5. Supplemented structure parameters and relations

Starting from the assumption that the subcell values which have been calculated for the various β_n modifications of trilaurin coincide approximately for all triglycerides from trilaurin to tristearin the theoretical [cf. equation (7)] and experimental values of crystal layer thicknesses can be compared in Table 1.

Furthermore, equation (7) allows theoretical equations for the crystal-layer thicknesses to be derived taking into account the computed subcell parameters of trilaurin. In Table 2 these equations are juxtaposed to the experimentally obtained relations.

Thanks are due to Deutsche Forschungsgemeinschaft for making available the equipment required

(X-ray diffractometer and electron microscope) in the experimental studies.

References

BLASENBREY, S. & PECHHOLD, W. (1967). Rheol. Acta, 6, 174–185.
BUCHHEIM, W. (1970). Kiel. Milchwirtsch. Forschungsber. 22, 3–61.
BUCHHEIM, W. & KNOOP, E. (1969). Naturwissenschaften, 56, 560–561.
FREDE, E. & PRECHT, D. (1977). Fette, Seifen, Anstrichm. 79, 69–75.
JENSEN, L. H. & MABIS, A. J. (1963). Nature (London), 197, 681.
JENSEN, L. H. & MABIS, A. J. (1966). Acta Cryst. 21, 770–781.
JONG, S. DE & VAN SOEST, T. C. (1978). Acta Cryst. B34, 1570–1583.
KNOOP, E. & SAMHAMMER, E. (1961). Milchwissenschaft, 16, 201–209.
LAGALY, G., FITZ, S. & WEISS, A. (1975). Clays Clay Miner. 23, 45–54.
LARSSON, K. (1964). Ark. Kemi, 23, 1–15.
PECHHOLD, W. (1968). Kolloid-Z. Z. Polym. 228, 1–38.
PECHHOLD, W., BLASENBREY, S. & WOERNER, S. (1962). Kolloid-Z. Z. Polym. 189, 14–22.
PRECHT, D. (1977). Kiel. Milchwirtsch. Forschungsber. 29, 287–298.
PRECHT, D., FREDE, E. & GREIFF, R. (1978). Fette, Seifen, Anstrichm. 80, 344–352.
PRECHT, D. & GREIFF, R. (1978). Kiel. Milchwirtsch. Forschungsber. 30, 157–178.
VAND, V., MORLEY, W. M. & LOMER, T. R. (1951). Acta Cryst. 4, 324–329.

Table 2. Relations for the crystal-layer thicknesses from trilaurin (N = 12) to tristearin (N = 18); comparison of experimental and theoretical results

Modification	$K (N)_{exp.}$ (Å)	$K (N)_{theor.}$ (Å)
$\beta_1(1,0,0)$	$2.496 N + 8.020$	$2.496 N + 8.001$
$\beta_{11}(2,0,0)$	—	$2.431 N + 5.383$
$\beta_{11}(1,1,0)$	$2.369 N + 7.354$	$2.369 N + 7.354$
$\beta_{111}(3,0,0)$	$2.255 N + 4.400$	$2.248 N + 4.418$
$\beta_{1V}(4,-1,1)$	$2.047 N + 3.567$	$2.064 N + 3.540$
$\beta_V(5,1,0)$	$1.890 N + 3.247$	$1.861 N + 2.770$

Neutron Diffraction at 15 and 120 K and *ab initio* Molecular-Orbital Studies of the Molecular Structure of 1,2,4-Triazole

BY G. A. JEFFREY, J. R. RUBLE AND J. H. YATES

Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260, USA

Abstract

The crystal structure of 1,2,4-triazole, $C_2H_3N_3$, has been refined using single-crystal neutron diffraction data [$\lambda = 1.0470 (1)$ Å] measured at 15 and 120 K. The crystal data at 15 K [120 K] are $M_r = 69.07$; Pbca; $Z = 8$; $a = 9.748 (2)$ [9.760 (2)], $b = 9.331 (2)$ [9.345 (2)], $c = 6.927 (2)$ [6.989 (2)] Å; $D_n = 1.456$ [1.439] g cm^{-3}. The final agreement factors are $R(F) = 0.039$ [0.055], $wR(F^2) = 0.050$ [0.054], $S = 1.309$ [1.114] for 1249 [1258] observations. The molecule is very close to planar, with the ring atoms deviating from their least-squares plane by less than 0.0015 (6) Å. The H atoms deviate from this plane by less than 0.061 (2) Å. Thermal-motion corrections based on rigid-body and segmented-body analyses resulted in differences of less than 0.005 Å in the corrected bond lengths from the two refinements. Ab initio molecular-orbital calculations were carried out at the Hartree–Fock (HF) 3-21G level, using GAUSSIAN83 to optimize the geometry of the isolated molecule for minimum energy. There are differences between the thermally corrected experimental and calculated bond lengths for the ring bonds of between 0.010 and 0.030 Å. These differences are largely accounted for by estimations of corrections for approximation in the

theoretical calculations based on higher-order calculations on simpler molecules. The agreement between the observed and theoretical C—H and N—H bond lengths is improved when an empirical anharmonic stretching correction is applied. *Ab initio* calculations, at the HF/STO-3G level, were carried out on formaldehyde hydrazone and formaldehyde hydrazone dimer to predict the effects of hydrogen bonding.

