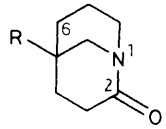
Conformational Study of Bridgehead Lactams. Preparation and *X*-Ray Structural Analysis of 1-Azabicyclo[3.3.1]nonane-2,6-dione

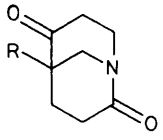
Peter H. McCabe, Neal J. Milne, and George A. Sim *
Department of Chemistry, University of Glasgow, Glasgow G12 8QC

3-(2-Carboxyethyl)-4-piperidone (**5**), prepared from *N*-benzyl-4-piperidone and benzyl acrylate (**9**), was thermally cyclized in the presence of dibutyltin oxide to 1-azabicyclo[3.3.1]nonane-2,6-dione (**4**), which possesses a bridgehead amide nitrogen. The boat–chair conformation of (**4**) in the solid state has been characterized by *X*-ray crystal structure analysis and the bridgehead amide shown to be appreciably distorted from planarity, with N(1) displaced by 0.37 Å from the plane of C(2), C(8), and C(9). Crystallographic data are $a = 6.214(4)$, $b = 6.845(5)$, $c = 17.850(8)$ Å, $Z = 4$, space group $P2_1cn$. *X*-Ray intensity measurements were made on a four-circle diffractometer and least-squares adjustment of the atomic parameters converged at $R = 0.038$ for 1 004 reflections.

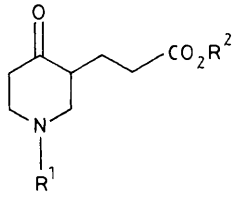
Spectroscopic and *X*-ray studies together with molecular mechanics calculations have established that bridged δ-lactams of type (**1**), incorporating a bridgehead nitrogen atom, adopt a boat–chair conformation with the lactam ring in the boat form to allow maximum p–π overlap within the amide function.[1,2] The *X*-ray characterization of (**2**) showed that the amide group is distinctly non-planar, with the N atom 0.36 Å out of the plane of the atoms to which it is bonded.[2] In an examination of the features that might favour a twin-boat conformation in related compounds, we noted that the chair/boat energy difference is substantially smaller in cyclohexanone than in cyclohexane.[3] Since molecular mechanics calculations indicated that a carbonyl group at C(2) in bicyclo[3.3.1]nonane derivatives results in a reduction in the energy difference between twin-chair and boat–chair conformations,[4] it is of some interest to determine the conformational effect of introducing a carbonyl group into the piperidine ring of (**1**). The molecular mechanics calculations for compound (**3**)[2] suggested that the boat–chair conformation is still preferred over the twin-boat form but only to the extent of 1.8 kJ mol^{-1} and since errors in such calculations are probably of the order of 2 kJ mol^{-1}, the preparation and characterization of (**4**) was undertaken to ascertain if the twin-boat conformer could be detected.



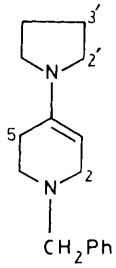
(**1**) R = H
(**2**) R = Ph



(**3**) R = Me
(**4**) R = H



(**5**) $R^1 = R^2 = H$
(**6**) $R^1 = CH_2Ph$, $R^2 = Et$
(**7**) $R^1 = R^2 = CH_2Ph$



(**8**)

$H_2C{=}CHCO_2CH_2Ph$
(**9**)

$BrCH_2CH_2CO_2CH_2Ph$
(**10**)

A synthesis of (**4**) by cyclization of 3-(2-carboxyethyl)-4-piperidone (**5**) was envisaged, since similar lactamizations had been achieved[1,5,6] in the syntheses of (**1**) and (**2**). Difficulty was foreseen in the isolation of the amino acid (**5**) at its isoelectric point from an acid or base hydrolysis of a simple ester precursor and the benzyl group, which can be hydrogenolysed in neutral media, was chosen to protect both the piperidone nitrogen and the carboxy group.

In exploratory approaches to the functionalization of *N*-benzyl-4-piperidone at C(3), attempted Michael condensation of ethyl acrylate with *N*-benzyl-4-piperidone enolate (generated by NaOH, NaOEt, or KOBu^t) and alkylation of the *N*-benzyl-4-piperidone enamine (**8**) with ethyl 3-bromopropanoate were unsuccessful. However, Michael condensation did take place between (**8**) and ethyl acrylate to form (**6**). For the synthesis of benzyl acrylate (**9**), 3-bromopropanoic acid was esterified with $PhCH_2OH$/*p*-TsOH and the resulting benzyl 3-bromopropanoate (**10**) was dehydrobrominated with NEt_3 in the presence of radical scavenger. Michael addition of the enamine (**8**) to (**9**) furnished the desired amino ester (**7**).

