References

ABRAHAMS, S. C. (1956). *Quart. Rev.* **10**, 407–436.
ANSELL, G. B., FORKEY, D. M. & MOORE, D. W. (1970). *Chem. Commun.* pp. 56–57.
ARONSON, YU. P. & BELEN'KII, S. M. (1965). *Zashch. Met.* **1**, 125–130.
BROWN, G. M. (1969). *Acta Cryst.* B**25**, 1338–1353.
CHESICK, J. P. & DONOHUE, J. (1971). *Acta Cryst.* B**27**, 1441–1444.
DOWNIE, T. C., HARRISON, W., RAPER, E. S. & HEPWORTH, M. A. (1972). *Acta Cryst.* B**28**, 1584–1590.
HARRISON, D. & RALPH, J. T. (1967). *J. Chem. Soc.* (*B*), pp. 14–15.
HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210–214.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
MARTÍNEZ-CARRERA, S. (1966). *Acta Cryst.* **20**, 783–789.
MONAHAN, J. E., SCHIFFER, M. & SCHIFFER, J. P. (1967). *Acta Cryst.* **22**, 322.
PATEL, N. K., MAKWANA, S. C. & PATEL, M. M. (1974). *Corros. Sci.* **14**, 91–93.
POLING, G. W. (1970). *Corros. Sci.* **10**, 359–370.
SLETTEN, J. & JENSEN, L. H. (1969). *Acta Cryst.* B**25**, 1608–1614.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
WHEATLEY, P. J. (1962). *J. Chem. Soc.* pp. 3636–3638.
WILL, G. (1969). *Z. Kristallogr.* **129**, 211–221.

Solid-State Phase Transition in Triethylenediamine, N(CH₂CH₂)₃N.
I. The Crystal Structure of Phase II at 298 K

BY J. K. NIMMO AND B. W. LUCAS

Department of Physics, University of Queensland, St. Lucia, Brisbane, Queensland, Australia

At atmospheric pressure, triethylenediamine, $N(CH_2CH_2)_3N$, undergoes a solid-state structural transition at 351 K; the so-called phase I is stable between 433 K (m.p.) and 351 K, phase II below 351 K. Single crystals of phase II have been grown by slow sublimation *in vacuo* and the crystal structure has been determined at 298 K (room temperature) from three-dimensional neutron diffraction data. The hitherto ambiguous situation concerning the molecular conformation has been resolved by considering the agreement of the following structural models, in turn, with the experimental neutron data: (i) an ordered structure of non-twisted molecules, (ii) an ordered structure of twisted (in the same sense) molecules, (iii) a disordered structure of composite molecules (each consisting of two half-weighted molecules twisted in opposing senses). [The twists refer to the upper half relative to the lower half of the molecule about the NN direction.] A hexagonal cell with $a = 6 \cdot 14$ (2), $c = 9 \cdot 46$ (2) Å and $Z = 2$ was employed for all models, but only the model with non-twisted molecules resulted in an acceptable structure. The space group was $P6_3/m$ and the molecular symmetry $\bar{6}m2$. Full-matrix least-squares refinements were used and all non-fixed positional and anisotropic thermal parameters were varied. Rigid-body motion is a reasonably good approximation for the thermal motion of the molecule. Intramolecular bond length and interbond angle magnitudes indicate good internal consistency and agree well with those values generally accepted for equivalent bonds in other compounds.

Introduction

Triethylenediamine, $N(CH_2CH_2)_3N$, formally known as 1,4-diazabicyclo[2,2,2]octane, is a globular molecule with a structural phase transition at 351 K (Chang & Westrum, 1960; Trowbridge & Westrum, 1963). In the room-temperature phase (phase II), X-ray diffraction studies have shown that the crystal system is hexagonal with two molecules per unit cell (Wada, Kishida, Tomiie, Suga, Seki & Nitta, 1960; Weiss, Parkes, Nixon & Hughes, 1964). Above 351 K, the compound structurally transforms to phase I for which a face-centred crystal system has been tentatively suggested (Brüesch, 1966; Brüesch & Günthard, 1966). [The structure of

phase I has been studied by the authors and details are given in part II (Nimmo & Lucas, 1976).]

