Reactions of Amidoximes with Orthoacetates

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The reaction of two amidoximes **4** with ethyl orthoacetate in the presence of an acid catalyst gave triazine *N*-oxides **7**. A mechanism *via* a Beckmann rearrangement to a carbodiimide, followed by reaction with amidoxime and the ortho ester, is proposed.

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Synthesis of fairly simple compounds by well-known methodology is usually not an exciting proposition. Therefore, when we recently needed to synthesize **5b**, we did not use the standard procedure of an amidoxime **4** and acetic anhydride [1], which usually gives the 1,2,4-oxadiazole **5** in excellent yield, but reacted **4b** with ethyl orthoacetate and an acid catalyst. The result was rather unexpected: instead of **5b**, we obtained a $C_{24}H_{20}N_6O$ compound, which was eventually determined to be **7b**, as the sole product (84% yield), whose spectral properties did not allow ready structure determination. The presence of exactly half of an equivalent of dioxane as a solvate which could not be removed under vacuum at 70° further confused the interpretation of the spectra and elemental analysis.

The same reaction with the unsubstituted analog **4a** gave a compound with very similar spectral properties. In this case the oxadiazole **5a** was the major product (58%), while the unknown **7a** was the minor (13%). This material could be recrystallized from hexanes, with which it did not form a solvate. Crystals suitable for X-ray analysis allowed structure determination, which showed **7a** to be a triazine *N*-oxide (Figure 1).

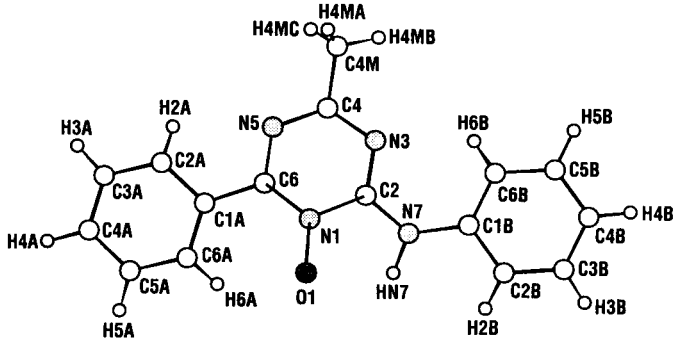


Figure 1

Although triazine *N*-oxides are not common, they have been previously prepared by three different methods: by oxidation of the corresponding triazine [2], by reaction of hydroxylamine with dicyanoamidine [2] or dicyanoguanidine [3], and by reaction of *N*-cyanoimidates with amidoximes [4].

Table 1

Fractional Coordinates (x10⁴) and B_{eq} (Å²). Estimated Standard Deviation are in Parentheses

$B_{eq} = 4/3(a^2B_{11}+b^2B_{22}+c^2B_{33} + abcos\gamma B_{12} + accos\beta B_{13} + bccos\alpha B_{23})$