The benzyl ester group of (**7**) was hydrogenolysed at room temperature in the presence of a catalytic amount of palladium black but the *N*-benzyl moiety remained intact even when the temperature and amount of catalyst were increased. Both benzyl groups of (**7**) were removed by hydrogen transfer from cyclohexa-1,4-diene in the presence of excess palladium black. The resulting amino acid (**5**) was used in a slightly impure state for the subsequent cyclization step, as repeated recrystallizations failed to yield material of analytical quality.

The bridged ketoamide (**4**) was formed in modest yield by lactamization[6] of (**5**) at high dilution (*ca.* 10^{-3} mol dm^{-3}), mediated by dibutyltin oxide.

Lactam (**4**) formed orthorhombic crystals. The crystal structure was determined by direct phasing[7] and the atomic co-ordinates adjusted by full-matrix least-squares calculations. The molecular structure is shown in Figure 1 and the torsion angles defining the ring conformations are in Table 1. There is no indication of disorder in the crystal structure and the molecules uniformly adopt the boat–chair conformation.

The N atom in (**4**) is displaced by 0.37 Å from the plane of C(2), C(8), and C(9), almost exactly as for compound (**2**).

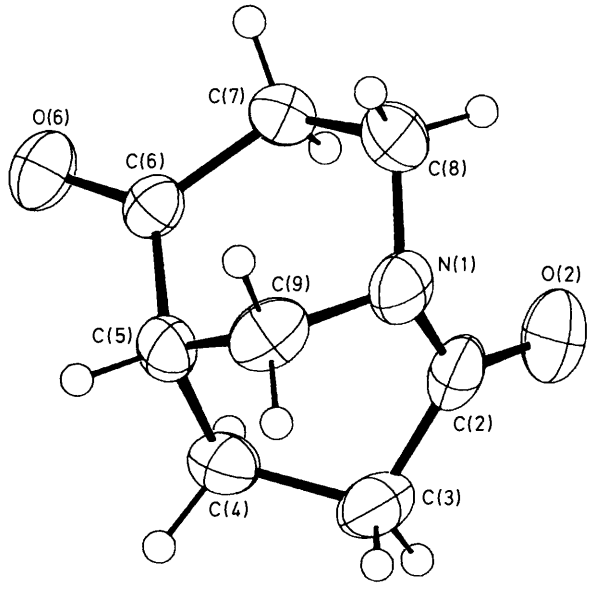


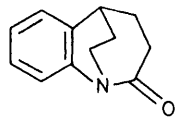
Figure 1. The molecular structure of 1-azabicyclo[3.3.1]nonane-2,6-dione (**4**). The thermal ellipsoids of the C, N, and O atoms are drawn at the 50% probability level. The H atoms are represented by spheres of radius 0.1 Å.

Table 1. Comparison of torsion angles / ° for 1-azabicyclo[3.3.1]nonane-2,6-dione (**4**) and 5-phenyl-1-azabicyclo[3.3.1]nonan-2-one (**2**).

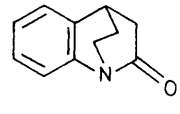
	(**4**)	(**2**)
C(9)–N(1)–C(2)–C(3)	−5.7	−0.8
N(1)–C(2)–C(3)–C(4)	57.8	54.2
C(2)–C(3)–C(4)–C(5)	−46.6	−49.9
C(3)–C(4)–C(5)–C(9)	−11.1	−4.2
C(4)–C(5)–C(9)–N(1)	62.6	58.2
C(5)–C(9)–N(1)–C(2)	−56.6	−59.3
C(9)–N(1)–C(8)–C(7)	−62.8	−65.1
N(1)–C(8)–C(7)–C(6)	36.7	50.9
C(8)–C(7)–C(6)–C(5)	−26.3	−47.2
C(7)–C(6)–C(5)–C(9)	36.4	50.3
C(6)–C(5)–C(9)–N(1)	−58.6	−60.2
C(5)–C(9)–N(1)–C(8)	76.2	73.5

