Formations of Novel Dimeric Cyclohexanone Oxime Compounds

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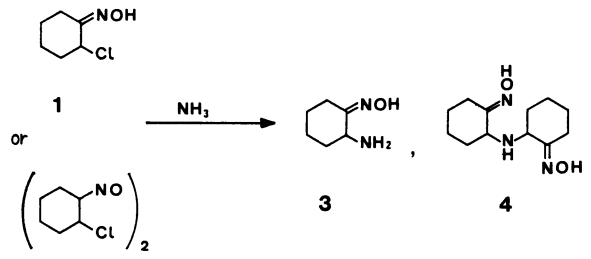
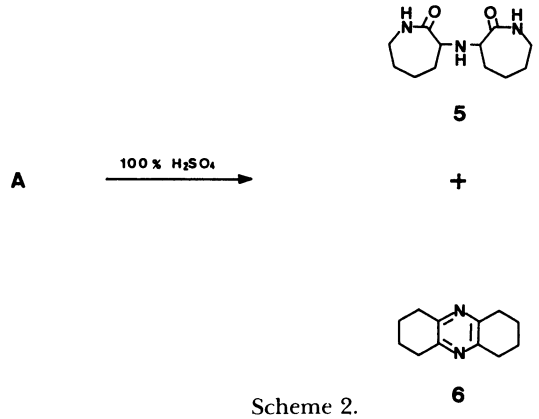
The structure of the dimeric oxime compound obtained by the reaction of 2-chlorocyclohexanone oxime or 1-chloro-2-nitrosocyclohexane dimer with stoichiometrical ammonia was established to be 14-oxa-7,15,16-triazatetracyclo[11.2.1.$0^{1,6}$.$0^{8,13}$]hexadecan-16-ol by spectroscopic methods and X-ray crystallography; the result leads to a revision of the previously proposed structure, bis(2-hydroxyiminocyclohexyl)amine.

2-Aminocycloalkanone oxime can be obtained by the reaction of 2-chlorocycloalkanone oxime or its dimer, 1-chloro-2-nitrosocycloalkane dimer, with a large excess of ammonia.[1] In the commercial chemico-enzymatic process[2] used to prepare L-lysine, 2-aminocyclohexanone oxime (**3**) is produced in large scale from 2-chlorocyclohexanone oxime (**1**) or 1-chloro-2-nitrosocyclohexane dimer (**2**). The structure of the principal by-product of the reaction (hereinafter named "compound **A**") was proposed to be bis(2-hydroxyiminocyclohexyl) amine (**4**) by Ohno *et al.*[3] and J. Beger *et al.*[4] (Scheme 1). However, while we were engaged in the further study of this reaction, we had some doubts about the chemical structure of compound **A**. Thus we have attempted the detailed instrumental analysis of compound **A** and its analog to elucidate the proper chemical structure.

The following experimental results may give support to assigning structure **4** to compound **A**. (i) In the reaction of **1** or **2** with ammonia, compound **A** increases with the decrease in the molar ratio of ammonia. Thus it is inferred from analogy with the reaction of alkyl halide and ammonia that compound **A** is an oxime having a imino group. (ii) 1,2,3,4,6,7,8,9-octahydrophenazine (**6**) was obtained as a major product when compound **A** was heated in acidic or alkaline aqueous solution. Moreover, bis(perhydro-2-oxo-3-azepinyl)amine (**5**), a plausible product from **4**, was formed as a major product by the Beckmann rearrangement of compound **A** in 100% sulfuric acid (Scheme 2). (iii) Compound **A** is obtainable in high yield by the reaction of **1** and **3**. (iv) The elemental analysis of compound **A** gave the empirical formula $C_{12}H_{21}N_3O_2$. However, when the properties of compound **A** are compared with those of **3**, the following different points are found: (v) The pattern of IR spectrum does not resemble to that of **3**. Particularly, the absorption at 1670 cm^{-1} arising from oxime group was missing in the spectrum of compound **A**. (vi) Compound **A** is only sparingly soluble in such solvents as chloroform and alcohols, while **3** is fairly soluble in them. (vii) The rate of the salt exchange reaction of compound **A** with ammonium chloride is lower than that of **3**. (viii) Compound **A** was formed by heating **3** with ammonia, but the reverse reaction did not proceed. Therefore, it is doubtful whether compound **A** and **3** have analogous functional groups or not.



