SHORT STRUCTURAL PAPERS

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Triethylenediamine. II. Phase I at 354K*

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Abstract. $N(CH_2CH_2)_3N$. f.c.c., $Fm3m$, $Z=4$, $a=$ 8·860 (5) Å, $D_x=$ 1·07 g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å. Source of material: B.D.H. It is proposed that molecules at each lattice site undergo hindered reorientations between eight equally weighted orientations, all centred on the site with coincident threefold molecular and crystal axes; around each [111] direction there are two orientations separated by a 60° rotation about that direction.

Introduction. In its high-temperature phase (above 351K) triethylenediamine (TEDA) assumes a 'plastic' nature. Various thermodynamic and spectroscopic studies have been made and it has been suggested that general molecular reorientation occurs (Chang & Westrum, 1960; Trowbridge & Westrum, 1963; Smith, 1965; Zussman & Alexander, 1968). In addition preliminary X-ray diffraction work has tentatively suggested a face-centred cubic crystal system (Brüesch, 1966; Brüesch & Günthard, 1966). However, until now no report of the structure has been published.

Although single-crystal and powder neutron diffractometry were attempted, because of sample-control difficulties it was found more profitable to collect X-ray powder-diffraction photographic data. With this method all diffracted intensities are recorded simultaneously and relatively quickly, thus reducing some of the major difficulties due to sample sublimation.

TEDA was purified and dried by subliming several times *in vacuo*. The sample was ground, loaded into a capillary tube and sealed in with epoxy resin, all within a dry box. The sample was then mounted in a Philips powder camera into which had been built a small electrical heater so designed that any sample sublimation occurred towards the X-ray beam. The phase I data were collected at 354 K with exposure times of 8,4,1,0·25 h. Nine lines were observed. The first two (111 and 200) were very intense and expected to suffer

Table 1. *The observed intensities (both uncorrected; and corrected for Lorentz, polarization and 'cones factor' effects) and the corresponding calculated data for the various models described in the text*

	Observed integrated intensities		(sc)$\lvert\mathscr{F}'(hkl)\rvert^2_{calc}$				
			Static disorder $\alpha_0=30°$ ($Fm3m$)		Free rotation	Free rotation about 3-fold axes	Hindered rotation about 3-fold axes
hkl	Uncorrected	Corrected: $\lvert\mathscr{F}'(hkl)\rvert^2_{obs}$					
111	11300	132	518	601	1081	604	561
200	6080	96	202	233	333	233	218
220	0	0 ± 2	1·64	2·14	0·807	1·29	1·15
311	475	22·3 ± 5·4	23·3	23·6	31·7	22·4	22·3
222	524	27·2 ± 1·4	28·8	27·5	13·7	29·3	29·4
400	162	11·7 ± 0·9	10·9	11·7	10·2	12·8	12·6
331	292	25·8 ± 2·8	19·2	21·7	26·1	18·8	19·1
420	168	15·8 ± 2·2	15·4	17·4	21·5	11·9	11·8
422	151	17·7 ± 4·8	18·2	16·2	8·43	16·9	16·6
511, 333	90	12·2 ± 4·0	20·5	18·2	4·60	22·5	22·4
		R	0·177	0·129	0·390	0·213	0·210
		(sc)	0·00843	0·0101	0·0183	0·0102	0·00925
		B_C(Å^2)	7·1	8·6	14·4	9·2	7·9
		B_N(Å^2)	7·1	8·6	14·4	9·2	7·9
		B_H(Å^2)	7·1	12·6	14·4	9·2	7·9

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* Supplementary notes to this paper detailing the experimental and mathematical procedures have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31384 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester, CH1 1NZ, England.

from secondary extinction, but at higher 2θ the intensities decreased rapidly. The films were scanned with a Joyce–Loebl microdensitometer and integrated intensities obtained; these intensities are given in Table 1, together with Lorentz–polarization-cones corrected values ($\mu R=0{\cdot}17$ so no absorption correction was required).

Phase I of TEDA has a disordered f.c.c. crystal system with four molecules per unit cell. Both static and dynamic disordered models were considered. For each model the centroids of the molecules were assumed to lie on the lattice points. Also the room-temperature molecular configuration and dimensions were assumed (see Fig. 1, Nimmo & Lucas, 1976). Multiplicity factors were applied to the calculated rather than the observed intensities.