Deviations from planarity in amides are not uncommon but are usually substantially smaller than in (**2**) and (**4**).[8] The out-of-plane distortions of the amide group can be assigned to out-of-plane bending at the nitrogen (χ_N) and the carbonyl carbon (χ_C) and twisting around the N–CO bond (τ).[9] The parameters for (**4**) are χ_N −49.1°, χ_C 5.8°, and τ 196.3° (*i.e.* a twist of 16.3°). The corresponding results for (**2**) are χ_N −48.8°, χ_C 5.9°, and τ 200.8° (*i.e.* a twist of 20.8°).[2]

The N–CO bond length in (**4**), 1.377(8) Å, is close to that in (**2**), 1.374(7) Å, and rather longer than the corresponding distances in less strained amides, *e.g.* 1.34 Å in caprylolactam[9] and 4-diethylcarbamoylcyclohex-1-ene-5-carboxylic acid.[10] The NC=O bond lengths in (**4**), 1.217(4) Å, and (**2**), 1.201(6) Å, are concomitantly shorter than the distances in caprylolactam, 1.23 Å, and 4-diethylcarbamoylcyclohex-1-ene-5-carboxylic acid, 1.24 Å. These results clearly mirror the decreased p–π overlap in (**2**) and (**4**). The amide C=O stretching frequency in (**4**) is 1 680 cm^{-1}, close to values of 1 680 cm^{-1} in (**1**) and 1 695 cm^{-1} in (**2**), whereas *N*-methyl-2-piperidone absorbs at 1 650 cm^{-1}, consistent with shorter and stronger C=O bonds in the bridgehead lactams. Mechanical models indicate that compounds (**11**) and (**12**) have larger twist angles about the N–CO bond and the C=O stretching frequency is 1 705 cm^{-1} in (**11**) and 1 755 cm^{-1} in (**12**);[11] an *X*-ray study of (**11**) gave N–CO and C=O bond lengths of 1.401 and 1.216 Å.[12]



(**11**)



(**12**)

The introduction of the C=O group at C(6) results in an appreciable flattening of the C(6)C(7)-region of the 4-piperidone ring in (**4**); the torsion angles in this ring are 26.5–76.7° whereas the corresponding angles in (**2**) are 47.2–73.5°.

A first-order analysis of decoupled 360 MHz ^1H n.m.r. spectra, partially assigned by chemical shift comparison, indicates that the lactam ring of (**4**) adopts a boat conformation in solution also. H–C(5) shows one large coupling (*ca.* 11 Hz) and one small coupling (*ca.* 1 Hz) with the methylene protons on C(4), consistent with approximate dihedral angles from a molecular model of *ca.* 10° with the pseudo-equatorial H–C(4) and *ca.* 100° with the pseudo-axial H–C(4); the appropriate angles in the crystal are 6(3)° and 111(3)°. In the alternative chair conformation, H–C(5) would project approximately equal dihedral angles (*ca.* 60°) and thus couple equally with both H–C(4) atoms. A further indication of the lactam boat conformation is that the pseudo-equatorial H–C(4) shows only a minor coupling (*ca.* 0.5 Hz) with the pseudo-equatorial H–C(3), whereas the H–C(3), H–C(4) diaxial coupling is *ca.* 5 Hz; the appropriate dihedral angles are *ca.* 80° and 150° on a molecular model and 67(3)° and 162(3)° in the crystal.

A molecular model in which the 4-piperidone ring has a chair conformation has the H–C(7), H–C(8) axial protons with a dihedral angle of *ca.* 175° and the equatorial protons with a dihedral angle of *ca.* 75°. In the crystal these angles are 168(3)° and 85(3)°. The large *vic*-diaxial coupling (*ca.* 10 Hz) and the small *vic*-diequatorial coupling (*ca.* 1 Hz) in the n.m.r. spectra are consistent with these angles being retained in solution. We conclude that the most likely conformation of (**4**) in solution is the boat–chair but, because of the complexity of the spectra, we cannot entirely exclude the possibility of an equilibrium with the conformationally mobile twin-boat, resulting in signal averaging.

Experimental

M.p.s were determined on a Reichert hot-stage apparatus and are uncorrected. Routine and high resolution mass spectra were recorded on AEI VG MS12 and MS902S instruments, respectively. I.r. spectra were obtained with a Perkin-Elmer 580 spectrometer. Routine ^1H n.m.r. spectra were recorded at 90 MHz with a Perkin-Elmer R32 instrument. Chemical shifts are expressed in ppm (δ) downfield from internal tetramethylsilane with deuteriochloroform as the solvent unless otherwise specified. Organic solutions were dried with anhydrous sodium sulphate.