Scheme 1.



Scheme 2.

Accordingly, we synthesized a reference compound and compared the data from instrumental analyses of the compound with those of compound **A** to elucidate the proper structure. We found that the reaction of 2-chlorocyclohexanone oxime or 1-chloro-2-nitrosocyclohexane dimer with stoichiometrical ammonia yields dimeric cyclohexanone oxime, 14-oxa-7,15,16-triazatetracyclo[11.2.1.$0^{1,6}$.$0^{8,13}$]hexadecan-16-ol.

Results and Discussion

2-Chlorocyclohexanone oxime (**1**) or 1-chloro-2-nitrosocyclohexane dimer (**2**) was treated with stoichiometrical ammonium chloride in a two-phase solvent system containing organic and aqueous alkaline layers to produce compound **A**. **1** or **2** was also reacted with stoichiometrical methylamine hydrochloride to produce compound **B**. 2-(methylamino)cyclohexanone oxime was obtained by the reaction of **1** or **2** with excess methylamine in organic solvents such as benzene and chloroform.

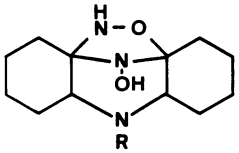
The structures of compound **A** and **B** were studied in the following procedure.

The elemental analyses gave the empirical formulae $C_{12}H_{21}N_3O_2$ and $C_{13}H_{23}N_3O_2$ to compounds **A** and **B**, respectively. Though ^{1}H-NMR spectrum of compound

A was not obtained due to its poor solubility, two kinds of protons exchangeable with deuterium in deuterium oxide were observed at δ=6.1 and 7.8 in the spectrum of compound **B**. ^{13}C-NMR spectra of both compounds showed analogous peak-patterns, the peaks to be noticed being observed at δ=100, 86, 60 (2 carbon atoms) in compound **A** and at δ=99, 85, 68, 63 in compound **B**. The peaks at δ=99—100 and 85—86 are reasonably assigned to quarternary carbon atoms, and the remaining peaks at δ=60—68 are also reasonably assigned to carbon atoms adjacent to the amino group. Thus, it is inferred that both compounds have two quarternary carbon atoms of considerably different natures and two similar carbon atoms adjacent to the amino group. Moreover, since no peaks were observed in the field lower than 100, it is suggested that neither of them has an oxime group.

In the IR spectra of both compounds, no absorption at 1670 cm^{-1} arising from oxime group was observed, but the bands due to amino groups and hydroxyl groups were observed at 3200—3100 cm^{-1}. Mass spectra of both compounds showed the fragment peaks at m/z (M-17)$^+$ resulting from the elimination of a hydroxyl radical, but no other useful information was obtained from them.

From these observations, we assigned 14-oxa-7,15,16-triazatetracyclo[11.2.1.0^{1,6}.0^{8,13}]hexadecan-16-ol (**7**) and 7-methyl-14-oxa-7,15,16-triazatetracyclo[11.2.1.0^{1,6}.0^{8,13}] hexadecan-16-ol (**8**) to the structures of compounds **A** and **B**, and the structure of **7** was definitely confirmed by X-ray diffraction analysis.



7 R = H
8 R = CH_3

The crystallographic structure of **7** is shown in Fig. 1. The atomic positional parameters are listed in Table 1 and Table 2 presents some of more important bond lengths and angles. The molecule has a fused ring structure. The two outer cyclohexane rings are attached equatorially to the central six-membered heterocyclic ring and is in a chair conformation. The bonding pattern within the three six-membered ring is normal with an average C–C bond length of 1.528 Å and C–N bond length of 1.471 Å. The longest of these, C(1)–C(6), 1.543 (3) Å and C(7)–C(12), 1.550(3) Å, can be ascribed to the high degree of substitution on these C atoms. The bond angle, C(1)–N(2)–C(12), is much less, 100.1(1)°, than expected as the effect of the ring strain of attached five-membered ring and has probably resulted in the long N(2)–O(2) length of 1.458(2) Å found at this point. The sum of the valency angles around N(2) is 314.6°. The dihedral angles between C(1)–C(6)–C(7)–C(12) and C(1)–C(3)–C(4)–C(6) and between C(1)–C(6)–C(7)–C(12)

