

Reaction Products of 2-Methylindole with Nitrosobenzenes: a Reinvestigation. X-Ray Analysis of 2-(Phenyl-*N*-oxidoiminomethyl)-3-phenylaminoindole

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2-Methylindole reacts with nitrosobenzenes to form 2-(aryl-*N*-oxidoiminomethyl)-3-arylaminoindoles (**4a–d**), which were previously described as 2-methyl-3-arylimino-3*H*-indoles (**3e** and **f**). The new structure was determined by X-ray analysis. The geometry of the molecule is discussed in the comparison with those reported in the literature for 2,3-diphenylindole, 3-arylaminoindoles, and analogous nitrone systems.

It has been reported that 2-methylindole (**1a**) reacts with nitrosobenzene (**2a**) and *p*-nitroso-*NN*-dimethylaniline (**2b**) to yield the corresponding 2-methyl-3-arylimino-3*H*-indoles (**3e** and **f**).¹ This incorrect interpretation is still current in the literature.² Angeli, the first to study this reaction, was misled by the fact that 2-phenylindole (**1b**) does lead to 2-phenyl-3-aryliminoindoles (**3a–d**) when it is treated with nitrosobenzenes.^{3,4}

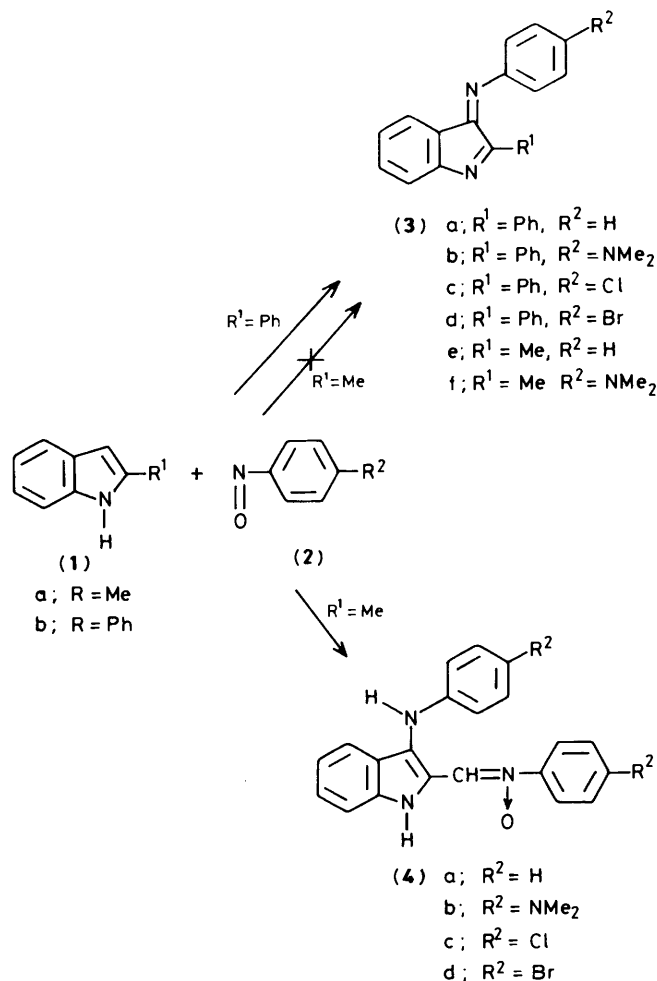
In this paper we describe the true structure of the products formed in the reaction of 2-methylindole (**1a**) with nitrosobenzenes (**2a–d**), and explain why it is impossible to obtain compounds such as (**3e** and **f**).

