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Structure of 1-Acetyl-7,8-dimethoxy-2(1*H*)-one

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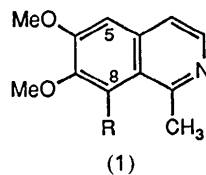
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Abstract. $C_{14}H_{12}N_2O_4$, $M_r = 272.3$, monoclinic, $P2_1/c$, $a = 10.385$ (2), $b = 16.419$ (3), $c = 7.539$ (5) Å, $\beta = 106.73$ (4)°, $V = 1231.0$ (9) Å³, $Z = 4$, $D_x = 1.47$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 1.19$ cm⁻¹, $F(000) = 568$, $T = 295$ K, $R = 5.9\%$ for 1363 observed [$I/\sigma(I) \geq 3$] reflexions. The title tricyclic is essentially flat, the 12 atoms of the ring system lying within 0.05 Å of their least-squares best plane. The two carbonyl groups of the imide functional group are oriented *anti*, with the substituent planar acetyl group making a dihedral angle of 18° with the five-membered ring. This close planarity forces the adjacent methoxy methyl out of the plane to the extent of 80°; the other methoxy lies essentially in the plane of the molecule. The structure of this tricyclic imide confirms that nitration of 6,7-dimethoxy-1-methylisoquinoline takes place at the more hindered benzene ring carbon, C8.

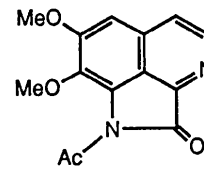
Introduction. In acid solution isoquinolines typically undergo electrophilic substitution *via* the isoquinolinium cation (Brown & Harcourt, 1960); nitration occurs at C5 and C8 with the former predominating to the extent of 9:1 (Dewar & Maitlis, 1957). Using 6,7-dimethoxy-1-methylisoquinoline (1*a*) (Spath & Polgar, 1929) as starting material and requiring from it an intermediate with a nitrogen substituent at C8, we initially assumed that the intrinsic isoquinoline 5 > 8 positional electrophilic substitution tendency would, if anything, be enhanced, in the undesired sense, by the presence of the 1-methyl group and

therefore that direct nitration of (1*a*) would lead predominantly to a 5-nitro derivative. Accordingly we explored the possibility of reversibly blocking the 5-position and indeed bromination did give (mainly) the 5-bromo derivative, which *via* subsequent 8-nitration and hydrogenolytic removal of halogen allowed entry to the desired series. However, we subsequently found that low temperature direct nitration of (1*a*) gave (mainly) a mononitro derivative (1*b*) (Balczewski, Street, Mallon & Joule, 1990) which did not have the predicted 5-nitro structure. It was shown to be the 8-nitro isomer by spectroscopic means, and by a chemical sequence which culminated in a tricyclic imide, shown by the X-ray crystallographic study described herein to have structure (2). One other compound with this ring structure has been reported (Kubo, Saito, Nakahara & Iwata, 1982).



(1)

R a H b NO₂ c NH₂ d NHAc



(2)

Experimental. Nitration of 6,7-dimethoxy-1-methylisoquinoline (1*a*) with fuming nitric acid at 223 K gave a mononitro derivative which was proved to be (1*b*). Thus, reduction of 6,7-dimethoxy-1-methyl-8-nitroisoquinoline (1*b*) gave the corresponding amine (1*c*) which, after *N*-acetylation

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Table 1. Crystal coordinates for (2)

The values given under B_{iso} are the equivalent isotropic values in the case of the non-hydrogen atoms and the refined values of B_{iso} for the hydrogen atoms.