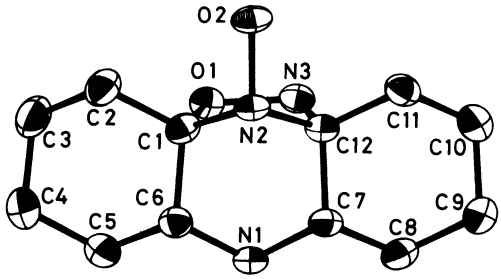


Fig. 1. Perspective view of the molecule **7** with atomic numbering scheme. The ellipsoids are drawn to enclose 50% probability.

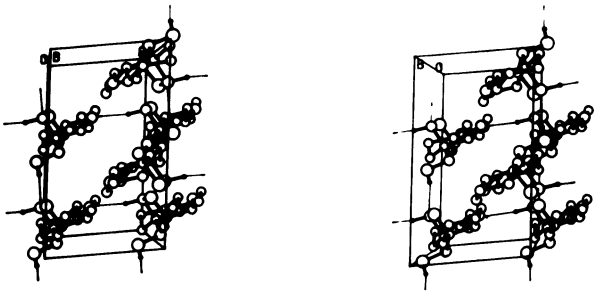


Fig. 2. Stereodrawing of the crystal structure. The hydrogen bonds are shown by fine lines. For H-atoms only the atoms contributed to the hydrogen bonds are drawn for clarity.

Table 1. Positional (×10^4) and thermal (×10) parameters

Atom	x	y	z	B_{eq}/Å^{2} [a]
C(1)	1707(2)	1674(1)	4115(1)	23
C(2)	1295(3)	930(1)	4504(2)	31
C(3)	1953(4)	419(1)	3502(2)	38
C(4)	4378(4)	515(1)	3271(2)	43
C(5)	4787(3)	1256(1)	2834(2)	32
C(6)	4117(3)	1795(1)	3791(1)	25
C(7)	3295(2)	3031(1)	3947(1)	24
C(8)	3262(3)	3708(1)	3198(2)	31
C(9)	2118(3)	4290(1)	3875(2)	39
C(10)	−256(3)	4077(1)	4062(2)	36
C(11)	−276(3)	3408(1)	4839(1)	28
C(12)	915(2)	2817(1)	4233(1)	22
N(1)	4384(2)	2491(1)	3250(1)	26
N(2)	1253(2)	2195(1)	5061(1)	22
N(3)	−420(2)	2569(1)	3066(1)	23
O(1)	204(2)	1835(1)	2975(1)	24
O(2)	−894(2)	2021(1)	5499(1)	27

a) The equivalent isotropic temperature factor defined by W. C. Hamilton (*Acta Crystallogr.*, **12**, 609 (1959)).

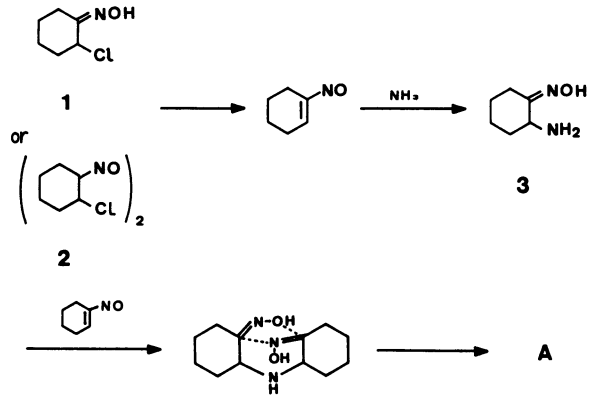
TABLE 2. IMPORTANT BOND LENGTHS AND ANGLES