Results

2-Methylindole (**1a**) reacted in absolute ethanol with nitrosobenzenes (**2a–d**) in 1:2 ratio in the presence of sodium ethoxide under reflux for 10 min to yield compounds (**4a–d**) (Scheme 1). The structure of (**4a**) was determined by X-ray analysis and the structures of compounds (**4b–d**) by comparing their spectroscopic data, which were all similar, with those of (**4a**). Compound (**4a**) shows a broad band at 3 250 cm⁻¹ in its i.r. spectrum, whereas two bands, due to the amine and indole NHs, are present in the i.r. spectra of compounds (**4b–d**) (Table 1). The broader band can most likely be attributed to the indole NH, which is engaged in a hydrogen bond as confirmed by X-ray analysis (see below). The bands at 1 600 and at *ca.* 1 520 cm⁻¹ can be attributed to the double bond of the pentatomic ring of the indole nucleus and to the C=N→O double bond, respectively. The value of 1 600 cm⁻¹ agrees with that previously described for 3-arylaminoindoles.³

The n.m.r. spectra show the absence of a methyl group at C-2. The singlet at δ 5.5 for compounds (**4c** and **d**), whose spectra were recorded in CDCl₃, is typical for the amine NH in 3-arylaminoindoles when the spectra are recorded in CDCl₃.⁵ The indole NH signal, which normally falls at *ca.* 8.2, overlaps those of the aromatic hydrogens.⁶ Compounds (**4a**, **c**, and **d**) show a singlet at δ *ca.* 8.1 due to the hydrogen of the CH=N→O group. Only in the case of compound (**4b**) does this signal fall together with the aromatic hydrogens. The two NMe₂ groups of compound (**4b**) give rise to a pseudo-triplet, which, in our opinion, is due to a singlet from the NMe₂ of the 3-arylamino-group, and a doublet from the NMe₂ of the arylimino-*N*-oxide group. Analytical and spectroscopic data are reported in Table 1.

Molecular Geometry of (4a).—Bond distances and angles are reported in Table 2, and the arbitrary numbering scheme used in the crystal analysis is shown in the Figure, which is a projection



Scheme 1.

of the molecule on the plane of the indole ring. The conformational geometry of the molecule can be deduced from the torsion angles listed in Table 2 and from the analysis of the mean plane calculation reported in Table 3. The intramolecular bond lengths and angles in the phenylaminoindole system are as expected from the hybridization of the atoms involved and compare favourably with those found in the related compounds

Table 1. Analytical and spectroscopic data of compounds (4a–d)

Compound ^a	M.p. (C) ^b	Formula	Found (%), (Calc.)	θ_{\max} , cm ⁻¹ ^g	¹ H Chemical shifts (δ)
(4a)	187 ^c	C ₂₁ H ₁₇ N ₃ O	C, 77.0; H, 5.2; N, 13.0	3 250 ^h 1 600 1 570 1 525	6.62–8.12 (14 H, m, arom.); 8.5 (1 H, s, CH=N→O) ^d
			(77.0) (5.2) (12.8)	3 400 ^h 3 220 ⁱ 1 610 1 520	3.06 (12 H, pseudo-t, 2NMe ₂), 3.54br (1 H, NH), 6.78–7.84 (14 H, m, arom.) ^e
(4b)	185	C ₂₅ H ₂₇ N ₅ O	C, 72.65; H, 6.45; N, 16.9	3 250 ^h 3 180 ⁱ 1 600 1 580 1 540	5.5 (1 H, s, NH), 6.7 (2 H, d, arom.), 7.1–7.56 (9 H, m, arom. + NH), 7.74 (2 H, d, arom.), 8.1 (1 H, s, CH=N→O) ^f
			(72.6) (6.6) (16.9)	3 380 ^h 3 250 ⁱ 1 600 1 515	5.54 (1 H, s, NH), 6.6 (2 H, d, arom.), 7.08–7.44 (9 H, arom. + NH), 7.64 (2 H, d, arom.), 8.1 (1 H, s, CH=N→O) ^f
(4c)	175	C ₂₁ H ₁₅ Cl ₂ N ₃ O	C, 63.35; H, 3.8; N, 10.8	3 250 ^h 3 180 ⁱ 1 600 1 580 1 540	5.5 (1 H, s, NH), 6.7 (2 H, d, arom.), 7.1–7.56 (9 H, m, arom. + NH), 7.74 (2 H, d, arom.), 8.1 (1 H, s, CH=N→O) ^f
			(63.65) (3.8) (10.6)	3 380 ^h 3 250 ⁱ 1 600 1 515	5.54 (1 H, s, NH), 6.6 (2 H, d, arom.), 7.08–7.44 (9 H, arom. + NH), 7.64 (2 H, d, arom.), 8.1 (1 H, s, CH=N→O) ^f
(4d)	188	C ₂₁ H ₁₅ Br ₂ N ₃ O	C, 52.05; H, 3.2; N, 8.9	3 250 ^h 3 180 ⁱ 1 600 1 580 1 540	5.5 (1 H, s, NH), 6.7 (2 H, d, arom.), 7.1–7.56 (9 H, m, arom. + NH), 7.74 (2 H, d, arom.), 8.1 (1 H, s, CH=N→O) ^f
			(52.0) (3.1) (8.7)	3 380 ^h 3 250 ⁱ 1 600 1 515	5.54 (1 H, s, NH), 6.6 (2 H, d, arom.), 7.08–7.44 (9 H, arom. + NH), 7.64 (2 H, d, arom.), 8.1 (1 H, s, CH=N→O) ^f