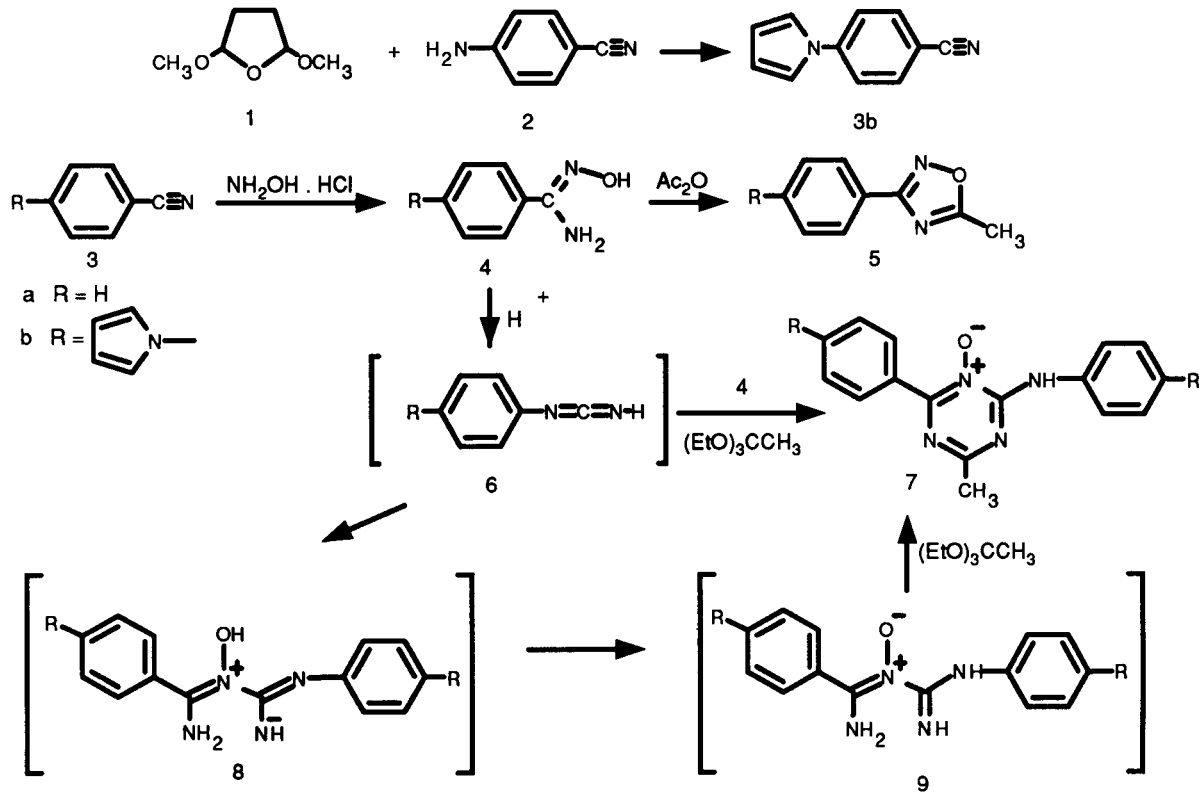
	x	y	z	B_{eq}
N(1)	1462(1)	1201(3)	5154(1)	1.77(6)
O(1)	1869(1)	1351(2)	4718(1)	2.21(5)
C(2)	1451(1)	2839(3)	5704(1)	1.74(6)
N(3)	1068(1)	2780(3)	6181(1)	1.91(6)
C(4)	700(1)	1047(3)	6113(1)	2.02(7)
C(4M)	292(1)	845(4)	6682(1)	2.61(8)
N(5)	668(1)	-501(3)	5590(1)	1.92(6)
C(6)	1050(1)	-397(3)	5102(1)	1.74(6)
N(7)	1855(1)	4424(3)	5701(1)	1.85(6)
C(1A)	999(1)	-2096(3)	4513(1)	1.82(6)
C(2A)	660(1)	-4061(3)	4612(1)	2.09(7)
C(3A)	566(1)	-5691(3)	4085(1)	2.38(7)
C(4A)	805(1)	-5381(3)	3438(1)	2.41(7)
C(5A)	1137(1)	-3434(3)	3330(1)	2.24(7)
C(6A)	1238(1)	-1803(3)	3860(1)	1.97(7)
C(1B)	1952(1)	6347(3)	6165(1)	1.76(6)
C(2B)	2393(1)	7811(3)	6022(1)	2.07(7)
C(3B)	2506(1)	9775(3)	6436(1)	2.21(7)
C(4B)	2189(1)	10292(3)	7008(1)	2.20(7)
C(5B)	1756(1)	8818(3)	7153(1)	2.27(7)
C(6B)	1631(1)	6862(3)	6741(1)	2.09(7)

Table 1a

Fractional Coordinates (x10³) and Isotropic Temperature Factors for Hydrogen Atoms

	x	y	z	B
H(4MA)	-7	61	647	3.0
H(4MB)	30	231	697	3.0
H(4MC)	39	-56	698	3.0
H(N7)	209	418	529	2.2
H(2A)	49	-421	503	2.4
H(3A)	33	-707	420	2.8
H(4A)	77	-664	307	2.8
H(5A)	130	-307	285	2.7
H(6A)	145	-42	379	2.4
H(2B)	264	729	565	2.5
H(3B)	282	1067	632	2.6
H(4B)	224	1170	729	2.6
H(5B)	151	918	758	2.7
H(6B)	135	589	684	2.5