N-Benzyl-4-pyrrolidinyl-1,2,5,6-tetrahydropyridine (**8**).—*N*-Benzyl-4-piperidone (0.93 cm^3, 5 mmol), pyrrolidine (1.25 cm^3, 15 mmol), and a trace of *p*-TsOH in dry benzene (50 cm^3) were heated under reflux for 1 h using a Dean–Stark apparatus. After rotary evaporation of the reaction solution, the residue was distilled to give (**8**) (0.624 g, 52%); b.p. 190 °C (0.15 mm, Kugelrohr); δ_H 1.6–1.9 [4 H, m, $H_2C(3')$], 2.2–2.85 [*ca.* 6 H, m, $H_2C(2)$, $H_2C(5)$, $H_2C(6)$], 2.85–3.15 [*ca.* 4 H, m, $H_2C(2')$], 3.55 (2 H, s, CH_2Ph), 4.1–4.25 (1 H, m, vinyl), and 7.15–7.4 (5 H, m, Ar); *m/z* (Found: 242.1760. $C_{16}H_{22}N_2$ requires 242.1782).

Table 2. Fractional atomic co-ordinates for compound (**4**), with standard deviations in parentheses.

Atom	*x*	*y*	*z*
C(2)	0.881 3(6)	0.147 2(3)	0.324 6(1)
C(3)	0.947 4(6)	0.322 8(4)	0.280 8(1)
C(4)	0.926 7(6)	0.501 3(3)	0.332 9(1)
C(5)	0.709 9(5)	0.501 2(3)	0.375 9(1)
C(6)	0.741 8(5)	0.455 0(3)	0.458 2(1)
C(7)	0.760 7(6)	0.244 0(3)	0.481 7(1)
C(8)	0.650 7(7)	0.095 6(3)	0.430 5(1)
C(9)	0.567 7(5)	0.346 5(4)	0.341 5(1)
N(1)	0.675 1(0)	0.160 3(3)	0.352 9(1)
O(2)	1.000 0(6)	0.012 1(3)	0.339 6(1)
O(6)	0.760 6(5)	0.584 2(2)	0.503 5(1)

Table 3. Bond lengths/Å and angles/° for compound (**4**).

Bond lengths	
C(2)–N(1)	1.380(4)
C(3)–C(4)	1.542(4)
C(5)–C(6)	1.515(3)
C(6)–C(7)	1.509(3)
C(7)–C(8)	1.528(4)
C(9)–N(1)	1.454(8)
C(2)–C(3)	1.492(4)
C(2)–O(2)	1.213(4)
C(4)–C(5)	1.550(5)
C(5)–C(9)	1.509(4)
C(6)–O(6)	1.204(3)
C(8)–N(1)	1.463(4)
Bond angles	
C(3)–C(2)–N(1)	113.3(3)
N(1)–C(2)–O(2)	122.2(3)
C(3)–C(4)–C(5)	111.7(3)
C(4)–C(5)–C(9)	108.0(2)
C(5)–C(6)–C(7)	118.7(2)
C(7)–C(6)–O(6)	120.5(2)
C(7)–C(8)–N(1)	108.6(4)
C(2)–N(1)–C(8)	115.0(8)
C(8)–N(1)–C(9)	110.5(5)
C(3)–C(2)–O(2)	124.2(4)
C(2)–C(3)–C(4)	107.4(2)
C(4)–C(5)–C(6)	111.4(3)
C(6)–C(5)–C(9)	108.9(2)
C(5)–C(6)–O(6)	120.7(2)
C(6)–C(7)–C(8)	115.8(2)
C(5)–C(9)–N(1)	106.8(5)
C(2)–N(1)–C(9)	115.6(5)

N-*Benzyl*-3-(2-*ethoxycarbonylethyl*)-4-*piperidone* (**6**).—Enamine (**8**) (1.916 g, 7.92 mmol) and ethyl acrylate (0.857 cm^3, 7.91 mmol) in dry MeCN (15 cm^3) under Ar were heated to reflux for 2 h. Water (5 cm^3) was added and the solution heated for a further 1 h. After rotary evaporation, the residue was taken into CH_2Cl_2, washed with water, dried, and the solvent removed *in vacuo*. The crude product was distilled (200–210 °C, 0.15 mmHg, Kugelrohr) to yield (**6**) (2.153 g, 94%); $\nu_{max.}(CCl_4)$ 1 735, 1 720 cm^{-1} (CO); δ_H 1.3 (3 H, t, *J* 8 Hz, CH_3), 2.0–3.2 (11 H, m, CH, CH_2), 3.7 (2 H, s, CH_2Ph), 4.18 (2 H, q, *J* 8 Hz, CH_2CH_3), and 7.4 (5 H, br s, Ar); (Found: M^+, 289.1688. $C_{17}H_{23}NO_3$ requires *M*, 289.1677).