Bond length	l/Å		l/Å
C(1)-C(2)	1.517(2)	C(2)-C(3)	1.528(3)
C(3)-C(4)	1.517(3)	C(4)-C(5)	1.527(3)
C(5)-C(6)	1.532(2)	C(6)-C(1)	1.543(2)
C(7)-C(8)	1.524(2)	C(8)-C(9)	1.529(3)
C(9)-C(10)	1.520(3)	C(10)-C(11)	1.528(3)
C(11)-C(12)	1.522(2)	C(12)-C(7)	1.550(2)
N(1)-C(6)	1.470(2)	N(1)-C(7)	1.467(2)
N(2)-C(1)	1.461(2)	N(2)-C(12)	1.484(2)
N(2)-O(2)	1.458(2)	N(3)-C(12)	1.480(2)
N(3)-O(1)	1.467(2)	O(1)-C(1)	1.462(2)
Bond angle	φ/°		φ/°
C(2)-C(1)-C(6)	112.8(1)	C(1)-C(2)-C(3)	111.1(2)
C(2)-C(3)-C(4)	110.9(2)	C(3)-C(4)-C(5)	110.5(2)
C(4)-C(5)-C(6)	111.9(2)	C(5)-C(6)-C(1)	111.2(1)
C(8)-C(7)-C(12)	111.4(1)	C(7)-C(8)-C(9)	111.5(2)
C(8)-C(9)-C(10)	109.8(2)	C(9)-C(10)-C(11)	110.9(2)
C(10)-C(11)-C(12)	111.9(1)	C(11)-C(12)-C(7)	111.7(1)
C(6)-C(1)-N(2)	107.2(1)	C(1)-C(6)-N(1)	111.5(1)
C(7)-C(12)-N(2)	104.8(1)	C(12)-C(7)-N(1)	112.4(1)
C(6)-N(1)-C(7)	112.2(1)	C(1)-N(2)-C(12)	100.1(1)
N(2)-C(1)-O(1)	105.9(1)	N(2)-C(12)-N(3)	105.1(1)
C(1)-O(1)-N(3)	106.9(1)	C(12)-N(3)-O(1)	104.1(1)
C(6)-C(1)-O(1)	107.6(1)	C(2)-C(1)-O(1)	108.5(1)
C(7)-C(12)-N(3)	111.0(1)	C(11)-C(12)-N(3)	110.6(1)
C(2)-C(1)-N(2)	114.5(1)	C(11)-C(12)-N(2)	113.4(1)
C(5)-C(6)-N(1)	108.3(1)	C(8)-C(7)-N(1)	109.2(1)
C(1)-N(2)-O(2)	107.5(1)	C(12)-N(2)-O(2)	107.5(1)

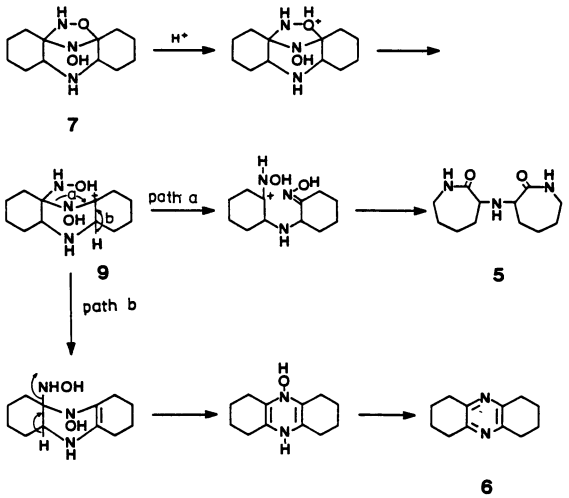
and C(7)–C(9)–C(10)–C(12) are 11.5(1)° and 7.4(1)°, respectively. O(1) and N(3) atoms axially attached to the C(1) and C(12) atoms respectively make five membered ring with the atom N(2) by an envelope conformation, with this atom 0.610(5) Å out of plane of the remaining four ring atoms. Figure 2 displays the packing. The molecules are linked by two types of intermolecular hydrogen bonds, such that the crystal contains an infinite two-dimensional net perpendicular to the b axis. One hydrogen bond exists between N(3)–H(N3) and N(1) of the molecules related by the c glide plane in the direction of a, the second between O(2)–H(O2) and N(3) of the successive molecules along the c. Thus each molecule is hydrogen bonded to four neighboring molecules. The plate-like morphology of the crystal parallels the orientation of the hydrogen-bonded nets. The hydrogen bond distances and angles are: N(3)···N(1), 3.158(2); H(N3)···N(1), 2.22(2) Å; N(3)–H(N3)···N(1), 163(2)°; O(2)···N(3), 2.807(2); H(O2)···N(3), 1.85(3) Å; O(2)–H(O2)···N(3), 170(3)°.