Scheme 1



Since our product contains an *N*-phenyl group, it obviously has to come from a rearrangement. Therefore we propose (Scheme 1) that the first step is a Beckmann type rearrangement to a carbodiimide **6**. The carbodiimide can then react with a second equivalent of the amidoxime to give **8** which tautomerizes to **9** and then reacts with the orthoacetate to give the observed product **7**.

The observation that the 4-pyrrolyl amidoxime **4b** yields the rearrangement product exclusively, while the unsubstituted compound **4a** gives **7a** as only the minor product, is consistent with a Beckmann rearrangement mechanism, which requires stabilization of a positive charge by the migrating group [5].

The proposed carbodiimides **6** are also likely intermediates for the rearrangement of amidoximes to ureas [6,7], although in one case a cyanamide was suggested [8].

EXPERIMENTAL

Melting points were determined on a Mettler FP61 melting point apparatus and are uncorrected. The ^1H and ^{13}C nmr spectra were recorded on a Bruker AM 300 spectrometer at 300 and 75 MHz, respectively, with tetramethylsilane as the internal standard. Elemental analyses were performed by the Physical and Analytical Chemistry unit of the Upjohn Company.

4-(1*H*-Pyrrol-1-yl)benzonitrile (**3b**) [9].

A solution of 2,5-dimethoxytetrahydrofuran (39.6 g, 0.300 mole) and 4-cyanoaniline (29.5 g, 0.250 mole) in glacial acetic acid (250 ml) was refluxed for 30 minutes, the solvent was evaporated, the residue was dissolved in chloroform and filtered through silica gel (200 g) to yield **3b** (36.7 g, 87%) as a pale yellow solid. The analytical sample, mp 104-105°, was obtained by recrystallization from 95% ethanol; ^1H nmr (deuteriochloroform): δ 6.37 (t, 2H), 7.11 (t, 2H), 7.42 (d, 2H), 7.69 (d, 2H).

Anal. Calcd. for $C_{11}H_8N_2$: C, 78.55; H, 4.79; N, 16.66. Found: C, 78.55; H, 5.07; N, 16.79.

N-Hydroxy-4-(1*H*-pyrrol-1-yl)benzenecarboximidamide (**4b**) [9].

A suspension of hydroxylamine hydrochloride (700 mg, 10.0 mmoles) in dimethylformamide (10 ml) was stirred with triethylamine (1.51 ml, 10.0 mmoles) for 15 minutes and filtered. The filtrate was stirred with the nitrile **3b** (840 mg, 5.00 mmoles) for 8 hours. The solution was diluted with ice-water, filtered, and the solids air dried overnight to yield **4b** (850 mg, 85%). The analytical sample, mp 195-197°, was obtained by recrystallization from ethanol; ^1H nmr (deuteriochloroform-DMSO-d_6): δ 5.53 (bs, 2H), 6.24 (t, 2H), 7.17 (t, 2H), 7.40 (d, 2H), 7.75 (d, 2H), 9.60 (s, 1H).

Anal. Calcd. for $C_{11}H_{11}N_3O$: C, 65.67; H, 5.51; N, 20.88. Found: C, 65.31; H, 5.49; N, 21.15.

2-Anilino-4-methyl-6-phenyl-1,3,5-triazine 1-Oxide (**7a**) and 5-Methyl-3-phenyl-1,2,4-oxadiazole (**5a**).