For the structurally similar compound bicyclo-[2,2,2]octane, Hendrickson (1961) has concluded from molecular orbital calculations that the molecule would be energetically most favourably arranged in a slightly twisted conformation. If the triethylenediamine (TEDA) molecule were also twisted and about the NN direction, the molecular symmetry would be 32 as compared with the more symmetric $\bar{6}m2$ of the non-twisted molecule. These molecular conformations are illustrated in Fig. 1.

Wada *et al.* (1960) have reported the phase II space group to be $P6_3/m$, which would preclude the twisted

molecular form. For the twisted molecular configuration the space group would be $P6_3$. An attempt to distinguish between structures based on these two space groups has been made by comparing the results of least-squares refinements of three-dimensional X-ray data (Weiss *et al.*, 1964). However, both models refined reasonably well and it was considered that a more extensive analysis would be necessary to distinguish unequivocally between the two models.

Other experimental techniques, for example proton magnetic resonance (Smith, 1965) and pure nuclear quadrupole resonance (Zussman & Alexander, 1968), have been employed, but again no conclusive distinction could be made between the models.

It was considered that a more accurate and detailed knowledge of the atomic positions (particularly for the H atoms) and the thermal motion of the atoms would assist in the solution of the problem. Hence, in view of the superiority of neutron diffraction over X-ray diffraction methods for these purposes, it was decided in the present work to collect a three-dimensional set of single-crystal neutron data.

Experimental

Crystal growth and sample preparation

Initially crystals were grown by slow evaporation of a saturated ethereal solution of commercially available

Fig. 1. Alternative molecular conformations proposed for the triethylenediamine molecule: (*a*) non-twisted, symmetry $\bar{6}m2$ and (*b*) twisted, symmetry 32. The molecule is shown in plan and elevation, wherein bonds represented in broken lines are at the bottom and rear respectively.

(laboratory grade) TEDA; however, suitably sized single crystals were of insufficient quality for use. Reasonably good-quality single crystals with dimensions up to ~5 mm were grown by slow sublimation of TEDA, across a temperature gradient of ~0·5 K, in an evacuated vessel, the starting material being the resultant of several previous sublimations to increase the purity of the sample.

The specimen chosen for the study (approximately $4 \times 2 \times 2$ mm) was transparent and showed well defined faces of the form $\{100\}$, $\{110\}$ and $\{111\}$. As the compound is highly hygroscopic, the crystal was removed from the sublimation growth vessel in a dry box, mounted on a small support strip of V foil, which had previously been attached by (epoxy resin) adhesive to a thin circular disc of silica glass, and the mounted sample encapsulated by a small hemispherical thin-walled dome of silica glass adhered by its rim to the disc to form an air-tight enclosed volume.

Single-crystal neutron-data collection

Data were collected from the encapsulated sample mounted on a computer-controlled four-circle single-crystal diffractometer used in conjunction with HIFAR, the research reactor of the Australian Atomic Energy Commission (AAEC) at Lucas Heights. ω–2θ scans were made for all Bragg intensity measurements, with a step size of 0·01° in 2θ. Background measurements were made for each Bragg reflexion, a standard reflexion being measured after every 20 reflexions to check stability of the specimen and the experimental system. Six equivalent sets of Bragg intensity data were collected.

Measurements were made to obtain a value for μ, the linear absorption coefficient, for TEDA by recording the reduction of the incident neutron beam intensity on passing normally through a parallel-sided single crystal slab of the material of known thickness. The value determined was 4 cm^{-1}, which is in good agreement with the calculated value.

Preliminary considerations of structural models

After considering the findings of previous investigations on TEDA, three structural models were regarded as possible alternatives:

(*a*) An ordered structure of non-twisted molecules with space group $P6_3/m$, as proposed by Wada *et al.* (1960).

(*b*) An ordered structure of twisted molecules with space group $P6_3$, as considered by Weiss *et al.* (1964). (It can be shown that as far as Bragg diffraction is concerned the sense of twist of the upper-half relative to the lower-half of the molecule is undetermined.)

