

Structure of Trimethylamine, C₃H₉N, at 118 K

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Abstract. $M_r = 59.1$, $P\bar{3}$, $a = 6.1366(29)$, $c = 6.8516(28)$ Å, $U = 223.5(3)$ Å³, $Z = 2$, $D_x = 0.878$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.058$ mm⁻¹, $F(000) = 68$, $R = 0.0559$ for 384 reflections. The structure consists of discrete molecules arranged head-to-tail in columns which run alternately parallel and antiparallel to the c crystallographic axis. Individual molecules have effective C_{3v} symmetry, with a pyramidal geometry at N [C–N–C = 110.40 (7)°], and the C–N bond length is 1.4535 (11) Å. The conformation about the C–N bond is such that the symmetry-unique H atom is *anti* to the N lone pair of electrons.

Introduction. Although the crystal structures of adducts of trimethylamine with iodine (Strømme, 1959), iodine chloride (Hassel & Hope, 1960), and sulphur dioxide (van der Helm, Childs & Christian, 1969), as well as the 10.25H₂O clathrate (Panke, 1968), have been known for several years, molecular parameters were not accurately determined. Moreover, no solid-state structure of NMe₃ itself has been published, although a gas-phase electron diffraction study (Beagley & Hewitt, 1968), and a microwave determination (Wollrab & Laurie, 1969) have been reported.

As part of continuing work in this Department on low-melting inorganic compounds, we are engaged in study of members of the homologous series N(CH₃)_{3-x}(SiH₃)_x ($x = 0-3$) (Barrow & Ebsworth, 1984; Blake, Ebsworth & Welch, 1984). Apart, therefore, from its intrinsic interest, the accurate crystal structure of trimethylamine serves as a basis for comparisons with the silylamines of this series.

Experimental. Colourless, cylindrical crystal, 0.05 × 0.04 × 0.04 cm, grown *in situ* on low-temperature-equipped Weissenberg goniometer from sample sealed in Pyrex capillary. Space group identified by combination of oscillation and Weissenberg photography, E statistics, and successful refinement. Crystal transferred without melting as described previously (Blake, Cradock, Ebsworth, Rankin & Welch, 1984) to similarly equipped CAD-4 diffractometer, 118 K, 25 reflections ($13 < \theta < 15^\circ$) centred, graphite-monochromated Mo $K\alpha$ radiation. For data collection θ_{\max}

= 30°, $\omega-2\theta$ scan in 96 steps, ω -scan width (0.8 + 0.35 tan θ)°. Rapid prescan after which reflections with $I \geq 0.5\sigma(I)$ remeasured such that final net intensity had $I > 33\sigma(I)$ subject to maximum measuring time of 90 s. No significant crystal decay or movement. 440 unique reflections over 26 X-ray hours. No absorption correction. For structure solution and refinement 384 amplitudes [$F \geq 2.0\sigma(F)$]. Automatic centrosymmetric direct methods (Sheldrick, 1976). Full-matrix least-squares (F), $w^{-1} = [\sigma^2(F) + 0.002064(F)^2]$, anisotropic thermal parameters for C and N, isotropic for H, $R = 0.0559$, $wR = 0.0681$, data:variable ratio 15:1. $(\Delta/\sigma)_{\max}$ in final cycle < 0.03. Max. peak and min. trough in final ΔF synthesis 0.43 and -0.25 e Å⁻³ respectively. No correction for secondary extinction. Neutral-atom scattering factors for C and N (Cromer & Liberman, 1970) and H (Stewart, Davidson & Simpson, 1965). Computer programs *SHELX76* (Sheldrick, 1976). *XANADU* (Roberts & Sheldrick, 1976), *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and *ORTEPII* (Johnson, 1976).

Discussion. Table 1 lists derived fractional coordinates and thermal parameters.* Fig. 1 is a projection of a single molecule in a direction normal to the crystallographically imposed C_3 molecular axis, and clearly demonstrates that the effective molecular symmetry is C_{3v} . Within this symmetry there are two possible molecular conformations, corresponding to *syn* and *anti* orientations of the unique H atoms relative to the N lone pair of electrons. The former would be severely crowded intramolecularly, and the determined structure clearly has the latter stereochemistry. Table 2 lists interatomic separations and interbond angles. Trimethylamine crystallizes head-to-tail in loosely packed (as evidenced by the relative U_{11} and U_{33} values) columns running alternately parallel and antiparallel to the c crystallographic axis, as shown in Fig. 2 (deposited).