	x	y	z	$B_{iso}(\text{\AA}^2)$
C1	0.0981 (4)	0.2401 (3)	0.3421 (6)	3.2
C2	0.0312 (4)	0.3111 (3)	0.2795 (6)	3.5
C3	0.1188 (5)	0.3793 (3)	0.3735 (7)	3.8
N4	0.2386 (4)	0.3411 (2)	0.4874 (5)	3.3
C5	0.2241 (4)	0.2547 (3)	0.4702 (6)	3.0
C6	0.2947 (4)	0.1880 (3)	0.5549 (6)	2.9
C7	0.2370 (4)	0.1079 (3)	0.5008 (6)	3.3
C8	0.1148 (5)	0.0955 (3)	0.3696 (7)	3.6
C9	0.0405 (4)	0.1641 (3)	0.2879 (6)	3.1
C10	-0.0875 (5)	0.1688 (3)	0.1585 (7)	4.1
C11	-0.1448 (5)	0.2432 (3)	0.1030 (7)	4.2
N12	-0.0902 (4)	0.3168 (2)	0.1617 (5)	4.1
O13	0.0979 (4)	0.4514 (2)	0.3570 (5)	5.4
C14	0.3585 (5)	0.3829 (3)	0.5760 (7)	4.2
C15	0.3524 (8)	0.4734 (3)	0.5999 (10)	5.5
O16	0.4628 (4)	0.3466 (2)	0.6285 (6)	6.4
O17	0.4085 (3)	0.1911 (2)	0.6989 (4)	4.0
C18	0.5286 (6)	0.1717 (5)	0.6509 (12)	5.9
O19	0.3148 (3)	0.0474 (2)	0.5961 (5)	4.3
C20	0.2621 (7)	-0.0342 (3)	0.5625 (10)	4.9
H8	0.0822 (45)	0.0408 (29)	0.3367 (62)	4.4 (11)
H10	-0.1282 (42)	0.1207 (27)	0.1075 (59)	3.3 (11)
H11	-0.2297 (46)	0.2429 (26)	0.0094 (60)	3.6 (10)
H151	0.4333 (55)	0.4892 (33)	0.6988 (77)	6.0 (14)
H152	0.2704 (70)	0.4899 (41)	0.6326 (88)	8.9 (20)
H153	0.3380 (58)	0.4968 (38)	0.4788 (87)	6.7 (17)
H181	0.5468 (67)	0.2108 (43)	0.5651 (97)	9.4 (22)
H182	0.5259 (68)	0.1192 (46)	0.5900 (97)	9.6 (23)
H183	0.6056 (79)	0.1780 (47)	0.7558 (112)	11.8 (25)
H201	0.1777 (45)	-0.0385 (27)	0.5946 (59)	3.5 (10)
H202	0.3271 (53)	-0.0687 (34)	0.6541 (73)	6.2 (14)
H203	0.2504 (53)	-0.0470 (33)	0.4254 (80)	6.8 (15)

Table 2. Molecular geometry for (2)