Introduction

The crystal structure of 1,2,4-triazole (I) was determined by Deuschl (1965) and refined by Goldstein, Ladell & Abowitz (1969) from X-ray diffractometer data at 113 and 296 K. The neutron diffraction refinements and theoretical calculations reported in this paper are a continuation of a series of comparisons of the experimental and theoretical molecular structures of small organic molecules. Molecules previously studied are acetamide (Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople, 1980), monofluoroacetamide (Jeffrey, Ruble, McMullan, DeFrees & Pople, 1981*a*), formamide oxime (Jeffrey, Ruble, McMullan, DeFrees & Pople, 1981*b*), *N,N'*-diformohydrazide (Jeffrey, Ruble, McMullan, DeFrees & Pople, 1982), and glyoxime (Jeffrey, Ruble & Pople, 1982). 1,2,4-Triazole is the first cyclic molecule in this series of investigations. The data were collected at 15 K to minimize the effects of thermal motion, and at 120 K for future use with X-ray data for deformation density analysis.

(I)
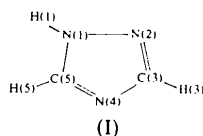
Experimental

The crystal structure refinements

The neutron diffraction data collection and structure refinement followed the same methods and procedures as described for formamide oxime (Jeffrey *et al.*, 1981*b*) except for the information provided below. Large prismatic rods of 1,2,4-triazole were obtained by slow evaporation of a 1:1 *n*-propanol/water solution. A specimen, $1.26 \times 1.40 \times 1.98$ mm, cut from a longer rod, had four natural faces {021} and two cut faces approximated by (311) and (510). The crystal was mounted with the *a* axis 17° off the φ axis of the diffractometer and was cooled at a rate of 1 K min^{-1} to a temperature of 15.0 ± 0.5 K for the first data set. It was then warmed to a temperature of 120.0 ± 0.5 K for the second data set. The lattice parameters given in Table 1 were determined from sin$^2 \theta$ values of 32

Table 1. *Crystal data for* 1,2,4-*triazole* ($C_2H_3N_3$; *Pbca; Z* = 8)

	This work		Deuschl (1965)	Goldstein, Ladell & Abowitz (1969)	
	15 K	120 K	298 K	113 K	296 K
a (Å)	9.748 (2)	9.760 (2)	9.69 (4)	9.729 (2)	9.769 (2)
b (Å)	9.331 (2)	9.345 (2)	9.38 (4)	9.334 (4)	9.366 (2)
c (Å)	6.927 (2)	6.989 (2)	7.14 (3)	6.977 (2)	7.195 (2)
V (Å^3)	630.1	637.4	649	633.6	658.3
D_x	1.456	1.439	1.40	1.448	1.394
λ (Å)	1.0470 (1)	1.0470 (1)	1.54	1.392*	1.392*

* Cu $K\beta$.

reflections at 15 K and 31 reflections at 120 K with $50° < 2\theta < 55°$. Neutron intensities were measured for one octant with scan widths of $\Delta(2\theta) = 3.8°$ for sin $\theta/\lambda \leq 0.48$ Å^{-1}, and varied according to the dispersion formula $\Delta(2\theta) = (3.410 + 1.906 \tan \theta)°$ for 0.48 Å$^{-1} < \sin \theta/\lambda < 0.79$ Å^{-1}. Neutron absorption corrections were applied using an analytical procedure (Templeton & Templeton, 1973). The linear absorption coefficient ($\mu = 155.6$ m^{-1}) was calculated assuming the mass absorption coefficient for chemically bonded H to be 2.4835 m^2 kg^{-1} at $\lambda = 1.0470$ Å (McMullan & Koetzle, 1980). The resulting transmission factors ranged from 0.78 to 0.86. Of the 1249 reflections in the 15 K data set and 1258 reflections in the 120 K data set, there were 11 and 9, respectively, with a negative net count; none significantly different from zero.