(*c*) A disordered structure consisting of twisted molecules as in (*b*), but with each molecule replaced by a composite of *two* molecules of opposite twist-sense and half-weight only. The two molecules are contrained so that the upper-half of one molecule always *eclipses* the
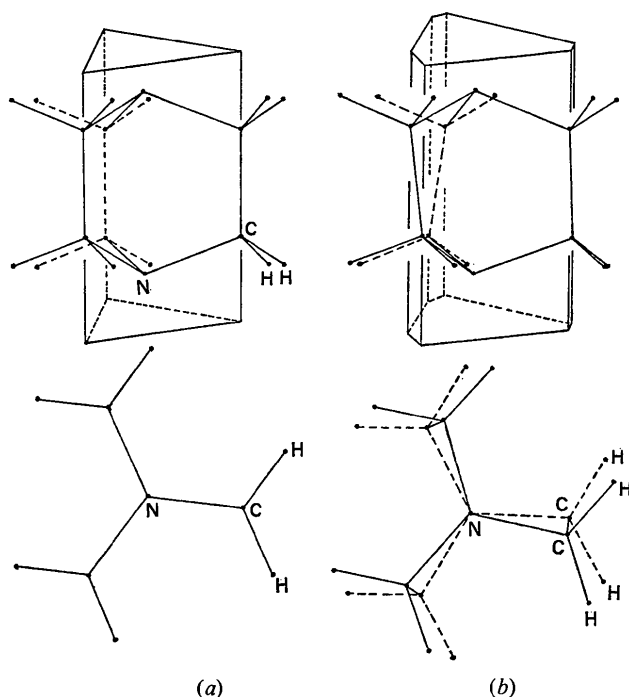
lower-half of the other molecule, when viewed along the NN direction, and *vice versa* (this implies a space group $P6_3/m$).

Note: model (c) is distinct from model (b) as regards Bragg diffraction.

The three structural models are illustrated in Fig. 2. It should be noted that the axes have been chosen differently from previous workers (Weiss *et al.*, 1964). Their axes are related to those of the present work as follows:

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix}_{Weiss} = \begin{pmatrix} 1 & 1 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{present}$$

Analysis of the data

The unit cell

Careful consideration of the measured Bragg intensities, with regard to the identification of systematic equivalent and non-equivalent reflexions, confirmed the crystal system as hexagonal (Wada *et al.*, 1960) and the cell dimensions $a=6\cdot14$ (2) and $c=9\cdot46$ (2) Å were equal to those given by Weiss *et al.* (1964).

Preparation of the measured data

The diffractometer-measured intensities $I(hkl)$, with their appropriate background intensities $B(hkl)$ subtracted, were corrected for absorption by the crystal sample using a computer program which numerically evaluates the correction to be applied for each reflexion, making use of the linear absorption coefficient, μ, the shape and measured external dimensions of the sample.

The equivalent sets of reflexions were compared by various statistical criteria to allow an estimate of the likely accuracy of each intensity. The squares of the structure amplitudes were obtained and equivalent reflexions combined to give a set of mean-square amplitudes $|F(hkl)|^2$ and standard deviations $\sigma\{|F(hkl)|^2\}$.

Least-squares structure refinements

All refinements were based on comparison of $|F(hkl)|^2$ values. (No reflexions allowed by the space groups were rejected in the refinement procedures.) The least-squares weighting factors used were $\omega(hkl) = [\sigma^2\{|F(hkl)|^2\}]^{-1}$. The discrepancy indices were $R_w = \{\sum w(F_o^2 - F_c^2)^2\}^{1/2}/\{\sum w(F_o^2)^2\}^{1/2}$ and $R = \sum|F_o^2 - F_c^2|/\sum|F_o^2|$. The nuclear coherent scattering amplitudes used

throughout were: N $0\cdot94$, C $0\cdot665$ and H $-0\cdot374$, all in units of 10^{-12} cm (Bacon, 1972).[*]