We speculate that this moderately complicated compound was formed by the reaction mechanism shown in Scheme 3. Hydrogen chloride was eliminated from **1** or **2** to give nitrosocyclohexene, and this was converted to **3** by addition of ammonia. When the molar ratio of ammonia was low, **3** reacted with another intermediary nitrosocyclohexene to give **4**. Spontaneous intramolecular 1,3-dipolar addition reaction between two oxime groups gave 14-oxa-7,15,16-triazatetracyclo-[11.2.1.$0^{1,6}$.$0^{8,13}$] hexadecan-16-ol (**7**).

A plausible mechanism for the formation of bislactam (**5**) and octahydrophenazine (**6**) are also illustrated in Scheme 4. Compound **7** was protonated in an acidic medium to produce a common intermediate (**9**). In 100% sulfuric acid, bislactam (**5**) was obtained by the



Scheme 3.



Scheme 4.

Beckmann rearrangement (path a). On the other hand, when **7** was heated in an acidic aqueous solution, **6** was formed by the elimination of hydroxylamino radical from **9** (path b).

Experimental

General. Melting points are uncorrected. The IR and mass spectra were recorded on Shimadzu IR-40 and Hitachi RMU-7M spectrometers respectively. ^{1}H-NMR and ^{13}C-NMR specra were recorded on Hitachi R-24B (60 MHz) spectrometer and JEOL FX-90Q pulse FT spectrometer (22.49 MHz) using TMS as internal standard.

Preparation of 2-Chlorocyclohexanone Oxime (1) and 1-Chloro-2-nitrosocyclohexane Dimer (2). **1** and **2** were prepared by the methods described in the patent.[5]

Preparation of 2-Aminocyclohexanone Oxime (3). In a 500 ml stainless steel autoclave, a mixture of 1-chloro-2-nitrosocyclohexane dimer (14.8 g, 0.05 mol), ammonia (170 g, 10 mol) and methanol 100 ml was heated at 70 °C. After 1 h, ammonia and methanol were removed under reduced pressure to give 15.7 g of crude 2-aminocyclohexanone oxime hydrochloride (95.3%). The crude product was purified by recrystallization from water to give (14.9 g, 90.6%) of 2-aminocyclohexanone oxime hydrochloride as white crystals; mp 212.0—213.0 °C. Found: C, 43.85; H, 8.00; N, 17.16; Cl, 21.49 %. Calcd for $C_6H_{13}N_2OCl$: C, 43.77; H, 8.02; N, 17.02; Cl, 21.53 %.

Preparation of 2-(Methylamino)cyclohexanone Oxime. To a solution of 1-chloro-2-nitrosocyclohexane dimer (14.8 g, 0.05 mol) in benzene (100 ml) was added dropwise at 60 °C a solution of methylamine (6.2 g, 0.2 mol) in benzene (50 ml) during 1 h, and the reaction mixture was heated at 60 °C for an additional 1 h. After the reaction, the mixture was cooled to room temperature and washed with a 100 ml portion of 10% sodium hydroxide. The benzene layer was dried over anhydrous magnesium sulfate, and benzene was removed under reduced pressure to give crude 13.5 g of 2-(methylamino)-cyclohexanone oxime (94.9%). The crude product was purified by recrystallization from methanol to give 10.8 g of 2-(methylamino)cyclohexanone oxime as white crystals (75.9%); mp 103—104 °C. Found: C, 59.18; H, 9.83; N, 19.75%. Calcd for $C_7H_{14}N_2O$: C, 59.12; H, 9.93; N, 19.71%.