(i) *Static disorder*

On the basis of the reflexions observed, five space groups were possible: $Fm3m$, $F432$, $F\bar{4}3m$, $Fm3$, $F23$. For static disorder models the threefold axis of the molecule was taken as always lying along a threefold axis of the unit cell. Consider a molecule located at the origin and lying along the [111] direction. Define α_0 as the angle between the vector $(\mathbf{a}+\mathbf{b}-2\mathbf{c})$ and the plane formed by the [111] direction and two bonded C atoms; α_0 then specifies the orientation of the asymmetric unit (see Fig. 2 for an example). As required by space-group considerations, the molecule on each lattice site was taken as disordered between orientations along each of the four threefold cubic axes, and also disordered between equivalent positions around each threefold axis (these latter positions depend on the space group as illustrated in Fig. 1). Each orientation of the molecule on a lattice site has equal weight.

Define $|\mathscr{F}'(hkl)|^2$ to be the sum of multiplicity-corrected structure amplitudes squared of non-equivalent reflexions superposed with reflexion hkl. A computer program was written to calculate $|\mathscr{F}'(hkl)|^2_{\text{calc}}$ for the first ten powder pattern lines in each of the five space groups as the molecular orientation angle α_0 was incremented in 3° steps from 0° to 30° (because of symmetry all information is contained in this angular range). For each α_0 the appropriate scale factor (sc) and temperature factors (B_j) for the various space groups were determined by least-squares refinement, minimizing R, where

$$R=\left[\frac{\sum w_{hkl}(|\mathscr{F}'(hkl)|^2_{\text{obs}}-(\text{sc})|\mathscr{F}'(hkl)|^2_{\text{calc}})^2}{\sum w_{hkl}(|\mathscr{F}'(hkl)|^2_{\text{obs}})^2}\right]^{1/2}$$

$$w_{hkl}=\left[0{\cdot}9-\left\{\frac{\sigma(|\mathscr{F}'(hkl)|^2_{\text{obs}})}{|\mathscr{F}'(hkl)|^2_{\text{obs}}}-0{\cdot}05\right\}\Big/0{\cdot}7\right]^2.$$

(The variation in conventional weights was considered to be too large.) Initially all temperature factors were confined to be equal. The results showed that the 111 and 200 reflexions were extinction-affected, as anticipated, and therefore these two reflexions were omitted from all least-squares refinements. From plots of R *versus* α_0 it was clear that for all space groups the best fit between observed and calculated data occurred for $\alpha_0=30°$, at which angle all space groups give equal $|\mathscr{F}'(hkl)|^2_{\text{calc}}$ for corresponding hkl. At this angle the models in space groups $Fm3m$, $F\bar{4}3m$, $Fm3$ become equivalent and likewise for $F432$, $F23$; *i.e.* there are two models, one has space group $Fm3m$, the other has $F432$. In Fig. 2 the former model is illustrated, viewed along the [111] direction; there are two equivalent positions about this axis. The space group $F432$ model consists of either one (but not both) of these positions and hence from symmetry considerations the $Fm3m$ model was favoured.

Thus the static disorder solution was taken to be the space group $Fm3m$ model with $\alpha_0=30°$. The values of $(\text{sc})|\mathscr{F}'(hkl)|^2_{\text{calc}}$ together with (sc), R and the B_j are given in Table 1 for the case $B_{\text{C}}=B_{\text{N}}=B_{\text{H}}$. Also given are the corresponding data with $B_{\text{C}}=B_{\text{N}}=8{\cdot}6$ Å^2, $B_{\text{H}}=B_{\text{C}}+4$Å^2, resulting in a significantly lower R. The coordinates of the asymmetric unit are given in Table 2.

Table 2. *Fractional coordinates of the asymmetric unit of phase* I *triethylenediamine* (*using phase* II *molecular dimensions*) *from the static disorder solution*

The effective space group is $Fm3m$.

	x	y	z
C	0·159	0·049	0·061
H(1)	0·185	0·156	0·113
H(2)	0·033	0·004	0·265
N	0·083	0·083	0·083

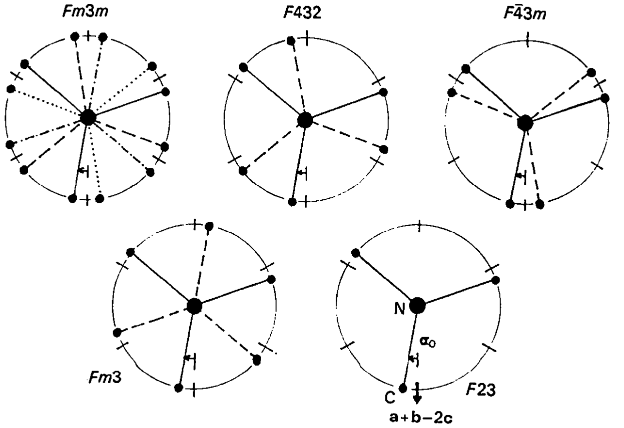

Fig. 1. Illustration of the static disorder arrangements around the cubic threefold axes for the five possible space groups, with a general molecular orientation angle α_0. For each space group the various molecular orientations around the [111] direction (centre of circle, out of the page) are indicated by the use of different types of line (*e.g.* dotted, dashed) for C–N bonds. H atoms have been omitted for clarity. Directly below each atom shown there is another of the same kind and in the case of carbon they are bonded. The centroid associated with each orientation lies on a lattice point.