^a All compounds gave the expected molecular ion peak in the mass spectrum. ^b From ethanol. ^c 183 °C. ^d In [2H₆]DMSO. ^e In [2H₆]acetone. ^f In CDCl₃. ^g From Nujol. ^h NH (broad). ⁱ NH (sharp).

Table 2. Bond distances (Å) and angles (°), with estimated standard deviations in parentheses

(a) Bond distances			
O(1)–N(2)	1.308(3)	C(6)–C(7)	1.366(5)
N(1)–C(1)	1.370(4)	C(7)–C(8)	1.392(4)
N(1)–C(8)	1.368(4)	C(10)–C(11)	1.355(5)
N(2)–C(9)	1.286(4)	C(10)–C(15)	1.360(5)
N(2)–C(10)	1.438(4)	C(11)–C(12)	1.373(7)
N(3)–C(2)	1.392(4)	C(12)–C(13)	1.356(8)
N(3)–C(16)	1.390(4)	C(13)–C(14)	1.343(8)
C(1)–C(2)	1.389(4)	C(14)–C(15)	1.390(6)
C(1)–C(9)	1.442(4)	C(16)–C(17)	1.372(4)
C(2)–C(3)	1.412(4)	C(16)–C(21)	1.378(4)
C(3)–C(4)	1.403(4)	C(17)–C(18)	1.375(4)
C(3)–C(8)	1.403(4)	C(18)–C(19)	1.370(5)
C(4)–C(5)	1.363(5)	C(19)–C(20)	1.362(6)
C(5)–C(6)	1.396(5)	C(20)–C(21)	1.378(5)
(b) Bond angles			
C(1)–N(1)–C(8)	108.9(3)	N(1)–C(8)–C(7)	129.4(3)
O(1)–N(2)–C(9)	123.1(4)	C(3)–C(8)–C(7)	122.2(4)
O(1)–N(2)–C(10)	116.6(3)	N(2)–C(9)–C(1)	124.4(3)
C(9)–N(2)–C(10)	120.3(3)	N(2)–C(10)–C(11)	121.3(4)
C(2)–N(3)–C(16)	123.3(4)	N(2)–C(10)–C(15)	118.1(4)
N(1)–C(1)–C(2)	108.6(4)	C(11)–C(10)–C(15)	120.6(5)
N(1)–C(1)–C(9)	126.8(3)	C(10)–C(11)–C(12)	119.4(5)
C(2)–C(1)–C(9)	124.4(3)	C(11)–C(12)–C(13)	121.1(6)
N(3)–C(2)–C(1)	124.4(4)	C(12)–C(13)–C(14)	119.0(6)
N(3)–C(2)–C(3)	128.2(3)	C(13)–C(14)–C(15)	121.2(5)
C(1)–C(2)–C(3)	107.3(3)	C(10)–C(15)–C(14)	118.7(4)
C(2)–C(3)–C(4)	134.1(3)	N(3)–C(16)–C(17)	121.9(3)
C(2)–C(3)–C(8)	106.7(4)	N(3)–C(16)–C(21)	119.1(5)
C(4)–C(3)–C(8)	119.2(4)	C(17)–C(16)–C(21)	119.1(5)
C(3)–C(4)–C(5)	118.6(3)	C(16)–C(17)–C(18)	119.9(3)
C(4)–C(5)–C(6)	120.9(5)	C(17)–C(18)–C(19)	121.1(5)
C(5)–C(6)–C(7)	112.4(4)	C(18)–C(19)–C(20)	119.2(4)
C(6)–C(7)–C(8)	116.7(3)	C(19)–C(20)–C(21)	120.4(4)
N(1)–C(8)–C(3)	108.4(4)	C(16)–C(21)–C(20)	120.4(4)