Benzyl 3-*Bromopropanoate* (**10**).—3-Bromopropanoic acid (14.3 g, 93 mmol), benzyl alcohol (10.4 cm^3, 100 mmol), and a catalytic amount of *p*-TsOH were boiled under reflux for 3 h using a Dean–Stark apparatus with dry benzene (100 cm^3). After rotary evaporation of the benzene, the crude product was taken into EtOAc, washed with aq. K_2CO_3, dried, and the solvent removed *in vacuo*. The residue, on distillation, gave two fractions, the first being benzyl alcohol and the second benzyl 3-bromopropanoate (**10**) (16.9 g, 74%) b.p. 110 °C (0.15 mmHg, Kugelrohr); δ_H 2.9 (2 H, t, *J* 7 Hz, CH_2CO), 3.55 (2 H, t, *J* 7 Hz, CH_2Br), 5.14 (2 H, s, CH_2Ph), and 7.3 (5 H, br s, Ar).

Benzyl Acrylate (**9**).—Ester (**10**) (14 g, 57 mmol), NEt_3 (12 cm^3, 86 mmol), and a trace of hydroquinone in $CHCl_3$ (50 cm^3) were heated under reflux for 1 h. The solution was washed with dil. HCl then water, dried, and the solvent was removed *in vacuo* and the residue distilled to yield (**9**) (7.965 g, 86%), b.p. 135 °C (3 mmHg, Kugelrohr) (lit.,[13] b.p. 228 °C); δ_H 5.22 (2 H, s, CH_2Ph), 5.75–6.6 (3 H, m, vinyl), and 7.36 (5 H, br s, Ar).

3-(2-*Benzyloxycarbonylethyl*)-N-*benzyl*-4-*piperidone* (**7**).—Enamine (**8**) (7.273 g, 30 mmol), benzyl acrylate (**9**) (4.862 g, 30 mmol), and a trace of hydroquinone in dry MeCN (20 cm^3) were heated to reflux for 1 h under argon. Water (10 cm^3) was added and the solution heated for an additional 0.5 h. After rotary evaporation of the solvent, the residue was taken into CH_2Cl_2, washed with water, dried, the solvent removed *in vacuo* and the benzyl alcohol distilled off at 70 °C (0.2 mmHg, Kugelrohr) to leave the crude ester (**7**) (6.463 g, 61%). This was passed through a column of silica gel with EtOAc–hexane (3:2) as the eluant and 30 fractions of 25 cm^3 were collected. Fractions 12–30 yielded (**7**) (4.780 g, 45%) as a light yellow oil; $\nu_{max.}(CCl_4)$ 1 740 and 1 720 cm^{-1} (CO); δ_H 1.2–3.15 (11 H, m, CH, CH_2), 3.6 (2 H, s, NCH_2Ph), 5.1 (2 H, s, OCH_2Ph), and 7.32 (10 H, br s, Ar); δ_C 22.69 (t), 31.73 (t), 40.71 (t), 48.62 (d), 53.35 (t), 58.65 (t), 61.54 (t), 66.05 (t), 126.86, 127.35, 128.17, 128.41, 128.89 (all d, Ar), 136.12, 137.98 (both s, Ar), 172.94 (s, CO), and 209.84 (s, CO); (Found: M^+, 351.1825. $C_{22}H_{25}NO_3$ requires *M*, 351.1834).

3-(2-*Carboxyethyl*)-4-*piperidone* (**5**).—Ketone (**7**) (0.319 g, 0.9 mmol), Pd black (0.319 g) and 1,4-cyclohexadiene (0.85 cm^3, 9 mmol) were stirred in EtOH (4 cm^3), at 60 °C under argon. The catalyst was removed by filtration through Celite 535 and the filter cake washed with hot EtOH. The filtrate and washings were rotary evaporated to yield crude amino acid (**5**) (0.117 g, 76%) as a colourless solid which was recrystallized with difficulty from aq. MeOH–CH_3COCH_3. Compound (**5**): (Found: C, 56.8; H, 7.9; N, 7.95. $C_8H_{13}NO_3$ requires C, 56.13; H, 7.65; N, 8.18%); δ_H([$^2H_3$] MeOD/D_2O) 1.2–6.0 (m, CH, CH_2); *m/z* (Found: 171.0896, $C_8H_{13}NO_3$ requires 171.0896).