A solution of *N*-hydroxybenzenecarboximidamide **4a** [10] (0.953 g, 7.00 mmoles), triethyl orthoacetate (2.271 g, 14.0

Table 2

Bond Lengths (Å), Angles (°), and Torsion Angles (°)

A. Bond Lengths (Å)

N(1)-O(1)	1.316(2)	C(1A)-C(6A)	1.399(2)
N(1)-C(2)	1.398(2)	C(2A)-C(3A)	1.378(2)
N(1)-C(6)	1.358(2)	C(3A)-C(4A)	1.390(3)
C(2)-N(3)	1.323(2)	C(4A)-C(5A)	1.385(3)
C(2)-N(7)	1.337(2)	C(5A)-C(6A)	1.386(2)
N(3)-C(4)	1.337(2)	C(1B)-C(CB)	1.394(2)
C(4)-C(4M)	1.499(2)	C(1B)-C(6B)	1.396(2)
C(4)-N(5)	1.326(2)	C(2B)-C(3B)	1.386(3)
N(5)-C(6)	1.338(2)	C(3B)-C(4B)	1.385(2)
C(6)-C(1A)	1.478(2)	C(4B)-C(5B)	1.382(2)
N(7)-C(1B)	1.417(2)	C(5B)-C(6B)	1.385(2)
C(1A)-C(2A)	1.401(2)		

B. Bond Angles (°)

O(1)-N(1)-C(2)	117.3(1)	C(6)-C(1A)-C(6A)	124.7(1)
O(1)-N(1)-C(6)	124.9(1)	C(2A)-C(1A)-C(6A)	118.4(1)
C(2)-N(1)-C(6)	117.8(1)	C(1A)-C(2A)-C(3A)	121.3(2)
N(1)-C(2)-N(3)	121.7(1)	C(2A)-C(3A)-C(4A)	119.8(2)
N(1)-C(2)-N(7)	114.3(1)	C(3A)-C(4A)-C(5A)	119.6(2)
N(3)-C(2)-N(7)	124.1(1)	C(4A)-C(5A)-C(6A)	120.9(2)
C(2)-N(3)-C(4)	116.2(1)	C(1A)-C(6A)-C(5A)	120.0(2)
N(3)-C(4)-C(4M)	116.6(1)	N(7)-C(1B)-C(2B)	116.8(1)
N(3)-C(4)-N(5)	125.6(1)	N(7)-C(1B)-C(6B)	124.1(1)
C(4M)-C(4)-N(5)	117.7(2)	C(2B)-C(1B)-C(6B)	119.1(2)
C(4)-N(5)-C(6)	117.6(1)	C(1B)-C(2B)-C(3B)	120.5(1)
N(1)-C(6)-N(5)	120.8(1)	C(2B)-C(3B)-C(4B)	120.5(2)
N(1)-C(6)-C(1A)	122.5(1)	C(3B)-C(4B)-C(5B)	118.6(2)
N(5)-C(6)-C(1A)	116.7(1)	C(4B)-C(5B)-C(6B)	121.9(2)
C(2)-N(7)-C(1B)	128.5(1)	C(1B)-C(6B)-C(5B)	119.3(2)
C(6)-C(1A)-C(2A)	116.8(1)		