Preparation of 14-Oxa-7,15,16-triazatetracyclo[11.2.1.0^{1,6}.0^{8,13}]-hexadecan-16-ol (7). To a mixture of 1-chloro-2-nitrosocyclohexane dimer (14.8 g, 0.05 mol), dichloromethane (200 ml), and 2 mol dm^{-3} sodium hydroxyde solution (100 ml) was added dropwise at room temperature a solution of ammonium chloride (5.4 g, 0.1 mol) in water (50 ml) during 30 min. The reaction mixture was stirred for an additional 2 h. A crystalline material suspended in the reaction mixture was filtered and washed with water. The crude product was purified by recrystallization from ethanol to give 11.3 g (94.6%) of **7** as a white solid ; mp 186—187 °C. ^{1}H-NMR (CD_3COOD) δ=1.3—2.2 (m 12H), 2.2—2.6 (t 4H), 3.4—3.8 (m 2H). ^{13}C-NMR CD_3COOD δ=22.5, 23.1, 23.6, 24.3, 27.2, 27.6, 28.7, 60.3, 60.4, 85.6, 100.0. IR (KBr): 3280, 3120, 2940, 2870, 1480, 1450, 1120, 958, 942, 905, 898, 860, 820, 795 cm^{-1}. Found: C, 60.58; H, 8.81; N, 17.69%. Calcd for $C_{12}H_{21}N_3O_2$: C, 60.23; H, 8.85; N, 17.56%.

Preparation of 7-Methyl-14-oxa-7,15,16-triazatetracyclo[11.2.1.-0^{1,6}.0^{8,13}]hexadecan-16-ol (8). In a similar manner to the above, **8** was prepared from methylamine hydrochloride in 90.7% yield; white solid; mp 157—158 °C. ^{1}H-NMR (DMSO-d_6) δ=1.0—2.0 (m 16H), 2.0—2.3 (m 2H), 2.1 (s 3H), 5.9—6.1 (1H), 7.8 (1H). ^{13}C-NMR ($CDCl_3$) δ=22.5, 23.0, 24.1, 27.8, 28.1, 29.2, 29.6, 36.4, 37.9, 62.6, 67.9, 85.0, 99.1. IR (KBr): 3210, 3100, 2930, 2850, 2770, 1450, 1360, 1350, 1260, 1250, 1190, 1150, 1120, 1040, 980, 950, 930, 900, 870, 830, 790, 700 cm^{-1}. Found: C, 61.77; H, 9.03; N, 16.62%. Calcd for $C_{13}H_{23}N_3O_2$: C, 61.63; H, 9.15; N, 16.59%.

Preparation of 1,2,3,4,6,7,8,9-Octahydrophenazine (6). A mixture of 14-oxa-7,15,16-triazatetracyclo[11.2.1.0^{1,6}.0^{8,13}] hexadecan-16-ol (**7**) (23.9 g, 0.1 mol) and 1 mol dm^{-3} sulfuric acid (100 ml) was heated at 60 °C. After 3 h, the reaction mixture was cooled to room temperature and adjusted to pH 10 with 2 mol dm^{-3} sodium hydroxide solution. The solution was extracted with three 100 ml portions of benzene and then dried over anhydrous magnesium sulfate. After removal of the benzene, the residue was distilled under reduced pressure, and the fraction at 128 °C/1.6 mmHg was collected; mp 108—109 °C. ^{1}H-NMR ($CDCl_3$) δ=1.6—2.2 (8H), 2.6—3.1 (8H). IR (KBr): 2920, 2860, 1460, 1430, 1420, 1390, 1335, 1240, 1210, 1190, 1130, 1120, 1070, 1060, 980, 925, 890, 870, 816, 750 cm^{-1}. Found: C, 76.30; H, 8.43; N, 14.67%. Calcd for $C_{12}H_{16}N_2$: C, 76.56; H, 8.57; N, 14.88%.