[*] A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31273 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
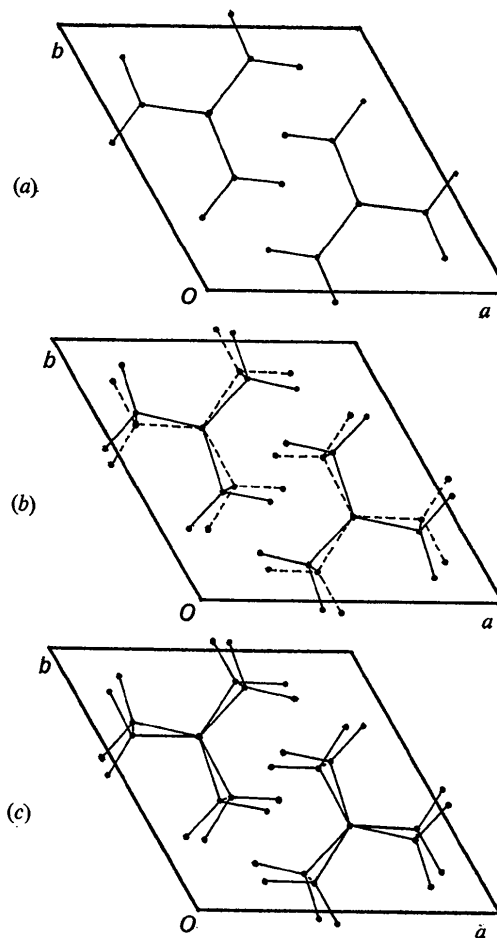

Fig. 2. Projections on the base of the unit cell of the alternative structural models proposed for phase II triethylenediamine: (a) an ordered structure of non-twisted molecules; (b) an ordered structure of twisted molecules; (c) a disordered structure of twisted molecules. (In each cell the molecule shown on the left is the upper half of the cell, the other molecule in the lower half.)

Table 1. *Atomic parameters of phase* II *triethylenediamine at* 298 K, *as given by least-squares refinement for the ordered structure of non-twisted molecules*

Temperature factor $= \exp\{-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\}$ (standard deviations are in parentheses and parameters without standard deviations were fixed in refinement by space group requirements). Other details of the refinement and final R values are also included.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N	$\frac{1}{3}$	$\frac{2}{3}$	0·6155 (4)	0·0289 (12)	$(=\beta_{11})$	0·0112 (6)	$(=\beta_{11/2})$	0	0
C	0·3010 (9)	0·4281 (9)	0·6700 (4)	0·0334 (21)	0·0293 (17)	0·0125 (4)	0·0170 (15)	−0·0002 (6)	−0·0039 (8)
H(1)	0·4491 (20)	0·4069 (18)	0·6281 (13)	0·0685 (59)	0·0748 (58)	0·0232 (15)	0·0558 (55)	0·0036 (26)	−0·0002 (29)
H(2)	0·1251 (21)	0·2770 (15)	0·6259 (11)	0·0712 (48)	0·0210 (28)	0·0192 (12)	0·0044 (39)	−0·0045 (24)	−0·0054 (17)

Number of independent reflexions $= 133$; number of variables refined $= 31$; $R_w = 0\cdot12$; $R = 0\cdot14$

Preliminary refinements for each of the models subsequently discussed indicated that the effects of extinction on the measured data were negligible and therefore no allowance was made for it in the final cycles of the refinements.

Details of the concluding stages of the refinements for the structural models are as follows:

(a) An ordered model of non-twisted molecules

A structure equivalent to that proposed by Wada *et al.* (1960) was used as the initial structure in the least-squares refinements. A scale factor and all non-fixed positional coordinates and anisotropic temperature factors were allowed to refine. The process converged and details of the final values are shown in Table 1.

(b) An ordered structure of twisted molecules

A structure equivalent to that obtained by Weiss *et al.* (1964) for their twisted-molecule model was used as the initial structure in the least-squares refinements.
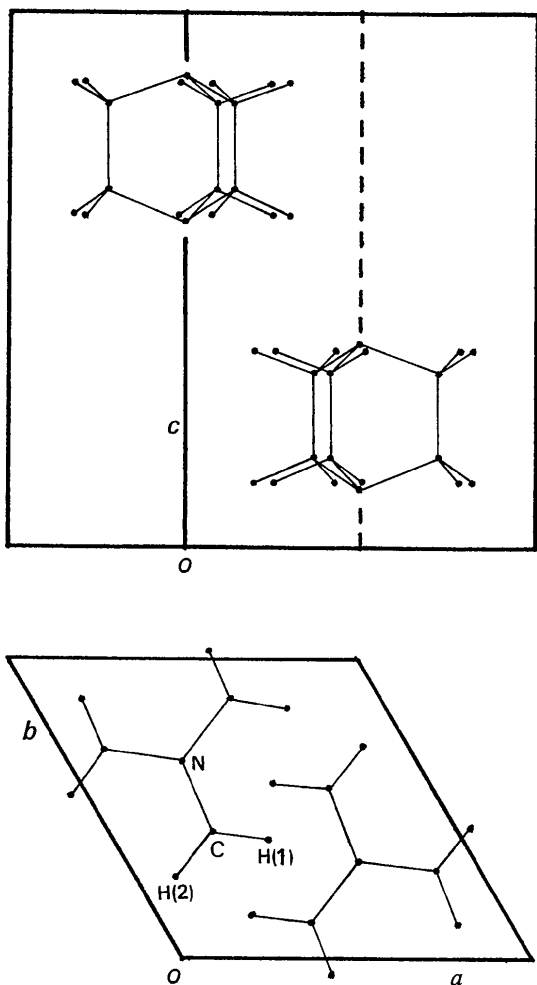