C. Torsion Angles (°)

O(1)-N(1)-C(2)-N(3)	-177.8(1)	N(5)-C(6)-C(1A)-C(2A)	17.6(2)
O(1)-N(1)-C(2)-N(7)	2.0(2)	N(5)-C(6)-C(1A)-C(6A)	158.6(2)
C(6)-N(1)-C(2)-N(3)	3.3(2)	C(2)-N(7)-C(1B)-C(2B)	-176.9(2)
C(6)-N(1)-C(2)-N(7)	-176.9(1)	C(2)-N(7)-C(1B)-C(6B)	2.2(3)
O(1)-N(1)-C(6)-N(5)	176.6(1)	C(6)-C(1A)-C(2A)-C(3A)	117.1(2)
O(1)-N(1)-C(6)-C(1A)	-3.3(2)	C(6A)-C(1A)-C(2A)-C(3A)	0.7(2)
C(2)-N(1)-C(6)-N(5)	-4.7(2)	C(6)-C(1A)-C(6A)-C(5A)	-176.1(2)
C(2)-N1-C(6)-C(1A)	175.4(1)	C(2A)-C(1A)-C(6A)-C(5A)	0.0(2)
N(1)-C(2)-N(3)-C(4)	1.0(2)	C(1A)-C(2A)-C(3A)-C(4A)	-0.8(3)
N(7)-C(2)-N(3)-C(4)	-178.8(2)	C(2A)-C(3A)-C(4A)-C(5A)	0.2(3)
N(1)-C(2)-N(7)-C(1B)	177.9(1)	C(3A)-C(4A)-C(5A)-C(6A)	0.6(3)
N(3)-C(2)-N(7)-C(1B)	-2.3(3)	C(4A)-C(5A)-C(6A)-C(1A)	-0.7(3)
C(2)-N(3)-C(4)-C(4M)	175.2(1)	N(7)-C(1B)-C(2B)-C(3B)	177.9(1)
C(2)-N(3)-C(4)-N(5)	-4.3(2)	C(6B)-C(1B)-C(2B)-C(3B)	-1.2(2)
N(3)-C(4)-N(5)-C(6)	3.0(3)	N(7)-C(1B)-C(6B)C(5B)	-178.7(2)
C(4M)-C(4)-N(5)-C(6)	-176.5(1)	C(2B)-C(1B)-C(6B)-C(5B)	0.3(2)
C(4)-N(5)-C(6)-N(1)	1.7(2)	C(1B)-C(2B)-C(3B)-C(4B)	1.2(3)
C(4)-N(5)-C(6)-C(1A)	-178.4(1)	C(2B)-C(3B)-C(4B)-C(5B)	-0.4(3)
N(1)-C(6)-C(1A)-C(2A)	162.3(2)	C(3B)-C(4B)-C(5B)-C(6B)	-0.4(3)
N(1)-C(6)-C(1A)-C(6A)	-21.6(2)	C(4B)-C(5B)-C(6B)-C(1B)	0.5(3)

Table 3

Close Intermolecular Contacts Between Non-hydrogen Atoms. Estimated Standard Deviations are in Parentheses

N(1).....C(2A)	x, y-1, z	3.466(2)
N(1).....C(3A)	x, y-1, z	3.451(2)
C(2).....C(2A)	x, y-1, z	3.318(2)
C(6).....C(3A)	x, y-1, z	3.481(2)
C(1B)....C(6)	x, y-1, z	3.495(2)
C(2B)....N(1)	x, y-1, z	3.387(2)
C(2B)....O(1)	x, y-1, z	3.420(2)
C(3B)....C(2)	x, y-1, z	3.394(2)
C(3B)....N(7)	x, y-1, z	3.362(2)
C(4B)....C(2)	x, y-1, z	3.371(2)
C(4B)....N(3)	x, y-1, z	3.447(2)
C(4B)....N(7)	x, y-1, z	3.498(2)
C(5B)....N(3)	x, y-1, z	3.341(2)
C(5B)....C(4)	x, y-1, z	3.473(2)
C(6B)....C(4)	x, y-1, z	3.483(2)
O(1).....N(7)	1/2-x, 1/2-y, 1-z	3.286(2)
O(1).....C(2B)	1/2-x, 1/2-y, 1-z	3.302(2)
C(5A)....C(3B)	1/2-x, 1/2-y, 1-z	3.444(2)
C(6A)....C(2B)	1/2-x, 1/2-y, 1-z	3.420(2)
O(1).....C(3B)	1/2-x, 11/2-y, 1-z	3.482(2)
C(4M)....C(4M)	-x, y, 11/2-z	3.461(2)

Table 4

Hydrogen Bonds

D Represents Donor, A Acceptor; Distances are in Å and Angles are in °. Standard Deviations are in Parentheses

D	A	A AT	D...A	H...A	<,D-H...A
N(7)	O(1)	x, y, z	2.552(2)	2.02	111

mmoles), and 1*S*-(+)-10-camphorsulfonic acid (14 mg) in 7 ml of toluene was refluxed for 3 hours. The solvent was evaporated, and the residue was chromatographed on silica gel with chloroform to yield **5a** (0.653 g, 58%) and then with 5% ethyl acetate in chloroform to yield **7a** (0.123 g, 13%).