(c) Selected torsion angles			
O(1)–N(2)–C(10)–C(15)	33.8(7)	C(9)–C(1)–C(2)–N(3)	–4.9(7)
O(1)–N(2)–C(9)–C(1)	–7.1(8)	N(1)–C(1)–C(9)–N(2)	6.9(8)
C(10)–N(2)–C(9)–C(1)	170.1(4)	C(2)–C(1)–C(9)–N(2)	–166.9(5)
N(1)–C(1)–C(2)–N(3)	–179.7(4)	C(16)–N(3)–C(2)–C(1)	121.3(5)

(d) Bond distances involving hydrogen atoms are in the range 0.92(3)–1.04(4) Å

Table 3. Analysis of the planarity

(a) Distances (in 10³ Å) of relevant atoms from the mean plane through the molecule with standard deviations in parentheses: starred atoms were not used to define the plane

Plane A: C(3)–C(8)
C(3) –4(5), C(4) 5(6), C(5) –1(6), C(6) –3(6), C(7) 2(5), C(8) 1(5),
C(2)* –35(5), N(1)* –15(5)

Plane B: N(1), C(1), C(2), C(3), C(8)
N(1) 13(5), C(1) –14(5), C(2) 10(5), C(3) –2(5), C(8) –6(5), N(3)*
–12(5), C(9)* –166(5)

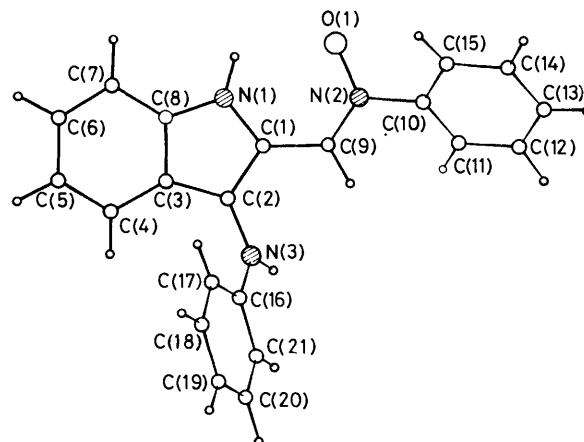
Plane C: C(16)–C(21)
C(16) –1(5), C(17) 3(5), C(18) –3(5), C(19) 0(5), C(20) 3(5), C(21)
–2(5), N(3)* –30(5)

Plane D: C(10)–C(15)
C(10) 9(5), C(11) –7(6), C(12) –3(7), C(13) 6(7), C(14) 0(6), C(15)
–8(6), N(2)* 35(5)

Plane E: O(1), C(9), C(10)
N(2)* –18(5)

(b) Dihedral angles (°) between planes

A–B 178.3; B–C 64.7; B–E 14.8; D–E 35.3



Projection of the molecule on the plane of the indole ring, and the atomic numbering scheme

2-phenyl-3-(*p*-methoxyphenyl)aminoindole⁶ and 2,3-diphenylindoles.⁷ The fused two-ring system is almost planar, the dihedral angle between the mean planes of the two individual rings being 178.3°. Significant deviations from planarity are observed only for the C(1) and N(1) atoms of the indole nucleus.