The initial parameters for the refinement using the 15 K data were those reported by Goldstein, Ladell & Abowitz (1969). The final parameters from that refinement were used as the initial parameters for the 120 K data refinement. Full-matrix least-squares refinement was carried out with a modified version of *ORFLS* (Busing, Martin & Levy, 1962). The quantity minimized was $\sum w|F_o^2 - kF_c^2|^2$, where $w = [\sigma_c^2 + (0.02F_o^2)^2]^{-1/2}$. After the final cycles of refinement, there were no changes greater than 0.01σ in any of the 74 parameters (72 atomic parameters, scale factor, and isotropic extinction parameter) for either refinement. The largest features in the final difference maps were 0.7σ (15 K) and 1.0σ (120 K), where the error in the neutron scattering density was estimated from $\sigma(F)$. These correspond to 1.1% (15 K) and 1.4% (120 K) of the largest peak in the scattering density maps. Extinction was moderate with 31 reflections (15 K) and 21 reflections (120 K) having correction factors for F_c^2 of less than 0.90. The most severe correction was for 021, with $F_o/F_c = 0.63$ (15 K) and 0.62 (120 K). The agreement factors for 15 K [120 K] data are: $R(F) = 0.039$ [0.055], $R(F^2) = 0.034$ [0.043], $wR(F) = 0.029$ [0.030], $wR(F^2) = 0.050$ [0.054], $S = 1.309$ [1.114]. The

Table 2. *Atomic parameters for* 1,2,4-*triazole*

The fractional atomic coordinates are $\times 10^5$ for non-hydrogen atoms and all other atomic parameters are $\times 10^4$ (except the X-ray values for the H atoms, $\times 10^3$). Anisotropic temperature factors are referred to the crystallographic axes and correspond to the temperature-factor expression $T = \exp(-2\pi^2 \sum_i \sum_j h_i h_j a_i^* a_j^* U_{ij})$. Isotropic $g = 0.185$ (7) $\times 10^4$ rad^{-1} for 15 K analysis, 0.207 (8) $\times 10^4$ rad^{-1} for 120 K. Estimated standard deviations given in parentheses refer to the least significant digit. The upper row refers to the 15 K analysis, the middle row to 120 K and the lower row gives the X-ray values ($\times 10^4$ for non-hydrogen, $\times 10^3$ for H atoms) at 113 K of Goldstein, Ladell & Abowitz (1969).

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	−764 (4)	−8391 (4)	20983 (6)	48 (2)	72 (1)	75 (2)	−1 (1)	3 (1)	−3 (1)
	−699 (5)	−8455 (6)	21013 (7)	123 (2)	205 (2)	197 (2)	−11 (2)	0 (2)	9 (2)
	−66 (2)	−846 (2)	2102 (2)	216 (10)	238 (4)	227 (7)	−2 (14)	−10 (14)	16 (14)
N(2)	2382 (4)	−20303 (5)	10576 (6)	73 (2)	69 (2)	82 (2)	−19 (1)	1 (1)	−12 (1)
	2508 (6)	−20288 (7)	10713 (8)	211 (2)	202 (2)	220 (2)	−54 (2)	−6 (2)	−19 (2)
	250 (2)	−2031 (2)	1072 (2)	326 (10)	230 (4)	254 (7)	−48 (14)	−2 (14)	−21 (14)
C(3)	15876 (6)	−19339 (7)	8742 (8)	67 (2)	65 (2)	77 (2)	11 (2)	9 (2)	−15 (2)
	15975 (8)	−19329 (9)	9074 (11)	195 (3)	197 (3)	208 (3)	23 (3)	26 (3)	−27 (3)
	1597 (2)	−1928 (2)	915 (3)	302 (10)	256 (8)	239 (7)	28 (14)	40 (14)	−5 (14)
N(4)	21498 (4)	−7571 (5)	17388 (6)	45 (2)	78 (2)	90 (2)	−2 (1)	0 (1)	−9 (1)
	21510 (5)	−7616 (6)	17721 (8)	121 (2)	224 (2)	248 (2)	−1 (2)	1 (2)	−14 (2)
	2149 (2)	−764 (2)	1775 (2)	206 (10)	278 (4)	276 (7)	7 (14)	−15 (14)	−5 (14)
C(5)	10602 (6)	−983 (6)	24949 (9)	55 (2)	57 (2)	81 (2)	1 (2)	0 (2)	−11 (2)
	10606 (8)	−1086 (8)	25088 (11)	135 (3)	164 (3)	223 (3)	0 (3)	−6 (3)	−22 (3)
	1064 (2)	−113 (2)	2505 (3)	225 (10)	225 (8)	254 (7)	0 (14)	−17 (14)	−12 (14)
H(1)	−1090 (1)	−664 (2)	2544 (2)	112 (5)	218 (6)	225 (6)	11 (5)	28 (4)	−26 (5)
	−1083 (2)	−669 (2)	2525 (3)	186 (6)	400 (8)	379 (8)	6 (7)	13 (6)	−1 (8)
	−106 (2)	−58 (2)	250 (4)	48 (6)					
H(3)	2189 (2)	−2732 (2)	110 (3)	218 (6)	213 (7)	284 (7)	52 (5)	49 (6)	−99 (6)
	2201 (2)	−2729 (2)	160 (3)	428 (10)	411 (12)	482 (11)	104 (9)	93 (9)	−145 (9)
	200 (2)	−267 (2)	21 (4)	38 (6)					
H(5)	1050 (2)	900 (2)	3301 (2)	234 (6)	162 (5)	285 (7)	−5 (5)	−2 (5)	−103 (5)
	1046 (2)	887 (2)	3306 (3)	371 (9)	299 (8)	516 (11)	−26 (8)	2 (9)	−163 (8)
	105 (2)	76 (2)	316 (4)	25 (6)					