The analytical sample of **5a**, mp 39° [11], was obtained by sublimation at 40 mm Hg; ^{1}H nmr (deuteriochloroform): δ 2.63 (s, 3H), 7.43-7.52 (m, 3H), 8.03-8.09 (m, 2H); ^{13}C nmr: δ 12.4, 126.8, 127.3, 128.8, 131.1, 168.4, 176.5.

Anal. Calcd. for $C_9H_8N_2O$: C, 67.49; H, 5.04; N, 17.49. Found: C, 67.47; H, 5.09; N, 17.46.

The analytical sample of **7a**, mp 137.7°, was obtained by recrystallization from hexanes; ir (Nujol mull): 3230, 1615, 1595, 1570, 1550, 1480, 1455, 1350, 1235, 745, 690 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.62 (s, 3H), 7.20 (t, 1H), 7.38 (t, 2H), 7.43-7.60 (m, 3H), 7.76 (d, 2H), 8.76 (d, 2H), 10.16 (s, 1H); ^{13}C nmr: δ 25.5, 120.8, 125.1, 128.1, 129.2, 130.6, 132.4, 136.2, 154.2, 155.5, 162.4.

Anal. Calcd. for $C_{16}H_{14}N_4O$: C, 69.05; H, 5.07; N, 20.13. Found: C, 68.98; H, 5.09; N, 20.15.

4-Methyl-2-(1*H*-pyrrol-1-yl)anilino-6-(1*H*-pyrrol-1-yl)phenyl-1,3,5-triazine 1-Oxide (**7b**).

A solution of **4b** (10.06 g, 50.0 mmoles), triethyl orthoacetate (18.3 ml, 0.100 mole), and 1*S*-(+)-10-camphorsulfonic acid (50 mg) in 60 ml of toluene was refluxed for 21 hours. After 1.5 hours another 50 mg of CSA was added, and after 2.75 hours another 18.3 ml of the orthoacetae. The reaction mixture was cooled to room temperature, the solids were filtered and washed with tolu-

Table 5

Anistoropic Thermal Parameters ($x10^4$)

The expression is of the form:

$\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-B_{12}hk-B_{13}hl-B_{23}kl)$

Estimated Standard Deviations are in parentheses

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	7(1)	172(5)	10(1)	0(2)	2(1)	0(2)
O(1)	8(1)	217(4)	13(1)	-19(2)	9(1)	-14(2)
C(2)	7(1)	159(5)	10(1)	3(2)	-1(1)	4(2)
N(3)	7(1)	196(5)	10(1)	-1(2)	1(1)	-3(2)
C(4)	7(1)	217(6)	11(1)	-1(2)	-0(1)	-0(3)
C(4M)	9(1)	306(7)	13(1)	-20(2)	4(1)	-22(3)
N(5)	7(1)	197(5)	11(1)	-5(2)	1(1)	-0(2)
C(6)	7(1)	157(5)	11(1)	3(2)	-1(1)	12(2)
N(7)	8(1)	163(5)	11(1)	-5(2)	4(1)	-2(2)
C(1A)	7(1)	160(5)	13(1)	6(2)	-1(1)	6(3)
C(2A)	9(1)	174(6)	13(1)	1(2)	1(1)	10(3)
C(3A)	10(1)	162(6)	19(1)	-7(2)	1(1)	0(3)
C(4A)	10(1)	184(6)	17(1)	5(2)	1(1)	-30(3)
C(5A)	9(1)	210(6)	13(1)	3(2)	3(1)	-10(3)
C(6A)	8(1)	166(6)	13(1)	-2(2)	1(1)	-3(3)
C(1B)	8(1)	143(5)	11(1)	4(2)	-2(1)	4(2)
C(2B)	7(1)	190(6)	14(1)	3(2)	1(1)	7(3)
C(3B)	8(1)	174(6)	18(1)	-8(2)	-2(1)	9(3)
C(4B)	9(1)	158(6)	16(1)	6(2)	-4(1)	-8(3)
C(5B)	10(1)	181(6)	14(1)	8(2)	3(1)	-7(3)
C(6B)	9(1)	164(6)	14(1)	-7(2)	4(1)	6(3)