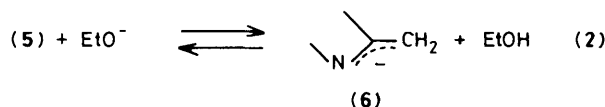
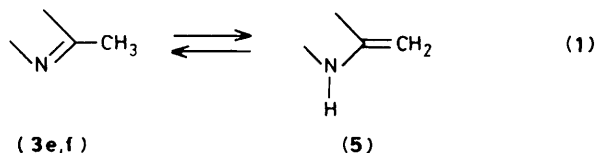
The comparison of our structure with that reported elsewhere,⁶ as regards the 3-phenylaminoindole moiety, shows the same bond distances and angles around the amine nitrogen and the same orientation of the phenyl to the indole ring (64.7°), confirming that in both these systems the probability of π -interaction of the nitrogen atom with the indole system and the phenyl group is minimal. Different features apply to the N(2) nitrogen atom of the nitrono moiety. In fact, the sum of the angles around the nitrogen atom (360.0°) indicates that this atom has sp^2 hybridization, as found for similar compounds, *viz.* oximes and amine oxides.⁸ On the other hand, the pyramidal nature of the N(2) atom, Plane E in Table 3, shows a low but significant deviation from a trigonal planar arrangement, the distance of N(2) from the O(1), C(9), C(10) plane being 0.018(5) Å. This distortion can be attributed to an interaction between O(1) and N(1) [O(1)⋯N(1) 2.578(4), O(1)⋯H(1) 2.25(3) Å], which justifies hydrogen-bond formation in the ring O(1), N(2), C(9), C(10), N(1), H(1) and the broad band at 3250 cm⁻¹ in the i.r. spectrum.

The N(2)–C(9) bond distance [1.286(4) Å], which is considerably shorter than the corresponding distance found in *xx*,*N*-triphenylnitrono⁹ (1.327 Å) and *N*-methyl-*p*-chlorobenzaldoxime⁸ [1.309(7) Å], is comparable with the N=C distance found in previously studied oximes and nitronos. The dihedral angle between the nitrono moiety and the phenyl ring C(10)–C(15) (35.3°) precludes any appreciable delocalization of the π -electrons into the aromatic system: more considerable conjugation seems to affect the indole ring, the mean plane of which forms a dihedral angle of 14.8° with the nitrono.

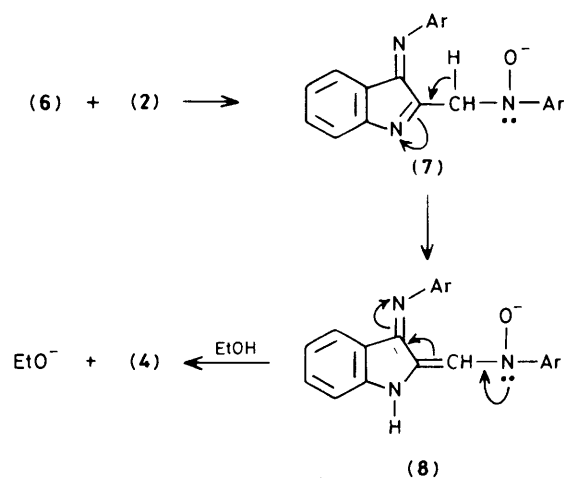
The molecular packing is determined by hydrogen bonds of the O⋯H–N type, in which the oxygen is involved with the nitrogen atom N(1) of an indole ring [O(1)⋯N(1)^{*i*} 2.875(5), O(1)⋯H(1)^{*i*} 2.05(3) Å; O(1)⋯H(1)^{*i*}–N(1)^{*i*} 143.3(2.0)°, *i* = 1 – *x*, –*y*, 1 – *z*] and with an amino nitrogen N(3) [O(1)⋯N(3)^{*ii*} 2.928(4), O(1)⋯H(3)^{*ii*} 1.98(4) Å; O(1)⋯H(3)^{*ii*}–N(3)^{*ii*} 175.4(2.0)°, *ii* = *x*, *y*, 1 + *z*]. The other contacts are consistent with van der Waals' interactions.