Atoms				Bond lengths (Å)			Bond angles (°)		τ (°)
A	B	C	D	A-B	B-C	C-D	ABC	BCD	
C1	C2	C3	N4	1.369 (6)	1.487 (7)	1.437 (6)	107.2 (4)	105.2 (4)	1.3 (5)
C1	C2	C3	O13			1.203 (6)		128.6 (4)	179.7 (5)
C1	C2	N12	C11		1.320 (6)	1.354 (7)	125.7 (4)	112.7 (4)	-0.9 (7)
C1	C5	N4	C3	1.406 (6)	1.428 (6)		106.5 (4)	109.2 (4)	-1.8 (5)
C1	C5	N4	C14			1.410 (6)		125.6 (4)	-168.3 (4)
C1	C5	C6	C7		1.368 (6)	1.454 (6)	116.9 (4)	118.0 (4)	2.5 (6)
C1	C5	C6	O17			1.356 (5)		124.7 (4)	-170.7 (4)
C1	C9	C8	C7	1.394 (6)	1.403 (6)	1.382 (7)	117.1 (4)	118.1 (4)	-1.8 (6)
C1	C9	C10	C11		1.406 (7)	1.371 (7)	113.2 (4)	120.1 (5)	-2.0 (7)
C2	C1	C5	C4				111.8 (4)		-1.0 (5)
C2	C1	C5	C6						174.1 (4)
C2	C1	C9	C8				122.0 (4)		-176.1 (4)
C2	C1	C9	C10						2.9 (6)
C2	C3	N4	C5						-1.9 (5)
C2	C3	N4	C14					124.4 (4)	168.3 (4)
C2	N12	C11	C10					126.3 (4)	1.8 (7)
C3	C2	C1	C5						-0.3 (5)
C3	C2	C1	C9						176.8 (4)
C3	C2	N12	C11				127.0 (4)		-178.8 (5)
C3	N4	C5	C6					136.3 (4)	-171.8 (5)
C3	N4	C14	C15			1.500 (9)			118.5 (5)
C3	N4	C14	O16			1.200 (7)			-161.0 (5)
N4	C3	C2	N12						179.6 (4)
N4	C5	C1	C9						126.2 (4)
N4	C5	C6	C7						-177.8 (4)
N4	C5	C6	O17						175.7 (5)
C5	C1	C2	N12						2.5 (8)
C5	C1	C9	C8						-178.5 (4)
C5	C1	C9	C10						0.5 (7)
C5	N4	C3	O13						179.4 (4)
C5	N4	C3	O13						179.7 (5)
C5	N4	C14	C15						-173.3 (5)
C5	N4	C14	O16						7.6 (7)
C5	C6	C7	C8						123.7 (4)
C5	C6	C7	O19			1.350 (6)			-0.4 (7)
C5	C6	O17	C18			1.432 (8)			112.4 (4)
C6	C5	C1	C9						-179.0 (4)
C6	C5	N4	C14						-106.6 (5)
C6	C7	C8	C9						-2.7 (7)
C6	C7	O19	C20			1.442 (7)			18.0 (8)
C7	C6	O17	C18				116.9 (4)		-1.8 (7)
C7	C6	O17	C18						175.6 (4)
C7	C8	C9	C10						80.1 (5)
C8	C7	C6	O17						129.7 (4)
C8	C7	O19	C20						-177.0 (5)
C8	C9	C10	C11						173.4 (4)
C9	C1	C2	N12				123.9 (4)		-2.9 (7)
C9	C8	C7	O19						176.8 (5)
C9	C10	C11	N12						-1.5 (7)
N12	C2	C3	O13						176.6 (4)
O13	C3	N4	C14						-0.3 (8)
O17	C6	C7	O19						-2.1 (8)
									-10.1 (8)
									-5.2 (6)

[giving (1d)], was then oxidized with 2 mol equivalents of selenium dioxide in refluxing dioxan. It was our anticipation that this would lead to the conversion of the 1-methyl substituent to carboxylic acid but in the event a crystalline tricyclic imide, (2), was obtained.

A sample, m.p. 477–448 K, suitable for crystallography was obtained by recrystallization from ethyl acetate as transparent, yellow, uniformly thin crystals, elongated in the c direction. A specimen of size 0.19 × 0.06 × 0.30 mm was cut and used for data collection up to 25° θ on the CAD-4 diffractometer system. Cell dimensions were determined by least-squares refinement of 25 automatically centred reflexions. Graphite-monochromated Mo $K\alpha$ radiation was monitored by repeated measurement of a standard reflexion and no drift correction was found to be necessary. Using $\omega/2\theta$ mode with ω scan width (0.75 + 0.35 tan θ)° and counting times up to 200 s per reflexion, 4732 data were measured in the hemisphere ($\pm h \pm k + l$). A unique non-zero set of 1671 of these were input to the MULTAN80 direct methods program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). A 20-atom solution was recognized from results of 280 E values > 1.35. F values < 2 $\sigma(F)$ were rejected to produce 1363 observations which were used in structure refinement and Fourier calculations. No absorption correction was made as $\mu R < 0.04$. The least-squares refinement program was written by one of us (OSM). The

maximum shift/e.s.d. in the final cycle was 0.46. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

After initial refinement of positional and isotropic temperature parameters it was possible to locate all 12 expected hydrogen atoms by difference Fourier synthesis at $R = 12\%$. The completed structure then refined to $R = 5.93\%$, $wR = 5.93\%$, with anisotropic temperature factors for the non-hydrogen atoms. All hydrogen atoms refined to acceptable positions with B values ranging from 3.3 Å² for H10, an aromatic ring hydrogen, to 11.4 Å² for H183, a methyl hydrogen. After consideration of (ΔF)² distributions over the F and $\sin\theta/\lambda$ ranges, unit weights were applied to the reflexions, $S = 1.10$. A final difference synthesis showed positive and negative peaks were within the range $\pm 0.2 e \text{ \AA}^{-3}$.