atomic parameters are given in Table 2. The atomic notation and thermal ellipsoids are shown in Fig. 1.*

The molecular dimensions derived from the two neutron diffraction refinements are compared with the

*Lists of observed and calculated structure factors (for both temperatures) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38373 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
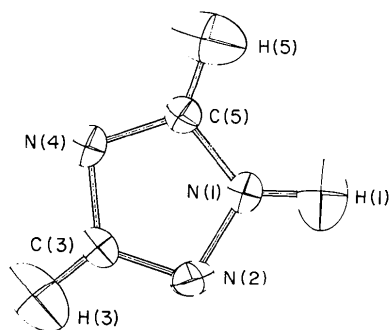

Fig. 1. Atomic notation and thermal-motion ellipsoids at 99% probability level (Johnson, 1976) for 1,2,4-triazole at 15 K.

previous X-ray results at 113 K in Table 3. For the non-hydrogen atoms, the difference between the X-ray values at 113 K and the neutron values at 120 K does not exceed the σ values for the X-ray data in the bond lengths, and is no more than 3σ in the bond angles. The X-ray thermal parameters are greater than the neutron values by factors ranging from 1·1 to 1·8.

Thermal-motion analysis and corrections

Rigid-body thermal-motion analysis is possible for this molecule only if the H atoms are included in the rigid body. The results of this analysis, shown in Table 4(a), gave fair agreement, with $\langle$r.m.s. U_{ij}(obs.) − U_{ij}(calc.)$\rangle$ = 0·0015 [0·0016] Å², with $\sigma(U_{ij})$ = 0·0019 [0·0020] Å². The internal motions of the H atoms were then calculated using the segmented-body analysis program *ORSBA* (Johnson, 1970), giving the results shown in Table 4(b). Those components greater than 2σ were then subtracted prior to a rigid-body analysis of the whole molecule. The results, shown in Table 4(c), had significantly better agreement factors with $\langle$r.m.s. U_{ij}(obs.) − U_{ij}(calc.)$\rangle$ = 0·0002 [0·0004] Å², with $\sigma(U_{ij})$ = 0·0003 [0·0006] Å². There was also better agreement between the directions of the motions at the two temperatures.

Table 3. *Experimental and theoretical molecular dimensions of* 1,2,4-*triazole*

Estimated standard deviations given in parentheses refer to the least significant figure.

	Experimental							
	Uncorrected			Corrected for thermal motion				
				Rigid body		ORSBA		
	15 K	120 K	(X-ray)* 113 K	15 K	120 K	15 K	120 K	Theoretical HF/3-21G
Bond lengths (Å)								
N(1)–N(2)	1·3599 (6)	1·3561 (8)	1·359 (3)	1·368	1·367	1·363	1·365	1·395
N(1)–C(5)	1·3345 (7)	1·3314 (9)	1·331 (3)	1·341	1·342	1·338	1·340	1·348
N(2)–C(3)	1·3245 (8)	1·3225 (10)	1·323 (3)	1·331	1·331	1·329	1·330	1·305
C(3)–N(4)	1·3656 (7)	1·3620 (10)	1·359 (3)	1·373	1·373	1·369	1·372	1·379
N(4)–C(5)	1·3343 (7)	1·3304 (9)	1·324 (3)	1·341	1·340	1·338	1·338	1·308
N(1)–H(1)	1·0478 (14)	1·0451 (18)		1·053	1·052	1·051	1·051	0·993
C(3)–H(3)	1·0855 (16)	1·0832 (21)		1·092	1·092	1·088	1·090	1·061
C(5)–H(5)	1·0858 (16)	1·0846 (20)		1·092	1·094	1·088	1·092	1·063
Bond angles (°)								
N(2)–N(1)–C(5)	110·19 (4)	110·12 (5)	110·2 (2)	†	†	110·1	110·2	109·2
N(1)–N(2)–C(3)	102·67 (4)	102·72 (6)	102·1 (2)			102·7	102·7	102·6
N(2)–C(3)–N(4)	114·27 (5)	114·22 (7)	114·6 (2)			114·3	114·2	114·1
C(3)–N(4)–C(5)	102·90 (4)	102·89 (6)	103·0 (2)			102·8	102·9	104·2
N(1)–C(5)–N(4)	109·97 (5)	110·05 (6)	110·1 (2)			110·0	110·0	110·0
N(2)–N(1)–H(1)	119·76 (9)	119·82 (12)				119·8	119·8	120·0
C(5)–N(1)–H(1)	129·89 (9)	129·93 (12)				129·9	129·9	130·8
N(2)–C(3)–H(3)	122·43 (10)	122·38 (15)				122·5	122·3	122·8
N(4)–C(3)–H(3)	123·29 (10)	123·40 (14)				123·2	123·4	123·1
N(1)–C(5)–H(5)	122·83 (10)	122·84 (13)				122·8	122·9	123·9
N(4)–C(5)–H(5)	127·20 (10)	127·10 (13)				127·2	127·1	126·2