The refinements did not converge. The C atoms, however, tended to move to positions corresponding to the non-twisted form and the H atoms to wander to physically unreasonable positions during the refinement procedure.

(c) A disordered structure of twisted molecules

A structure similar to that obtained by Weiss *et al.* (1964) but with each molecule replaced by *two* molecules of opposite twist-sense and half-weight was used as the initial structure in the least-squares refinements. Again the refinements did not converge.

Each refinement for the models (*a*), (*b*) and (*c*) was repeated from different starting values to ensure the possibility of convergence. Model (*a*) converged after a few cycles only, but neither model (*b*) nor model (*c*) converged satisfactorily.

For model (*a*) the minimum residual R_w was 0·12. Although somewhat larger than usual for a structure of this complexity, it was not unexpected in view of the following:

(i) The crystal perfection attainable for a relatively large single crystal that sublimes readily is rather limited.

(ii) The crystal was enclosed in a silica glass capsule to prevent absorption of atmospheric water vapour and also sublimation, leading to increased background scattering.

(iii) The accuracy of the numerically evaluated correction for absorption effects is limited by the number of volume elements into which it is economic, in computer time, to divide the crystal. For high linear absorption coefficients, this deficiency can lead to errors in the corrections. In the present instance, μ is quite large (4 cm^{-1}); the crystal sample was divided into 125 volume elements.

Description of the structure

(i) Positional parameters

The refinements showed that the structure consists of two non-twisted molecules per unit cell (Fig. 3); the parameters are given in Table 1. The structure is compatible with the ordered structure obtained by Weiss *et al.* (1964), but now the H atom positions have been determined, and the thermal parameters and other positional coordinates are known more accurately.

(ii) Atomic thermal parameters and rigidity of the tri-ethylenediamine molecule

Table 1 includes the components of the thermal parameter tensors for the N, C and H atoms of the molecule The magnitudes and orientations of the thermal ellipsoid for each atom are given in Table 2, where *l*, *m* and *n* are the direction cosines relative to the orthogonal axes *a*, *b** and *c*.

The possibility was investigated of fitting a rigid-body motion for the molecule as a whole to the observed thermal parameters of the atoms, in terms of

Fig. 3. The structure of phase II triethylenediamine, as determined in the present work, showing the plan and elevation of the unit cell.

Table 2. *Orientation and magnitudes of thermal ellipsoids* (*direction cosines, l, m and n give the orientation relative to the orthogonal axes a, b* and c*)

	B (Å^2)	$(\bar{u}^2)^{1/2}$(Å)	l	m	n
	5·88	0·273	0·8660	−0·5000	0·0000
N	2·52	0·179	0·5000	0·8660	0·0000
	4·07	0·227	0·0000	0·0000	1·0000
	6·14	0·279	0·8850	−0·4553	0·0971
C	2·60	0·182	0·4545	0·8902	0·0318
	4·51	0·239	−0·1009	0·0160	0·9948
	13·23	0·409	0·8251	−0·5585	0·0853
H(1)	6·46	0·286	0·5445	0·8264	0·1437
	8·09	0·320	−0·1507	−0·0721	0·9859
	12·02	0·390	0·9880	−0·1067	−0·1121
H(2)	2·03	0·160	0·1138	0·9917	0·0593
	6·13	0·279	0·1048	−0·0713	0·9919

translation T and libration ω tensors using the least-squares procedure described by Cruickshank (1956). The elements of the T and ω tensors for the molecule are given in Table 3.