1-*Azabicyclo*[3.3.1]*nonane*-2,6-*dione* (**4**).—Ketone (**5**) (0.0816 g, 0.475 mmol) and dibutyltin oxide (0.1183 g, 0.475 mmol) in dry toluene (125 cm^3) were heated under reflux for 6 h using a Dean–Stark trap. The toluene was removed *in vacuo* and the residue taken into $CHCl_3$, filtered through Celite 535 and the $CHCl_3$ removed *in vacuo*. The residue was sublimed at 100 °C (0.15 mm) to furnish the pure lactam (**4**) (0.022 g, 30%) as a colourless solid m.p. 65–66 °C. (Found: C, 62.7; H, 7.4; N, 8.9. $C_8H_{11}NO_2$ requires C, 62.73; H, 7.24; N, 9.14%); $\nu_{max}(CHCl_3)$ 2 960, 1 705, (CO), 1 680 (amide CO), 1 489, 1 461, 1 435, 1 410, 1 381, 1 348, 1 289, 1 135, 1 048, 1 022, 990, 975, and 943 cm^{-1}; δ_H(360 MHz) 1.55–1.67 [1 H, m; H–C(4) pseudo-ax.], 2.30–2.49 [3 H, m; H–C(3) pseudo-ax.; H–C(4) pseudo-eq.; H–C(7) eq.], 2.53–2.66 [2 H, m; H–C(3) pseudo-eq.; H–C(7) ax.)], 2.90–2.96 [1 H, dm; H–C(5)], 2.99–3.09 [1 H, dq; H–C(8) ax.], 3.30–3.36 [1 H, dm, H–C(9) ax.], 3.62–3.70 [1 H, dq, H–C(9) eq.], and 4.33–4.42 [1 H, qt, H–C(8) eq.]; δ_C 23.76 (CH_2), 31.22 (CH_2), 32.53 (CH_2), 46.22 (CH_2CO), 42.45 (CH), 49.28 (CH_2CO), 182.33 [C(2)], and 209.32 [C(6)]; (Found: M^+, 153.0792. $C_8H_{11}NO_2$ requires *M*, 153.0790).

Crystal Data.—1-Azabicyclo[3.3.1]nonane-2,6-dione (**4**), $C_8H_{11}NO_2$, $M = 153.2$, orthorhombic, $a = 6.214(4)$, $b = 6.845(5)$, $c = 17.850(8)$ Å, $V = 759$ Å^3, $D_c = 1.34$ g cm^{-3}, $Z = 4$, $F(000) = 328$, $\mu(\text{Mo}-K_\alpha) = 1.04$ cm^{-1}, systematic absences *hkl*: $h + k = 2n + 1$, h0*l*: $l = 2n + 1$, space group $P2_1cn$ ($\bar{c}ba$ setting of C_{2v}^9, No. 33, *Pna*2).

Crystallographic Measurements.—Cell dimensions were derived from least-squares treatment of the setting angles of 25 reflections measured on an Enraf–Nonius CAD4 diffractometer with Mo–K_α radiation. For the intensity measurements, 1 322 *hkl* reflections were surveyed in the range $\theta < 30°$ and 1 004 satisfied the criterion $I > 2.5\sigma(I)$.

Structure Analysis.—The crystal structure was elucidated with the direct-phasing procedure MITHRILL.[7] After preliminary least-squares adjustment of the co-ordinates of the C, N, and O atoms, the H atoms were located in a difference electron-density distribution. Refinement with anisotropic thermal parameters for the C, N, and O atoms and isotropic parameters for the H atoms converged at $R = 0.038$, $R_w = 0.048$, with weights $w = 1/\sigma^2(|F|)$. Fourier, least-squares, geometry and ORTEP calculations were performed with the GX system of programs.[14] Atomic co-ordinates are listed in Table 2 and bond lengths and angles in Table 3. Tables of thermal parameters, hydrogen atom co-ordinates, and C–H bond lengths have been deposited at the Cambridge Crystallographic Data Centre.*

* *Supplementary data:* for details of the Supplementary Publications Scheme see 'Instructions for Authors (1989),' *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

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