* From Goldstein, Ladell & Abowitz (1969).
† Not significantly different from ORSBA values.

The thermally corrected values for the bond lengths and bond angles are given in Table 3. The effect of excluding the H atoms from the rigid-body analysis decreases the average bond-length correction from 0·007 to 0·003 Å at 15 K and from 0·010 to 0·008 Å at 120 K. When corrected for thermal motion, the two sets of neutron values differ by less than 0·002 Å from the rigid-body analysis and less than 0·004 Å from the segmented-body analysis.

Ab initio molecular-orbital calculations

The theoretical calculations were carried out at the Hartree–Fock (HF) level using both the STO-3G and 3-21G split-valence basis sets (Binkley, Pople & Hehre, 1980) as incorporated in Harris *GAUSSIAN*83 (De-Frees, Levi, Pollack, Blurock, Hout, Pietro, Francl & Hehre, 1983). Minimization of the total energy at the HF/3-21G level with respect to all in-plane geometrical parameters led to the molecular dimensions given in
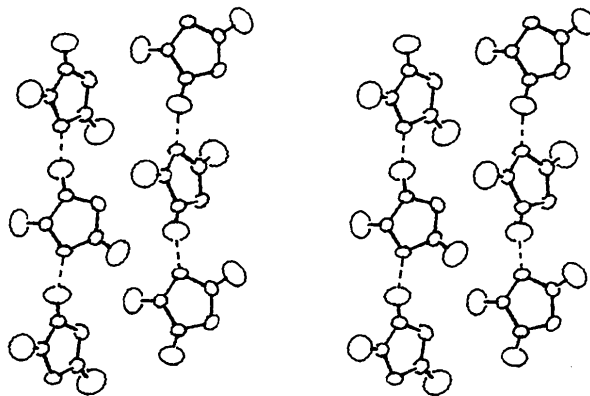
Description of the structure

The molecules are close to being exactly planar. The largest deviation of the ring atoms from their mean plane at 15 K [120 K] is 0·0015 (6) [0·0010 (8)] Å for C(5). The H atoms are out of this plane by +0·061 (2) [+0·056 (2)] Å for H(1), +0·006 (2) [+0·010 (2)] Å for H(3) and −0·011 (2) [−0·014 (2)] Å for H(5).

The hydrogen bonding forms corrugated sheets of molecules approximately parallel to (001), as described by Goldstein, Ladell & Abowitz (1969) and shown in Fig. 2. The N–H⋯N hydrogen-bond length is 1·789 (2) Å and the N–H⋯N angle is 168·2 (1)°. This is comparable to the values of 1·809 (2) Å and 173·3 (1)° for the N–H⋯N values in imidazole by neutron diffraction at 103 K (McMullan, Epstein, Ruble & Craven, 1979).

Fig. 2. Stereoview of the chains of hydrogen-bonded 1,2,4-triazole molecules in the crystal structure.

Table 4. *Thermal-motion analysis*

Rigid-body-motion analysis with respect to origin at center of mass, X and Y in the plane of the molecule with X nearly parallel to N(2)–C(3) and Y nearly parallel to C(5)–H(5). Z is normal to the plane of the molecule. First line 15 K, second line 120 K.