Table 3. *Translation and libration tensors describing the thermal vibrations of the triethylenediame molecule at 298 K* (*tensor elements* $T_{13}, T_{23}, \omega_{13}, \omega_{23}$ *are zero by symmetry*)

$$T = \begin{pmatrix} 0·0264 \ (27) & 0·0000 \ (52) & 0 \\ & 0·0285 \ (32) & 0 \\ & & 0·0450 \ (24) \end{pmatrix} \text{Å}^2$$

r.m.s. amplitude of translation: 0·16 (5), 0·17 (5), 0·21 (7) Å

$$\omega = \begin{pmatrix} 26·9 \ (4·8) & 0·4 \ (3·1) & 0 \\ & 29·1 \ (4·5) & 0 \\ & & 51·5 \ (6·5) \end{pmatrix} (°)^2$$

r.m.s. amplitude of libration: 5·18 (2·20), 5·40 (2·64), 7·18 (1·77)°.

Burns, Ferrier & McMullan (1967) have proposed the use of the following quantities in consideration of the rigidity of atoms in the molecule: $U^o(U^c)$ is the trace of the observed (calculated) U matrix ($U_{ij} = a_i a_j \beta_{ij}/2\pi^2$), $\sigma[U^o]$ is the standard deviation in U^o, S represents the degree of mismatch between the shapes, and θ represents the mismatch in orientation between the observed and calculated thermal ellipsoids of each atom. Burns *et al.* (1967) suggest an acceptable degree of rigidity exists if $(U^o - U^c) < 2\sigma[U^o]$, $S < 150$ and $\theta < 25°$, but effective non-rigidity if $(U^o - U^c) > 3\sigma[U^o]$, or $S > 200$, or $\theta > 30°$. Values of these quantities for the atoms in the TEDA molecule are given in Table 4(a). The criteria suggested for the assignment of rigidity to the molecule are satisfied for all parameters, with the exception of the shape factor S for C and H(1) for which, although the shape factor is greater than the suggested value of 150 for rigidity, in both instances the values obtained are less than the 200 value set for definite assignment of non-rigidity. It would seem therefore that, with respect to its thermal motion, the molecule may be considered to behave as a reasonably rigid body in the room-temperature phase of the crystal. To allow detailed comparison, the complete set of U^o_{ij}, U^c_{ij} and $\sigma(U^o_{ij})$ is included in Table 4(b).

Table 4(a). *Values used in assessing the rigidity of the triethylenediamine molecule, according to Burns et al.* (1967)

	Tr $U^o(\sigma[U^o])$	Tr $(U^o - U^c)$	S	$\theta(°)$
N	0·1334 (37)	0·0060	34	3·6
C	0·1441 (187)	−0·0114	193	13·8
H(1)	0·2722 (553)	0·0484	17	23·0
H(2)	0·2549 (488)	0·0274	191	10·6

Table 4(b). *Observed and calculated atomic vibration tensor components* (Å^2)

		Observed	Calculated
N	U_{11}	0·0414 (14)	0·0408
	U_{22}	0·0414 (14)	0·0417
	U_{33}	0·0507 (27)	0·0450
	U_{12}	0·0000 (0)	−0·0002
	U_{13}	0	0
	U_{23}	0	0
C	U_{11}	0·0474 (28)	0·0610
	U_{22}	0·0400 (27)	0·0334
	U_{33}	0·0567 (18)	0·0605
	U_{12}	0·0020 (2)	0·0023
	U_{13}	0·0018 (64)	0·0009
	U_{23}	−0·0110 (23)	−0·0085
H(1)	U_{11}	0·0828 (73)	0·0882
	U_{22}	0·0842 (68)	0·0550
	U_{33}	0·1051 (91)	0·0803
	U_{12}	0·0386 (35)	0·0278
	U_{13}	0·0103 (85)	0·0105
	U_{23}	−0·0039 (62)	−0·0170
H(2)	U_{11}	0·1209 (85)	0·0977
	U_{22}	0·0469 (67)	0·0481
	U_{33}	0·0872 (45)	0·0802
	U_{12}	−0·0403 (369)	−0·0224
	U_{13}	−0·0095 (42)	−0·0073
	U_{23}	−0·0113 (42)	−0·0186