(ii) *Free rotation*

The scattering function for a spherically symmetric atom freely rotating at radius r from a point (xyz) is

$$f(s)\exp\left[2\pi i(\xi x+\eta y+\zeta z)\right]\frac{\sin 2\pi sr}{2\pi sr}$$

where $s=2\sin\theta/\lambda$ and $(\xi\eta\zeta)$ is a position in reciprocal space (*International Tables for X-ray Crystallography*, 1968). $|\mathcal{F}'(hkl)|^2_{\rm calc}$ were calculated for TEDA molecules freely rotating around the f.c.c. lattice points (space group $Fm3m$) and R minimized by least squares refinement, varying (sc) and B_j (with constraints) as in the static disorder case. The results for the case $B_{\rm C}=B_{\rm N}=B_{\rm H}$ are given in Table 1.

(iii) *Free rotation about threefold axes*

The scattering function for a spherically symmetric atom rotating about an axis at radius r from a centre (xyz) is $f(s)\exp[2\pi i(\xi x+\eta 4+\zeta z)]J_0(2\pi tr)$, where t is the distance in reciprocal space from $(\xi\eta\zeta)$ to an axis through the origin parallel to the axis of rotation (*International Tables for X-ray Crystallography*, 1968). One molecule of TEDA was considered to lie on each f.c.c. lattice point and each molecule was disordered between the threefold crystal axes and rotating around them. The effective space group is $Fm3m$. $|\mathcal{F}'(hkl)|^2_{\rm calc}$ were calculated and refinements made; the results are given in Table 1.

(iv) *Hindered rotation about threefold axes*

Atoji & Watanabé (1953) have derived the effect of a generalized potential on the X-ray scattering of a hindered rotator. Using the case of a simple potential function $V=-\frac{1}{2}V_0\cos n(\theta-\gamma)$, where γ is the rotation angle corresponding to a potential minimum and n the number of potential minima, $|\mathcal{F}'(hkl)|^2_{\rm calc}$ were calculated for a model similar to that of §(iii) but where the rotation was hindered with equilibrium positions given by the static disorder solution. Refinements were made and the results are given in Table 1.

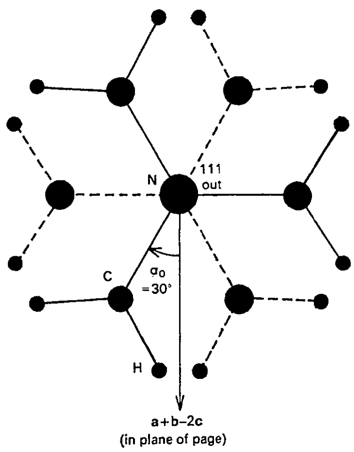

Fig. 2. The static disorder solution showing the disordered arrangement of the triethylenediamine molecule (centred on a lattice point) around the [111] direction. Two molecular orientations are shown (solid, dashed line). Directly below each atom shown there is another of the same kind and in the case of carbon they are bonded. α_0 is measured in the plane of the page.

Discussion. Because of data limitations, the refinements were made with the constraints $B_{\rm H}=B_{\rm C}+B_1^0$, $B_{\rm N}=B_{\rm C}+B_2^0$, where B_1^0 and B_2^0 were fixed for a particular refinement. Values of B_1^0 and B_2^0 between 0 and 6 Å^2 were used. It was found for each set of restrictions on the B_j, irrespective of whether unit-weighted or variable-weighted R indices were used, that the static disorder model ($Fm3m$, $\alpha_0=30°$) always gave the best fit between calculated and observed intensities, followed by the other models in the same sequence as shown in Table 1. For ease of comparison, only the results for the cases with $B_{\rm C}=B_{\rm H}=B_{\rm N}$ are given in Table 1 with the exception of the static disorder model with $B_{\rm C}=B_{\rm N}$, $B_{\rm H}=B_{\rm C}+4$ Å^2 for which the best fit of all was obtained.