(a) Rigid-body analysis including H atoms

		I_1	I_2	I_3
T	0·075 Å	55·6°	131·1°	119·9°
	0·130	73·7	139·1	126·3
	0·070	34·2	58·6	78·0
	0·113	22·5	67·7	92·5
	0·014	83·0	121·9	32·9
	0·102	74·8	122·4	36·6
ω	5·00°	180·0°	90·0°	90·0°
	5·98	13·8	96·1	102·4
	4·21	98·6	34·6	56·8
	4·91	81·0	48·8	42·6
	3·51	95·4	56·9	146·6
	4·43	83·4	138·8	49·6

(b) Internal motion of H atoms from *ORSBA*

	Radial	In-plane	Out-of-plane
H(1)	0·0067 Å²	0·0090 Å²	—
	0·0072	0·0061	—
H(3)	0·0074	0·0132	0·0040 Å²
	0·0076	0·0119	—
H(5)	0·0059	0·0135	0·0040
	0·0058	0·0123	—

(c) Rigid-body analysis with H motions from (b) subtracted

		I_1	I_2	I_3
T	0·073 Å	89·0°	175·9°	94·0°
	0·129	85·3	170·6	98·1
	0·069	1·0	89·0	90·4
	0·112	18·7	83·0	107·3
	0·036	89·6	94·0	4·0
	0·107	71·9	96·2	19·2
ω	4·44°	5·6°	84·4°	89·7°
	5·69	1·0	106·7	93·0
	4·19	95·6	6·5	86·7
	4·98	73·1	18·7	82·3
	2·21	93·3	93·3	3·3
	3·66	89·4	98·2	8·3

Table 3 and a total energy of −239·42802 hartrees (−628·6182 × 10³ kJ mol⁻¹). Subsequent calculation of the gradient force field at the minimum-energy geometry and determination of the vibration frequencies gave only positive frequencies, indicating that the planar molecule is an energy minimum.

As in the previous studies in this series, theoretical values of the bond lengths are corrected for approximation in the theory and for hydrogen-bonding effects. For the approximation in the theory, the difference between the HF/3-21G results and higher-level approximations for similar bonds in smaller

molecules is used (DeFrees, Krishnan, Schlegel & Pople, 1982). For consistency, the same small-molecule calculations are used for the same bond types as in the preceding papers in this series.

To study the effect on the bond lengths of hydrogen bonding, the difference between the monomer and hydrogen-bonded dimer geometries was calculated at the HF/STO-3G level for formaldehyde hydrazone, $H_2C=N-NH_2$. In the closed-dimer model, shown in Fig. 3, the atoms were constrained to be planar. The details of the optimized calculated geometries of the formaldehyde hydrazone monomer and closed-dimer are given in Table 5. It is interesting to note that in the
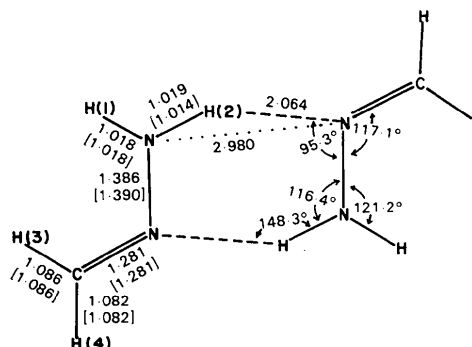

Fig. 3. Model for hydrogen bonding. Formaldehyde hydrazone dimer calculated at HF/STO-3G level. Bond lengths (Å) in parentheses are those for the isolated molecule.

Table 5. *Calculated geometries for the isolated molecule and closed hydrogen-bonded dimer of formaldehyde hydrazone*

The atomic notation is given in Fig. 3.

	Isolated molecule			Hydrogen-bonded dimer
	HF/STO-3G		HF/3-21G	HF/STO-3G
	Planar	Twisted	Planar	Planar
Bond lengths (Å)				
N–N	1·390	1·361	1·373	1·386
C=N	1·281	1·235	1·262	1·281
N–H(1)	1·018	1·038	0·997	1·018
N–H(2)	1·014	1·038	0·990	1·019
C–H(3)	1·086	1·098	1·079	1·086
C–H(4)	1·082	1·098	1·070	1·082
Bond angles (°)				
N–N–C	116·0	175·3	119·8	117·1
N–N–H(1)	122·1	111·3	121·7	121·2
N–N–H(2)	117·3	111·3	116·1	116·4
N–C–H(3)	124·1	123·0	123·7	123·8
N–C–H(4)	118·1	123·0	118·5	118·3
Torsion angles (°)				
H(1)–N–N–C	0	+119·9	0	0
H(2)–N–N–C	180	−118·6	180	180
H(3)–C–N–N	0	+89·9	0	0
H(4)–C–N–N	180	−91·0	180	180
E_{min} (kJ mol⁻¹ × 10³)*	−386·2726	−386·1051	−389·0677	−772·5707

* Hydrogen-bond energy = 25·5 kJ mol⁻¹.

twisted conformation of formaldehyde hydrazone, which is a local minimum less stable than the planar conformation, the C=N and N—N bonds are both shorter than in the planar conformation and nearly collinear. The effects of hydrogen bonding on the dimensions of formaldehyde hydrazone, shown in Fig. 3, are very small for the N—N bond and negligible for the C—N bond. The donor N—H bond is lengthened, as expected. This contrasts with the formamide hydrogen-bonded dimer calculations reported by Jeffrey *et al.* (1981*b*), where the stronger N—H···O=C hydrogen bonds were calculated to shorten the C—N bonds by 0·023 Å and lengthen the C=O bonds by 0·018 Å. The calculated lengthening of the donor N—H bond was also greater, 0·018 Å, in that molecule.