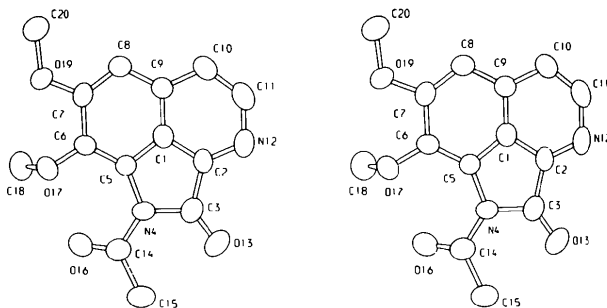


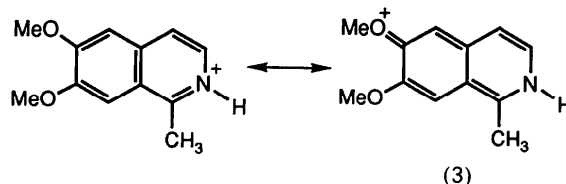
Fig. 1. Stereodrawing, after Johnson (1976), of (2) showing numbering scheme, and the 50% probability ellipsoids.

Discussion. The atomic parameters for 1-acetyl-7,8-dimethoxypyrrolo[2,3,4-*ij*]isoquinolin-2-one, (2), are listed in Table 1.* Table 2 lists the total molecular geometry for (2), and Fig. 1 shows a stereoscopic drawing of the molecule with the numbering system used in the tables. The tricyclic heterocycle is essentially planar, each of the 12 ring atoms lying within 0.05 Å of their least-squares best plane. The five-membered ring is planar to within 0.012 Å and the benzene and pyridine rings to within 0.018 Å. The two imide carbonyl groups are arranged in an *anti* fashion. The extent of conjugation in the imide grouping is reflected in the dihedral angle of only 18° between the ring and its acetyl substituent. This near coplanarity in turn forces the adjacent methoxy group out of the plane of the benzene ring (80°); the

* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53831 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

remaining methoxy group achieves planarity (-3°) with the benzene ring by twisting its methyl away from its adjacent methoxy.

One may rationalize the preferred regioselectivity of electrophilic nitration of (1a) by assuming that substitution involves the 2-protonated species (1a)—H⁺ and that this reduces [*cf.* resonance contributor (3)] the electron-releasing ability of the 6-methoxy group, allowing the influence of the 7-methoxy group to control the position of introduction of the electrophile.



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Structure of 3-Methyl-1,2,3,4,5,6-hexahydro-1,6-methano-3-benzazocinium Hydrogen Oxalate

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Abstract. C₁₃H₁₈N⁺.C₂H₂O₄⁻, *M_r* = 277.3, orthorhombic, *P*2₁2₁2₁, *a* = 5.752 (1), *b* = 15.502 (2), *c* = 15.910 (2) Å, *V* = 1418.6 (6) Å³, *Z* = 4, *D_x* = 1.298 g cm⁻³, *Mo Kα* (*λ* = 0.71069 Å), *μ* = 1.01 cm⁻¹, *F*(000) = 592, *T* = 295 K. Final *R* = 0.035, *wR* = 0.042 for 1003 reflections with *I* > 3σ(*I*). The compound is an ammonium hydrogen oxalate.

Both O atoms of the ionized carboxyl group act as acceptors in the formation of two hydrogen bonds: (a) an N—H⋯O bond linking the cation and anion with N⋯O and H⋯O distances of 2.722 (4) and 1.78 (5) Å and (b) a strong O—H⋯O bond linking a chain of oxalate ions along *a* with O⋯O and H⋯O distances of 2.578 (4) and 1.59 (6) Å. The relative