(iii) *Interatomic distances and angles*

The molecular configuration and packing arrangement is represented in Fig. 3. The calculated interatomic distances and angles are given in Table 5. As the atoms forming the molecule are bonded to form a reasonably rigid unit [see § (ii)], the motion of the individual atoms will be correlated in some way, giving bond lengths which are shorter than their actual values [see Cruickshank (1956)]. The expression for the mag-

Table 5. *Interatomic distances and angles for triethylenediamine and calculated corrections for bond lengths based on rigid-body motion*

Uncorrected interatomic distances (Å)

C–N	1·470 (7)	C–H(1)	1·06 (2)
C–C	1·513 (5)	C–H(2)	1·09 (1)

Corrections to be added (Å), assuming rigid-body motion of the molecule

C–N	0·016 (2)	C–H(1)	0·011 (2)
C–C	0·013 (6)	C–H(2)	0·015 (2)

Uncorrected bond angles (°)

C–N–C	108·4 (2)	N——C–H(1)	107·2 (7)
C–C–N	110·5 (4)	N——C–H(2)	107·2 (8)
C–C–H(1)	112·0 (7)	H(1)–C–H(2)	107 (1)
C–C–H(2)	112·4 (6)		

nitude of the corrections to be made to the bond lengths, if the molecule is assumed to behave as a rigid unit, has been given by Busing & Levy (1964). Values for these corrections are given in Table 5.

The magnitudes of the interbond angles C–C–H(1) and C–C–H(2); N–C–H(1) and N–C–H(2) are respectively closely equal. Agreement is also obtained, within estimated errors, with the previously reported X-ray determined bond lengths and interbond angles (Weiss *et al.*, 1964) and the values obtained for the molecules in the gaseous phase by electron diffraction (Yokezeki & Kuchitsu, 1971).

Concluding remarks

The present neutron diffraction study of TEDA indicates an ordered structure of non-twisted molecules, in preference to an ordered or disordered structure of twisted molecules.

It has been previously suggested that, in addition to the lattice thermal motion already discussed, the molecules undergo hindered reorientation in both phases (Smith, 1965; Zussman & Alexander, 1968). Molecular reorientation is considered to occur above 190 K with jumps between structurally equivalent orientations about the (threefold) NN direction, increasing in frequency to $\sim 5 \times 10^7$ Hz at 350 K, just below the structural transition. More general reorientation is considered to occur in phase I with a frequency $\gg 3 \times 10^4$ Hz (for further details, see part II). It is not unexpected, therefore, that for such relatively low frequencies in phase II, the present neutron diffraction study should indicate an ordered structure with relatively small translational and librational molecular motions only.

References

BACON, G. E. (1972). *Acta Cryst.* A**28**, 357–358.
BRÜESCH, P. (1966). *Spectrochim. Acta*, **22**, 861–865, 867–875.
BRÜESCH, P. & GÜNTHARD, H. H. (1966). *Spectrochim. Acta*, **22**, 877–887.
BURNS, D. M., FERRIER, W. G. & McMULLAN, J. T. (1967). *Acta Cryst.* **22**, 623–629.
BUSING, W. R. & LEVY, H. A. (1964). *Acta Cryst.* **17**, 142–146.
CHANG, S. S. & WESTRUM, E. F. (1960). *J. Phys. Chem.* **64**, 1551–1552.
CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 754–756.
HENDRICKSON, J. B. (1961). *Chem. Eng. News*, **39**, 40.
NIMMO, J. K. & LUCAS, B. W. (1976). *Acta Cryst.* B**32**, In the press.
SMITH, G. W. (1965). *J. Chem. Phys.* **43**, 4325–4336.
TROWBRIDGE, J. C. & WESTRUM, E. F. (1963). *J. Phys. Chem.* **67**, 2381–2385.
WADA, T., KISHIDA, E., TOMIIE, Y., SUGA, H., SEKI, S. & NITTA, I. (1960). *Bull. Chem. Soc. Japan*, **33**, 1317–1318.
WEISS, G. S., PARKES, A. S., NIXON, E. R. & HUGHES, R. E. (1964). *J. Chem. Phys.* **41**, 3759–3767.
YOKOZEKI, A. & KUCHITSU, K. (1971). *Bull. Chem. Soc. Japan*, **44**, 72–77.
ZUSSMAN, A. & ALEXANDER, S. (1968). *J. Chem. Phys.* **48**, 3534–3539.