Comparison of experimental and theoretical results

Large and systematic differences are observed between the uncorrected theoretical and experimental N—N and C—N bond lengths, as shown in Table 6. These differences appear to be due primarily to the limitations of the HF/3-21G basis set, since they are almost cancelled by the corrections derived by extrapolation from higher-level theory. The residual discrepancies are still significant in terms of the experimental errors, for which $3\sigma = 0\cdot002$ Å, but are small in comparison with the changes in bond length with level of theory for

Table 6. *Analysis of bond-length discrepancies* (Å)

Bond	Theory —Exp.[a]	High-level extrapolation to MP3/6-31G	H-bonding dimer — monomer	Residual discrepancy
N(1)—N(2)	+0·030	−0·027[b]	−0·004	−0·001
N(1)—C(5)	+0·010	−0·005[c]	—	+0·005
N(4)—C(3)	+0·010	−0·006[c]	—	+0·004
N(2)=C(3)	−0·024	+0·019[d]	—	−0·005
N(4)=C(5)	−0·030	+0·019[d]	—	−0·011
N(1)—H(1)	−0·058	+0·014[c]	+0·005	−0·039
C(3)—H(3)	−0·027	+0·008[e]	—	−0·019
C(5)—H(5)	−0·025	+0·008[e]	—	−0·017

Notes: (*a*) the 15 K values corrected by the *ORSBA* method. (*b*) From planar hydrazine. (*c*) From methylamine. (*d*) From methylimine. (*e*) From methane.

the N—N and C=N bonds. It is interesting to note that although the formal single and double C—N bonds in triazole do not differ markedly in length, 1·369 and 1·338 Å *versus* 1·338 and 1·329 Å, the differences between theory and experiment are reversed in sign, and this is compensated by an opposite reversal in the correction terms based on methylamine with C—N = 1·471 Å and methylimine with C=N = 1·273 Å. At the HF/3-21G level there appears to be a trend to underestimate the electron delocalization around the five-membered ring.

As in previous studies, the C—H and N—H bond lengths agree better with theory if the thermal-motion corrections are omitted. This is believed to be due to anharmonicity of the bond-stretching motion. The application of the Kuchitsu & Bartell (1961) semi-empirical anharmonic correction reduced this discrepancy to values comparable to that for the non-hydrogen bond lengths, as shown in Table 7. The expression used was $-\frac{3}{2}a\langle U_{XH}^2\rangle$, where $\langle U_{XH}^2\rangle$ is the relative mean-square amplitude of H and X atoms along the X—H bond; $a = 1\cdot98$ Å^{-1} for the C—H bonds from Kuchitsu & Morino (1965) and $a = 2\cdot19$ Å^{-1} for N—H bonds.

Bond angles are relatively insensitive to thermal-motion corrections and, because of the constraint of ring closure in this molecule, are less affected by approximations in the theory than for acyclic molecules. The agreement between experiment and theory is excellent. The principal features observed are reproduced by the theory; notably the 103° ring angles at N(2) and N(4), the 110° angles at N(1) and C(5), and the 114° angle at C(3). The mean difference in ring bond angles is 0·5° and the maximum difference is 1·4°. For the exocyclic angles, the mean difference is 0·6°, and the maximum is 1·1°.

Table 7. *Effect of anharmonicity correction on* N—H *and* C—H *bond lengths* (Å)

First line 15 K, second line 120 K.

	Experimental value	Segmented-motion correction	Anharmonicity correction	Corrected value	Corrected theoretical value
N(1)—H(1)	1·0478 (14)	+0·003	−0·017	1·033	1·007
	1·0451 (18)	+0·006	−0·021	1·030	—
C(3)—H(3)	1·0855 (16)	+0·002	−0·016	1·072	1·069
	1·0832 (24)	+0·007	−0·018	1·072	—
C(5)—H(5)	1·0858 (16)	+0·002	−0·015	1·073	1·071
	1·0846 (22)	+0·007	−0·015	1·077	—

Sciences. We wish to thank Dr R. K. McMullan for his help and advice and Mr Joseph Henriques for his technical assistance.

References

BINKLEY, J. S., POPLE, J. A. & HEHRE, W. J. (1980). *J. Am. Chem. Soc.* **102**, 939–947.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS.* Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

DEFREES, D. J., KRISHNAN, R., SCHLEGEL, H. B. & POPLE, J. A. (1982). *J. Am. Chem. Soc.* **104**, 5576–5580.