If it is assumed that the change in entropy of the material on being heated through the transition is given by

$$\Delta S=k_B\ln\frac{\Omega(\text{phase I})}{\Omega(\text{phase II})},$$

where k_B is Boltzmann's constant and Ω the number of degrees of freedom of the molecule, then using $\Delta S=4{\cdot}99\times10^{-23}$ J(molecule K)$^{-1}$ (Trowbridge & Westrum, 1963) it is found that $\Omega_{\rm I}/\Omega_{\rm II}=37{\cdot}3$. Therefore there must be more disorder than the static disorder model allows ($\Omega_{\rm I}/\Omega_{\rm II}\sim8$). Spectroscopic studies (Smith, 1965; Zussman & Alexander, 1968) also suggest more disorder and indeed that general molecular reorientation occurs. It would seem probable then that the correct structure is a dynamically disordered one with equilibrium positions given by the static disorder solution. The extra disorder could either be hindered spherical rotation or hindered rotation about the cubic threefold axes, but probably a combination of both. As this hindered rotational disorder is not detected from Bragg intensity measurements, it is evident that the reorientation frequency is $<10^{18}$ Hz ($\sim$frequency of X-radiation).

Owing to the nature and limited amount of the present experimental data, a conventional least-squares refinement was not possible. An attempt at refinement using Kubic Harmonics (von der Lage & Bethe, 1947; Seymour & Pryor, 1970) was made, but unsuccessfully.

We wish to thank Dr J. C. Taylor (AAEC) who supplied a Kubic Harmonics refinement program and CSIRO Protein Chemistry Division for the use of their microdensitometer. The support of the Australian

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Nalidixic Acid

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Abstract. 1-Ethyl-1,4-dihydro-7-methyl-1,8-naphthyridin-4-one-3-carboxylic acid, $C_{12}H_{12}N_2O_3$, monoclinic, $P2_1/c$, $a=8{\cdot}913$ (3), $b=13{\cdot}133$ (4), $c=9{\cdot}371$ (3) Å, $\beta=99{\cdot}75$ (4)°, $D_m=1{\cdot}41$, $D_c=1{\cdot}425$ g cm^{-3} for $Z=4$. Equi-inclination Weissenberg intensities, scanned with an automatic densitometer. The structure, solved by direct methods, refined to $R=0{\cdot}0968$.

Introduction. Prismatic crystals, elongated along **c**, were grown from an ethanol/water solution. Oscillation and Weissenberg photographs indicated that the crystals were monoclinic, with systematic absences $h0l$, $l=2n+1$ and $0k0$, $k=2n+1$, thus determining the space group to be $P2_1/c$. Cell dimensions were determined from calibrated Weissenberg (Cu $K\alpha$) and precession photographs (Mo $K\alpha$). Intensities were collected by the equi-inclination Weissenberg method with multi-film packs. Layers $hk0$–$hk7$ and $0kl$–$1kl$ were photographed with Ni-filtered Cu $K\alpha$ radiation. The films were scanned by the Science Research Council microdensitometer service, with an Optronics P-1000 Photoscan. 797 unique observed reflexions were obtained after inter-layer scaling and merging of equivalent reflexions. The structure was solved by direct methods with the *PHASE* link of the X-RAY System (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), and all non-hydrogen atoms were located in the first E map. All subsequent calculations were carried out with a set of computer programs written by Dr G. M. Sheldrick. Full-matrix least-squares refinement with individual isotropic thermal parameters, gave an R of 0·133. A difference synthesis failed to reveal all except one hydrogen position, H(12), and so contributions from H atoms initially in calculated positions were included. The refinement was terminated after eight cycles of full-matrix least-squares refinement with all non-hydrogen atoms assigned individual anisotropic thermal parameters. The positional parameters of the H atoms were allowed to refine, but with the C–H vectors constrained in magnitude. The parameters were refined in two overlapping blocks. A weighting scheme $w=1/\{\sigma^2|F|+0{\cdot}040198F^2\}$ was used, and the final R was 0·0968. Tables 1 and 2 list the positional and thermal parameters.*

Discussion. Nalidixic acid (Fig. 1) is a clinically useful antibacterial drug (Gale, Cundliffe, Reynolds, Richmond & Waring, 1972) which acts by inhibiting nucleic acid synthesis in an, as yet, unknown manner. We have determined the structure of this compound as part of a series of studies on such drugs (Neidle & Jones, 1975; Jones & Neidle, 1975).

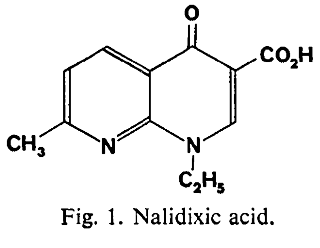

Fig. 1. Nalidixic acid.

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* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31453 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.