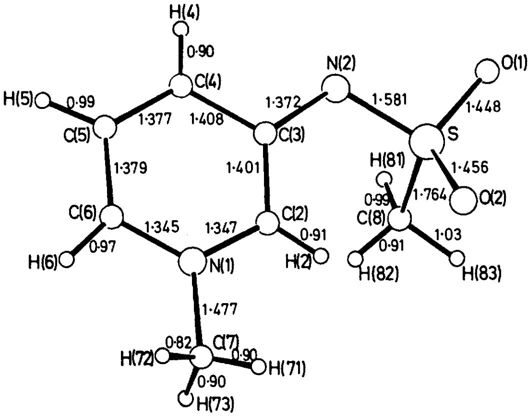

FIGURE 1 Bond lengths for molecule (7)

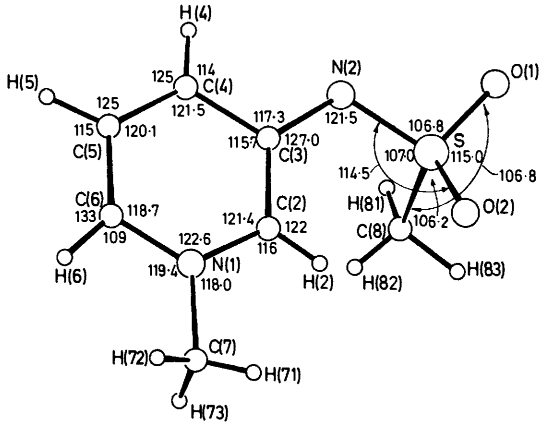

FIGURE 2 Bond angles for molecule (7)

The geometry of the pyridinium ring is significantly different from that reported for pyridine itself.[11] The presence of the methyl group on N(1) gives rise to a marked increase of the C(2)–N(1)–C(6) angle (122.6 *vs.* 116.9°), as expected on the basis of the VSEPR theory.[12]

Interestingly, the expected C_{2v} symmetry of the ring is destroyed by the presence of the substituent on C(3), which gives rise to (i) a 0.02—0.03 Å lengthening of the C(2)–C(3) and C(3)–C(4) bonds, as compared with C(5)–C(6) and C(4)–C(5), respectively, and (ii) a 4° decrease of the angle C(2)–C(3)–C(4) with respect to the angle C(4)–C(5)–C(6). According to Coulson *et al.*[13] the two effects are indicative of extensive conjugation between the substituent and the ring. The rather short C(3)–N(2) bond [1.372(2) Å] is consistent with this result. The dihedral angle between the least-squares plane of the pyridinium ring and the plane through atoms C(3), N(2), and S is 13.9°, and the dihedral angle between the latter and the plane through atoms N(2), S, and C(8) is 70.6°.

The sulphur–nitrogen and sulphur–oxygen bond distances are in good agreement with literature values.[14] It is worth remarking that one of the two oxygen atoms, O(2), has a close contact with a C–H group of the pyridinium ring, C(2)–H(2). The O(2) · · · C(2) distance [2.953(2) Å] is in agreement with values reported by Donohue for a number of similar interactions.[15]

EXPERIMENTAL

The m.p.s were determined with a Reichert apparatus. Spectra were recorded with a Perkin-Elmer model 257 grating spectrophotometer, a Hitachi–Perkin-Elmer RMU 6E mass spectrometer, a Unicam SP 800A spectrophotometer, and a Varian HA 100 n.m.r. spectrometer.

1-*Methyl*-3-(2-*nitroanilino*)*pyridinium Iodide* (3).—3-(2-Nitroanilino)pyridine (6) (1.08 g, 0.005 mol) [m.p. 95—96 °C (lit.,[6] 95—96 °C)] and MeI (2.2 g, 0.015 mol) in tetrahydrothiophen 1,1-dioxide (25 ml) were heated (60 °C) for 72 h. Evaporation of solvent *in vacuo* (130 °C at 7 mmHg) gave the *quaternary salt* (3) (1.25 g, 70%) as yellow needles (EtOH), m.p. 155—156 °C (Found: C, 40.1; H, 3.5; N, 11.6. $C_{12}H_{12}IN_3O_2$ requires C, 40.4; H, 3.4; N, 11.8%).