The structure of trimethylamine in the crystal is very similar to that determined in the vapour phase by

* Lists of structure factors, Fig. 2, and Table 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38977 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

electron diffraction (ED) (Beagley & Hewitt, 1968), and by microwave spectroscopy (MW) (Wollrab & Laurie, 1969), not only in terms of C_{3v} molecular symmetry and *anti* conformation, but also in respect of the specific molecular parameters C–N [1.4535 (11) (crystal); 1.455 (2) (ED); 1.451 (3) Å (MW)] and C–N–C [110.40 (7) (crystal); 110.6 (6) (ED); 110.9 (6)° (MW)]. These observations are entirely consistent with the absence of any significant intermolecular contacts in the crystalline phase.

The largest residue in the ultimate ΔF synthesis is the major lobe of a $2p_z-2s$ hybrid orbital of the N atom, classically the 'N lone pair'. This residue, together with its minor-lobe component, is plotted in Fig. 3(a) with contours drawn at intervals of $0.085 e \text{ \AA}^{-3}$. Extended Hückel molecular-orbital (EHMO) calculations (Howell, Rossi, Wallace, Haraki & Hoffmann, 1977), of the self-consistent charge and configuration type, have confirmed that this $2p_z-2s$ hybrid orbital is the major component of the highest occupied molecular orbital (HOMO) of NMe_3 , Fig. 3(b). Trimethylamine, *inter alia*, has been the subject of recent MO calculations at both semi-empirical (MNDO) and *ab initio* levels (Livant, McKee & Worley, 1983), but the results of these calculations were mainly addressed to the questions of planarity at N in the series $\text{N}(\text{CH}_3)_{3-x}(\text{SiH}_3)_x$ ($x = 0-3$), and of matching theoretical MO levels to photoelectron spectra. We have employed the EHMO approach to probe intramolecular bonding.

Table 1. Positional (fractional coordinates) and thermal (\AA^2) parameters with standard deviations

The anisotropic temperature factor is defined as $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl + 2U_{12}a^*b^*hk)]$. The isotropic temperature factor is defined as $\exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$.

	x	y	z			
N	0.33333	0.66667	0.34010 (14)			
C	0.57546 (15)	0.86815 (14)	0.27271 (14)			
H(1)	0.600 (3)	1.023 (3)	0.3212 (16)			
H(2)	0.5965 (24)	0.8768 (23)	0.1296 (17)			
H(3)	0.708 (3)	0.842 (3)	0.3193 (20)			
	U or U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N	0.0133 (4)	0.0133	0.0341 (6)	0.0000	0.0000	0.0066
C	0.0176 (5)	0.0190 (5)	0.0471 (6)	0.0027 (3)	0.0042 (3)	0.0061 (3)
H(1)	0.049 (3)					
H(2)	0.038 (3)					
H(3)	0.056 (3)					

Table 2. Interatomic distances (\AA) and interbond angles ($^\circ$)

Primed atom generated by operation of the crystallographic threefold rotation axis.

N–C	1.4535 (11)	C–H(2)	0.987 (14)
C–H(1)	0.946 (17)	C–H(3)	0.961 (17)
C–N–C'	110.40 (7)	H(1)–C–H(2)	110.1 (13)
N–C–H(1)	108.9 (10)	H(1)–C–H(3)	109.3 (14)
N–C–H(2)	114.3 (8)	H(2)–C–H(3)	103.9 (13)
N–C–H(3)	110.1 (10)		

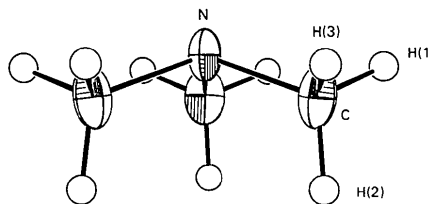


Fig. 1. Trimethylamine, with thermal ellipsoids drawn at the 50% electron probability level, except for H atoms which have an artificial radius of 0.1 Å for clarity.

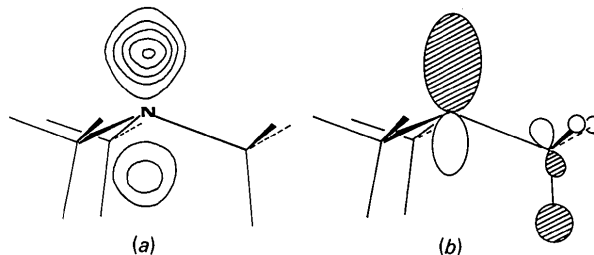


Fig. 3. (a) Experimental electron density contours of the N lone pair of trimethylamine. (b) The HOMO of NMe_3 , as given by the extended Hückel method. The composition of this molecular orbital (only one asymmetric fraction of which is drawn here) is approximately $87\% \psi_{\text{N}2p_z} + 2\% \psi_{\text{N}2s} + 4\% \psi_{\text{H}(2)1s}$.