Discussion

We propose that the products described by Angeli¹ are in fact formed, and that they are intermediates in the formation of compounds (4a–d). Compounds (3e and f), which have a methyl group at C-2, give rise to a tautomeric equilibrium, as shown in equation (1). In addition the presence of EtO⁻



produces the anion (6) [equation (2)] which could react with nitrosobenzenes to yield compounds (4a–c), as described in Scheme 2.



Scheme 2.

The equilibrium (1) has already been confirmed for other systems, such as 2-methylthiazoline¹⁰ and 2-methyl-oxazoline,¹¹ which have the methyl group in the α -position to the N=C double bond, as for compounds (3e and f). To isolate compounds such as (3e and f), *i.e.* the proposed intermediates, we tried to stop the reaction after a few minutes, performing it with the reagents in a 1:1 ratio; however the expected compounds were not obtained. Because 2-phenylindole (1b) reacts with phenylhydroxylamine in the presence of hydrogen iodide to form (3a),¹² we tried the same experiment with 2-methylindole (1a). Even with this method the expected (3e) was not isolated at all.

In summary, the proposed intermediates (3; R¹ = Me) cannot be synthesized owing to the high reactivity of the 2-methyl group, which is probably favoured by the C=N group at C-3, as shown in Scheme 2.

Experimental

M.p.s are uncorrected. I.r. spectra were recorded on a 257 Perkin-Elmer spectrophotometer. ¹H N.m.r. spectra were recorded on a Varian XL-100 spectrometer using Me₄Si as internal standard. Mass spectra were recorded on a Varian 112-S apparatus. 2-Methylindole (1a) and nitrosobenzene (2a) were Fluka products. Nitrosobenzenes (2b),¹³ (2c),¹⁴ and (2d)¹⁴ were prepared as described in the literature.

Reaction of 2-Methylindole (1a) with Nitrosobenzenes (2a–d).
General Procedure.—10% Sodium ethoxide in absolute ethanol (1 ml) was added dropwise to a boiling solution of 2-methylindole (1a) (5 mmol) and nitrosobenzenes (2a–d) (10 mmol) in absolute ethanol (20 ml). After the addition of sodium ethoxide, which caused an exothermic reaction, the reaction mixture was refluxed for 10 min. Compounds (4a, c, and d) precipitated with cooling of the reaction solution, and were purified by recrystallization from ethanol. Yields were: (4a) (85%), (4c) (75%), and (4d) (83%). The mother liquor was chromatographed on a SiO₂ column eluting with benzene and benzene–acetone (9:1). In all cases, compounds such as (3e and f) were not isolated, but only traces of (4a, c, and d) were obtained.

In the reaction of (1a) with (2b), compound (4b) was not precipitated from the reaction solution. Thus, the solvent was evaporated and the residue was extracted with benzene (30 ml); the benzene solution was chromatographed on a SiO₂ column eluting with benzene–acetone (9:1). From the red-brown fraction compound (4b) was isolated in 15% yield.

Crystal Structure of 2-(Phenyl-N-oxidoiminomethyl)-3-phenylaminoindole (4a).—Crystals obtained from ethanol

Table 4. Fractional co-ordinates ($\times 10^4$, $\times 10^3$ for hydrogen) with estimated standard deviations in parentheses