ene to yield **7b** (5.46 g, 48%). The filtrate was evaporated to dryness and diluted with absolute ethanol to yield more **7b** (3.08 g, 27%). The analytical sample, mp 251.1° dec, was obtained as the solvate with 0.5 dioxane by recrystallization from dioxane; ir (Nujol mull): 3229, 1616, 1606, 1584, 1577, 1552, 1584, 1528, 1472, 1423, 1332, 729 cm^{-1}; ms: (70 eV, electron impact) m/z 408 (molecular ion), 183, 392, 168; ^1H nmr (deuteriochloroform): δ 2.66 (s, 3H), 3.71 (s, 4H, 0.5 dioxane), 6.37 (t, 2H), 6.41 (t, 2H), 7.10 (t, 2H), 7.23 (t, 2H), 7.50 (d, 2H), 7.84 (d, 2H), 10.15 (s, 1H); ^{13}C nmr: δ 25.6, 67.1 (dioxane), 110.6, 111.6, 118.9, 119.0, 119.3, 121.2, 121.9, 127.0, 132.6, 133.7, 138.0, 143.6, 154.4, 154.7, 162.7.

Anal. Calcd. for $C_{24}H_{20}N_6O\cdot\frac{1}{2}C_4H_8O_2$: C, 69.01; H, 5.35; N, 18.57. Found: C, 69.41; H, 5.30; N, 18.81.

Crystal Data for **7a**.

(**I**): $C_{16}H_{14}N_4O$, M_r = 278.31, monoclinic, C2/c, a = 24.608(2), b = 5.634(2), c = 19.080(2)Å, β = 91.18(2), V = 2644.7(7)Å^3, Z = 8, D_c = 1.40 gm/cm^3, graphite monochromatized CuKα, λ = 1.5418, μ(CuKα) = 6.52 cm^{-1}, T = 123°K, R = 0.048 for 2454 unique reflections. A clear, thin plate of dimensions 0.11 x 0.21 x 0.50 mm was used for intensity measurements on a Siemens $P2_1$ diffractometer controlled by a Harris computer. CuKα radiation and a graphite monochromator were used for intensity measurement. The step-scan technique was used with a scan rate of 4°/min, a scan width of 3.4°, and a $2\theta_{max}$ = 136°. Ten reflections periodically monitored showed no loss of intensity during the data collection. Of the 2454 unique reflections measured, 2014 had intensities $>3\sigma$. Standard deviations in the intensities were approximated by the equation:

$$\sigma^2(\mathbf{I}) = \sigma^2(\mathbf{I})_{counting\ statistics} + 0.0171\mathbf{I}^2$$

where the coefficient of **I** was calculated from the variations in intensities of the monitored reflections. Unit cell parameters were determined accurately by least squares fit of CuKα_1 2θ values (λ(CuKα_1) = 1.5402) for 25 high 2θ reflections [12]. Polarization corrections appropriate for a monochromator with 50% perfect character were applied. No absorption correction was applied. A partial trial solution, 14 atoms, was obtained by direct methods, using MULTAN [13]. The trial solution was extended using successive Fourier syntheses. Hydrogen atoms were clearly found in a difference map. The structure was refined by least squares with the coordinates and anisotropic thermal parameters for nonhydrogen atoms included in the refinement. Isotropic thermal parameters for hydrogen atoms were set ½ unit higher than the isotropic equivalent of the thermal parameters of the attached heavier atom. The function minimized in the refinement was $\Sigma w(F_o^2-F_c^2)^2$, where weights w were $1/\sigma^2(F_o^2)$. Atomic form factors were from Doyle & Turner [14], except for hydrogens, which were from Stewart, Davidson & Simpson [15]. In the final refinement cycle, all shifts were $<0.70\sigma$. The final R was 0.048, and the goodness of fit was 2.88. A final difference map showed no peaks $>0.34 e Å^{-3}$. The CRYM system of computer programs was used [16]. A ball & stick drawing with atom numbering is shown in Figure 1. The final coordinates are shown Table 1 and other pertinent X-ray data in Tables 1a-5.

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