Preparation of Bis(perhydro-2-oxo-3-azepinyl)amine (5). To 100% sulfuric acid (98 g, 1 mol) was added at 60 °C 14oxa-7, 15, 16-triazatetracyclo[11.2.1.0^{1,6}.0^{8,13}]hexadecan-16-ol (23.9 g, 0.1 mol) over 30 min. The reaction mixture was heated at 60 °C for an additional 1 h. After the reaction mixture was cooled to 10—20 °C, water (200 ml) was added at 0—5 °C. The resulting solution was adjusted to pH 10 with 30% sodium hydroxide solution and was extracted with three 300 ml portions of chloroform; then the chloroform extract was dried over anhydrous magnesium sulfate. After removal of the chloroform, the residue was distilled under reduced pressure, and the fraction at 220 °C/0.25 mmHg was collected. ^{1}H-NMR (DMSO-d_6) δ=1.2—2.4 (12H), 2.5 (NH), 2.9—3.4 (4H), 4.0—4.5 (2H), 8.0—8.6 (-NH-C(=O)-, 2H). IR (KBr): 3300, 3200, 3070, 2970, 2920, 2840, 1660, 1470, 1450, 1420, 1380, 1350, 1320, 1300, 1260, 1150, 1130, 1110, 980, 970, 820 cm^{-1}. Found: C, 60.56; H, 8.51; N, 17.79%. Calcd for $C_{12}H_{21}N_3O_2$: C, 60.23; H, 8.85; N, 17.56%.

X-Ray Crystal Structure Determination. Crystal data: $C_{12}H_{21}N_3O_2$, Mr=239.32, monoclinic, $P2_1/c$, a=6.022(1), b=19.245(4), c=10.560(1) Å, β=95.94(1)°, V=1217.4 Å^3, Dm=1.298, Dx=1.306 Mg m^{-3}, Z=4, F(000)=520, μ(Cu $K\alpha$)=0.74 mm^{-1}, the final R was 0.0464 for 2022 unique reflections.

Crystals of compound **7** suitable for X-ray diffraction were obtained upon recrystallization from an ethanol solution. Preliminary film work revealed the material to be monoclinic with systematic absences (h0l, $l=2n+1$; 0k0, $k=2n+1$) strongly indicative of the centrosymmetric space group C_{2h}^6 $-P2_1/c$. The density was measured by flotation in chloroform-cyclohexane solution. The unit cell parameters were obtained by least-squares from 2θ values for 15 reflections measured on a diffractometer. The intensities of 2022 (1990 non-zero) independent reflections were collected on a Rigaku automatic four-circle diffractometer up to an angle of 2θ=125° with graphite monochromated Cu $K\alpha$ radiation, using the $2\theta-\omega$ scan technique and scan range of $(0.8+0.142\tan\theta)°(\omega)$. The scan speed and the background counting time were 10°/min and 3s at each terminus of the scans for $0°<2\theta\leqq 80°$, 5°/min and 6s for $80°<2\theta\leqq 100°$, and 2°/min, 15s for $110°<2\theta\leqq 125°$. Three standard reflections were measured every 100 measurements with no significant deterioration in intensity. Lorentz and polarization correction were applied, but not that for absorption.

The structure was solved with the MULTAN 78 program[6] which located all the non-hydrogen atoms. Isotropic and anisotropic block-diagonal least-squares refinement with HBLS VI program[7] reduced R to 0.070. A difference synthesis at this stage clearly indicated all H atoms, which were included in the refinement with isotropic temperature factors. In the refinement, the function minimized was $\sum\omega(|F_o|-|F_c|)^2$

with $\omega=[\sigma^2(F_o)+a|F_o|+b|F_o|^2]^{-1}$ for $F_o\neq 0$ and $\omega=c$ for $F_o=0$, where $\sigma(F_o)$ is the standard deviation based on counting statistics. Final refinement ($a=0.0006$, $b=5.7428$ and $c=0.01379$) gave $R=0.0464$ ($\omega R=0.0639$) for all reflections and $R=0.0459$ for non-zero reflections. No significant peaks were observed in the final difference map, except for a few peaks of *ca* 0.3 eÅ^{-3}. All calculations were performed with the UNICS programs on a FACOM M-200 computer.[8]

References

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