The EHMO calculations, performed in strict C_{3v} symmetry with parameters specified in Table 3 (deposited), have reproduced the relative weakness of the C–H(2) bond that is consistent with its crystallographically observed (albeit not statistically significant) relative lengthening; C–H overlap populations are 0.796 to H(1,3) and 0.793 to H(2). Furthermore, larger $\text{N}\cdots\text{H}(2)$ than $\text{N}\cdots\text{H}(1,3)$ repulsive interactions (computed overlap populations -0.054 and -0.045 , respectively) account for the wider N–C–H(2) angle observed in the X-ray study. The origin of these repulsions derives largely from the form of the HOMO, and thus the outward displacement of H(2) atoms does not arise from simple $\text{H}(2)\cdots\text{H}(2')$ steric contact. This is apparent from both the crystallographic and the theoretical studies – from the former $\text{H}(2)\cdots\text{H}(2')$ is 2.562 (17) Å, well outside the van der Waals sum, and from the latter the $\text{H}(2)\cdots\text{H}(2')$ overlap population is actually positive although very small (0.0014).

It is encouraging to note that both aspects of the asymmetry of the CH_3 function are also observed in the microwave study (Wollrab & Laurie, 1969).

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Structure of *trans*-1,9-Dichloro-1,2,3,4,6,7,8,9-octahydrophenazine 5-Oxide, C₁₂H₁₄Cl₂N₂O

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Abstract. $M_r = 273.025$, monoclinic, $P2_1/c$, $a = 6.155$ (1), $b = 11.390$ (2), $c = 20.200$ (4) Å, $\beta = 119.85$ (3)°, $V = 1228.25$ (1) Å³, $Z = 4$, $D_m = 1.479$, $D_x = 1.487$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu(\text{Cu } K\alpha) = 3.15$ mm⁻¹, $F(000) = 568$, room temperature. Final $R = 0.039$ for 1671 reflections. The central ring is almost flat and both unsaturated six-membered rings exist in the crystal in half-chair conformations with both C–Cl bonds lying in axial positions, in the *trans* configuration.

Introduction. 1,9-Dichloro-1,2,3,4,6,7,8,9-octahydrophenazine 5-oxide was first obtained by Fischer & Weitz (1975) as two isomers which were resolved by column chromatography on silica gel. The authors suggested that the compound with m.p. 443 K has the *cis* configuration and that with m.p. 439 K the *trans* configuration of Cl atoms. The compound was obtained again and resolved by thin-layer chromatography by Hahn, Muszkiet, Rybczyński & Skrzypek (1983). One of the isomers has m.p. 447 K and the other decomposes in the temperature range 433–448 K with no clear melting point. This does not allow identification of the isomers and we have therefore investigated the crystal structures of both isomers to

identify them. We first solved the structure of the isomer having no clear melting point.

Experimental. Recrystallization from ethanol, D_m by flotation, thin colourless single-crystal fragments $\sim 0.4 \times 0.4 \times 0.1$ mm, Syntex $P2_1$ diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, θ – 2θ scan, unit-cell parameters refined from accurately measured 2θ values of 25 high-angle reflections, L_p and empirical absorption corrections (transmission 0.159 to 0.275), $\sin\theta/\lambda \leq 0.546$ Å⁻¹, 1671 reflections measured ($0 \leq h \leq 6$, $0 \leq k \leq 12$, $-22 \leq l \leq 19$), all unique, 1278 considered observed with $F_o \geq 2\sigma(F_o)$; three standard reflections varied in intensity by <3% throughout data collection. Direct methods [*MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978)] revealed positions of all non-hydrogen atoms; refinement (on F) by full-matrix least squares with anisotropic temperature factors for non-hydrogen atoms, all H atoms located in difference Fourier synthesis and refined isotropically using mixed method, final $R = 0.039$, $R_w = 0.042$, $S = 1.53$ for the observed reflections, $w = 1/\sigma^2$, $(\Delta/\sigma)_{\max}$ for non-H atoms = 0.38 [U_{12} for C(7)], $(\Delta/\sigma)_{\text{ave}} = 0.12$, final $\Delta\rho$ excursions $\leq |0.21| e \text{ Å}^{-3}$; atomic scattering factors from *International Tables for X-ray Crystallography* (1974) for neutral atoms, and anomalous-dispersion corrections for non-hydrogen atoms from Cromer & Liberman (1970). All calculations except for *MULTAN* performed using *XRAY76* (Stewart, 1976).

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