	x/a	y/b	z/c
O(1)	4 881(2)	1 277(2)	4 253(3)
N(1)	6 439(2)	98(2)	1 831(4)
N(2)	4 819(2)	1 911(2)	2 409(4)
N(3)	6 893(2)	1 543(2)	-3 689(4)
C(1)	6 176(2)	893(2)	239(4)
C(2)	6 911(2)	849(2)	-1 719(4)
C(3)	7 676(2)	31(2)	-1 279(4)
C(4)	8 612(3)	-364(3)	-2 547(5)
C(5)	9 196(3)	-1 162(3)	-1 553(6)
C(6)	8 867(3)	-1 588(3)	674(6)
C(7)	7 955(2)	-1 237(3)	1 963(5)
C(8)	7 362(2)	-418(2)	951(4)
C(9)	5 353(2)	1 724(2)	536(5)
C(10)	4 153(2)	2 885(2)	2 564(5)
C(11)	3 548(3)	3 212(4)	1 001(7)
C(12)	2 944(4)	4 164(4)	1 191(9)
C(13)	2 936(4)	4 776(4)	2 924(9)
C(14)	3 524(4)	4 433(4)	4 482(8)
C(15)	4 141(3)	3 471(3)	4 338(6)
C(16)	7 824(2)	2 315(2)	-4 851(4)
C(17)	8 761(2)	2 615(3)	-3 949(5)
C(18)	9 650(3)	3 406(3)	-5 138(6)
C(19)	9 623(3)	3 897(3)	-7 230(6)
C(20)	8 696(3)	3 596(3)	-8 133(6)
C(21)	7 795(3)	2 811(3)	-6 953(5)
H(1)	610(3)	-4(3)	335(5)
H(3)	626(3)	143(3)	-441(5)
H(4)	883(3)	-8(3)	-403(5)
H(5)	985(3)	-150(3)	-242(5)
H(6)	932(3)	-220(3)	131(5)
H(7)	770(3)	-152(3)	360(5)
H(9)	531(2)	231(2)	-72(5)
H(11)	351(3)	277(4)	-23(7)
H(12)	256(4)	443(4)	-8(7)
H(13)	247(3)	541(4)	312(6)
H(14)	354(3)	483(3)	573(6)
H(15)	464(3)	325(3)	541(6)
H(17)	882(2)	225(3)	-259(5)
H(18)	1 033(3)	363(3)	-450(5)
H(19)	1 028(3)	445(3)	-800(6)
H(20)	866(3)	397(3)	-972(6)
H(21)	717(3)	259(3)	-760(5)

solution were red prisms elongated on [001]. Lattice constants were determined using the CTDIF program¹⁵ which repeatedly improves the diffractometer values of $(\theta, \chi, \psi)_{hkl}$ angles for 18 reflections until these angles do not move more than 0.01° .

Crystal data. $C_{21}H_{17}N_3O$, $M = 327.4$. Triclinic, $a = 11.982(4)$, $b = 11.462(4)$, $c = 6.253(2)$ Å; $\alpha = 83.4(1)$, $\beta = 80.1(1)$, $\gamma = 95.7(1)^\circ$; $Z = 2$; $D_c = 1.30$ g cm⁻³; $U = 834.1$ Å³; Cu- K_α radiation, $\lambda = 1.5418$ Å, μ (Cu- K_α) = 6.16 cm⁻¹. Space group $P\bar{1}$ from structure determination.

Intensity data were collected with a Siemens AED single-crystal diffractometer up to $\theta = 70^\circ$. 3 172 Independent reflections were measured, of which 1 578 were used for the crystal analysis; the intensities were $> 2[\sigma^2(I) + 10^{-4}I^2]^{\frac{1}{2}}$,

where I is the relative intensity of $\sigma^2(I)$ its variance. The dimensions of the crystal roughly in the x, y, z directions were 0.14, 0.10, and 0.58 mm. No absorption correction was made.

Structure analysis and refinement. The structure was solved by direct methods by use of the set of computer programs written by Sheldrick.¹⁶ After refinement of the non-hydrogen atoms with anisotropic thermal parameters (R 0.089), a difference map revealed significant residual peaks near the positions where all the hydrogen atoms were expected to occur. All the atomic parameters were then refined, hydrogens isotropically, with full-matrix least-squares cycles. The weighing function was of the form $1/w = \sigma^2(F_o) + 0.005 F_o^2$. The final agreement factor R was 0.045 and R_w was 0.044. Positional parameters together with their standard deviations are given in Table 4. The atomic scattering factor for oxygen, nitrogen, and carbon are from ref. 17 and those for hydrogen from ref. 18. Observed and calculated structure factors and thermal parameters are given in Supplementary Publication No. SUP 23691 (10 pp).^{*} All calculations were carried out on the CDC Cyber 76 computer at the Consorzio per la Gestione del Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna. Bibliographic searches were carried out using the Cambridge Crystallographic Data files which were obtained through the Servizio Italiano di Diffusione Dati Cristallografici, Parma.

^{*} For details of Supplementary Publications see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.

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