DEFREES, D. J., LEVI, B. A., POLLACK, S. K., BLUROCK, E. S., HOUT, R. F. JR, PIETRO, W. J., FRANCL, M. M. & HEHRE, W. J. (1983). To be published.

DEUSCHL, H. (1965). *Ber. Bunsenges. Phys. Chem.* **69**, 550–557.

GOLDSTEIN, P., LADELL, J. & ABOWITZ, G. (1969). *Acta Cryst.* **B25**, 135–143.

JEFFREY, G. A., RUBLE, J. R., McMULLAN, R. K., DEFREES, D. J., BINKLEY, J. S. & POPLE, J. A. (1980). *Acta Cryst.* **B36**, 2292–2299.

JEFFREY, G. A., RUBLE, J. R., McMULLAN, R. K., DEFREES, D. J. & POPLE, J. A. (1981a). *Acta Cryst.* **B37**, 1885–1890.

JEFFREY, G. A., RUBLE, J. R., McMULLAN, R. K., DEFREES, D. J. & POPLE, J. A. (1981b). *Acta Cryst.* **B37**, 1381–1387.

JEFFREY, G. A., RUBLE, J. R., McMULLAN, R. K., DEFREES, D. J. & POPLE, J. A. (1982). *Acta Cryst.* **B38**, 1508–1513.

JEFFREY, G. A., RUBLE, J. R. & POPLE, J. A. (1982). *Acta Cryst.* **B38**, 1975–1980.

JOHNSON, C. K. (1970). *Thermal Neutron Diffraction*, edited by B. T. M. WILLIS, ch. 9. Oxford Univ. Press.

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

KUCHITSU, K. & BARTELL, L. S. (1961). *J. Chem. Phys.* **35**, 1945–1949.

KUCHITSU, K. & MORINO, Y. (1965). *Bull. Chem. Soc. Jpn*, **38**, 805–813.

McMULLAN, R. K., EPSTEIN, J., RUBLE, J. R. & CRAVEN, B. M. (1979). *Acta Cryst.* **B33**, 688–691.

McMULLAN, R. K. & KOETZLE, T. (1980). Unpublished results.

TEMPLETON, L. K. & TEMPLETON, D. H. (1973). Am. Crystallogr. Assoc. Meet., Storrs, CT. Abstr. E-10.

The Structure of 2-Methyl-2-propanol at 293 K

BY A. MIKUSIŃSKA-PLANNER

Optics Laboratory, Institute of Physics, A. Mickiewicz University, 60-780 Poznań, Poland

Abstract

The angular distributions of the scattered X-ray intensity from 2-methyl-2-propanol in the liquid phase were measured with Cu $K\alpha$ and Mo $K\alpha$ radiation lines. From these an experimental pair-function distribution was calculated. This is compared with the pair-function distributions from several models. Good agreement is obtained for two types of association. The first is a dimer with an open hydrogen-bond structure. The second is a cyclic trimer. The average length of the hydrogen bond in the dimers and the trimers is 3·08 and 2·46 Å, respectively. Association involving more than three molecules having the chain or cyclic structure is excluded.

Introduction

The association of 2-methyl-2-propanol in the liquid state has been investigated by Liddel & Becker (1957), who assumed dimers with a cyclic structure only, and by Bellamy & Pace (1966) and by Korppi-Tommola (1977), who assumed an open structure.

The coexistence of dimers with higher polymers is favoured by Davis, Pitzer & Rao (1960) and Van Ness, Van Winkle, Richtol & Hollinger (1967). Saunders & Hyne (1958), Huyskens, Henry & Gillerot (1962) and Storek & Kriegsmann (1968) exclude the dimers and suggest the occurrence of trimers only. Tucker, Farnham & Christian (1969) and Tucker & Becker (1973) assume the coexistence of trimers and higher polymers.

X-ray diffraction studies were undertaken by Narten & Sandler (1979), who have determined the hydrogen-bond length from the maximum in the intermolecular radial-distribution function. This paper is a determination of a structural model of 2-methyl-2-propanol using the pair-function method, which permits a more exact interpretation of the X-ray diffraction data.

Experimental

The sample obtained from recrystallization of analytically pure 2-methyl-2-propanol was measured at 293 ± 0.2 K in a thermostated cuvette 1 mm thick with mica windows. The intensity of the scattered beam was measured between $s_0 = 4\pi \sin \theta_0/\lambda = 0.300$ Å^{-1} and $s_m = 11.831$ Å^{-1} using Cu $K\alpha$ ($\lambda = 1.5418$ Å) and Mo $K\alpha$ ($\lambda = 0.7107$ Å) radiations. A transmission arrangement has been used with a flat-crystal mono-