1-*Methyl*-3-(2,4,6-*trinitroanilino*)*pyridinium Iodide* (2).—3-(2,4,6-Trinitroanilino)pyridine [1.5 g, 0.005 mol, m.p. 173 °C (lit.,[5] 173 °C)] and MeI in propan-1-ol (50 ml) were heated under reflux (97 °C) for 24 h. After cooling, the red precipitate was collected and crystallised from EtOH to give the *iodide* (2) (1.15 g, 70%) as red needles, m.p. 200 °C (Found: C, 32.6; H, 2.4; N, 15.9. $C_{12}H_{10}IN_5O_6$ requires C, 32.2; H, 2.3; N, 15.7%); δ (D_2O) 4.31 ($N-CH_3$).

1-*Methyl*-3-(2,4,6-*trinitrophenylimido*)*pyridinium* (8).—The quaternary salt (2) (0.9 g, 0.002 mol) in MeCN (20 ml) was treated with Et_3N (1 g, 0.01 mol) at room temperature for 12 h. The filtered product crystallised from EtOH to give *compound* (8) (0.6 g, 90%) as red plates, m.p. 258—259 °C (decomp.) (Found: C, 45.0; H, 3.2; N, 21.5. $C_{12}H_9N_5O_6$ requires C, 45.2; H, 2.8; N, 21.9%); *m/e* 319.

1-*Methyl*-3-*methylsulphonylaminopyridinium Iodide* (1).—3-Methylsulphonylaminopyridine (3.5 g, 2.03×10^{-2} mol) [m.p. 140 °C (lit.,[3] 140—141 °C)] and MeI (6 g, 4.2×10^{-2} mol) were heated under reflux in dry MeOH (20 ml) for 5 h. The cooled yellow solution deposited the *quaternary salt* (1) (4.2 g, 65.9%) as colourless plates from MeOH, m.p. 209—210 °C (Found: C, 26.9; H, 3.3; N, 8.7. $C_7H_{11}IN_2O_2S$ requires C, 26.8; H, 3.5; N, 8.9%); $\nu_{max.}$ (Nujol) 1 630, 1 590, 1 503, 1 464, 1 380, 1 350, 1 317, 1 265, 1 160, 980, 955, 867, 809, and 788 cm^{-1}.

1-*Methyl*-3-*methylsulphonylimidopyridinium* (7).—The

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1976, Index issue.

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[12] R. J. Gillespie and R. S. Nyholm, *Quart. Rev.*, 1957, **11**, 339.

[13] A. Domenicano, A. Vaciago, and C. A. Coulson, *Acta Cryst.*, 1975, **B31**, 221.

[14] M. Alléaume, A. Gulko, F. H. Herbstein, M. Kapon, and R. E. Marsh, *Acta Cryst.*, 1976, **B32**, 669.

[15] J. Donohue, in 'Structural Chemistry and Molecular Biology,' ed. A. Rich and N. Davidson, Freeman, San Francisco, 1968, p. 443.

quaternary salt (1) (15 g, 4.78 × 10^{-2} mol) in 200 ml water was treated with Amberlite IRA 401 (OH) (250 g) to give the *betaine* (7) as colourless plates (7.22 g, 81.2%), m.p. 209—210 °C (from MeOH) (Found: C, 44.8; H, 5.4; N, 15.3. $C_7H_{10}N_2O_2S$ requires C, 45.1; H, 5.4; N, 15.1%); $\nu_{max.}$ (Nujol) 1 600, 1 570, 1 380, 1 337, 1 321, 1 245, 1 195, 1 160, 1 100, 1 030, 985, 960, 830, 815, 798, 761, and 715 cm^{-1}; *m/e* 186.

3-*Amino*-1-(2,4-*dinitrophenyl*)*pyridinium chloride* (9).—3-Aminopyridine (1.88 g, 0.02 mol) and 2,4-dinitrochlorobenzene (4.05 g, 0.02 mol) in $HCONMe_2$ were heated at 20 °C for 20 h. The collected precipitate was washed with $HCONMe_2$ (5 ml), and dried to give the required *chloride* (9) (5.6 g, 95%) as yellow needles, m.p. 240 °C (lit.,[7] 238—240 °C) (Found: C, 44.6; H, 3.3; N, 18.7. Calc. for $C_{11}H_9ClN_4O_4$: C, 44.5; H, 3.1; N, 18.8%).

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