Acta Cryst. (1974). B30, 568

The Structure and Absolute Configuration of the Spin-Label *R*-(+)-3-Carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy

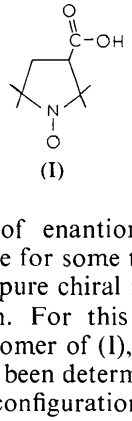
By Joseph B. Wetherington, Susan S. Ament and J. William Moncrief
Department of Chemistry, Emory University, Atlanta, Georgia 30322, *U.S.A.*

(*Received* 6 *October* 1973; *accepted* 8 *October* 1973)

The structure of the title compound, $C_9H_{16}NO_3$, has been determined by direct methods and refined to $R_1=0.054$ from three-dimensional Cu $K\alpha$ diffractometer data. The space group is $P2_12_12_1$ with $a=8.089$ (16), $b=10.097$ (10), $c=12.404$ (24) Å, $Z=4$. The absolute configuration was established by direct measurement of twenty enantiomer-sensitive Bijvoet reflection pairs. The –C(NO)C– group is essentially planar with an angle of 3·3° between the N–O bond and the plane C–N–C. The five-membered ring has an envelope conformation with a C(3) displacement of 0·57 Å. Molecules are linked translationally parallel to x by hydrogen bonds between the carboxy hydroxyl group and the oxygen of the nitroxide with an O···O distance of 2·681 Å.

Introduction

Nitroxides are paramagnetic compounds widely used in recent years for spin-label studies of biological systems (Hamilton & McConnell, 1968). 3-Carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (I) is a readily resolvable chiral nitroxide (Flohr & Kaiser, 1972) useful as a reporter group in studies of enzyme catalysis. At acid *p*H, the *p*-nitrophenyl ester of (I) forms a stable acyl-enzyme with α-chymotrypsin (Berliner & McConnell, 1971). The hydrolysis of this ester with α-chymotrypsin has been found to exhibit enantiomeric specificity, the (+)-isomer being the more active. A similar asymmetric effect has been observed in hydrolysis of the *m*-nitrophenyl ester of (I) with the model carboxylic esterase cyclohexaamylose (Flohr, Paton & Kaiser, 1971).



(I)

Spin-label studies of enantiomeric specificity in biological systems have for some time been hampered by a lack of optically pure chiral nitroxides of known absolute configuration. For this reason the crystal structure of the (+)-isomer of (I), including the absolute configuration, has been determined. A preliminary report of the absolute configuration has been published (Ament, Wetherington, Moncrief, Flohr, Mochizuki & Kaiser, 1973).

Experimental

Pale yellow crystals of (+)-(I), prepared as previously described (Flohr & Kaiser, 1972), were examined and found to be orthorhombic, space group $P2_12_12_1$, $Z=4$. A summary of physical and crystallographic data is given in Table 1.

Table 1. *Summary of physical and crystallographic data for* (+)-(I)

$C_9H_{16}NO_3$	
M.W.	186·2
m.p.	205–207°
Space group	$P2_12_12_1$
a	8·089 (16) Å
b	10·097 (10)
c	12·404 (24)
Density (obs)	1·22 g cm^{-3}
Density (calc)	1·22
Z	4
Reflections	
$F_o^2>2\sigma(I)$	995
Total	1071
R_1 (observed data)	0·054
R_1 (all measured data)	0·080

Two crystals of (+)-(I) were reduced in size by dissolution in pentyl acetate and mounted for data collection on an automated Supper–Pace diffractometer possessing Weissenberg geometry. Two axes of diffraction data (a,c) were measured with nickel-filtered Cu $K\alpha$ radiation. Following Lp corrections the data were correlated (Simpson, 1963) to give 1071 independent reflections, 995 of which were considered observed, having intensities greater than $2\sigma(I)$ (Parker, Flynn & Boer, 1968). An additional 243 high-angle reflections accessible in principle were not measured owing to physical limitations of the diffractometer.

The structure was solved by direct methods with the 100 reflections with $E>1.50$ and the program *MULTAN* (Germain, Main & Woolfson, 1971). Reflections in the starting set were 741, 419, 151, 646, 712, 249, and 080 with the first three used for origin and enantiomer specification. An E map computed from one of the several sets of phases showing high figures of merit clearly revealed the positions of the 13 non-hydrogen atoms. A structure-factor calculation based on these 13 positions resulted in $R_1=0.32$.

Refinement

Eight cycles of full-matrix least-squares refinement with individual anisotropic temperature factors with the program *ORXFLS* (Busing, Martin & Levy, 1962) reduced R_1 to 0·11. Three intense low-angle reflections (020, 002, and 022) affected by non-linearity of the proportional counter and secondary extinction were removed, thereby reducing R_1 to 0·093. A difference map revealed the positions of all 16 hydrogen atoms. Four additional cycles of full-matrix least-squares refinement of all positional and thermal parameters (individual isotropic temperature factors for hydrogens) produced a final $R_1=0{\cdot}054$ and $wR=0{\cdot}055$ where $R=\sum||F_o|-|F_c||/\sum|F_o|$ and $wR=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$. The weighting scheme $w=1/\sigma_F^2$ was employed. The atomic scattering factors used are those given in *International Tables for X-ray Crystallography* (1968).

Determination of the absolute configuration

The absolute configuration of (+)-(I) was determined by the direct measurement of Bijvoet pairs of reflections with subsequent application of empirical absorption corrections by the method of Moncrief & Sims (1969). After the final cycle of refinement, values of I_{hkl} and $I_{\overline{hkl}}$ were calculated for the S configuration with the f'' values of Cromer & Liberman (1970) for O, N, and C. Accessible reflections with a calculated $\text{IDEL}=(I_{hkl}-I_{\overline{hkl}})/I_c$ greater than 2·5% (hereafter referred to as enantiomer-sensitive reflections) were ranked ac-

Table 2. *Comparison of the signs of the observed Bijvoet differences and those calculated for the S configuration*

The consistent disagreement of the signs establishes the absolute configuration of (+)-(I) as *R*.

	Observed sign of IDEL before and after absorption correction								Average*		Calculated sign of IDEL‡
	$I_{hkl}-I_{\bar{h}kl}$		$I_{hkl}-I_{h\bar{k}l}$		$I_{\bar{h}\bar{k}l}-I_{\bar{h}kl}$		$I_{\bar{h}\bar{k}l}-I_{h\bar{k}l}$		$I_{hkl}-I_{\overline{hkl}}$		
Reflection	Before	After	Before	After	Before	After	Before	After	Before	After†	$I_{hkl}-I_{\overline{hkl}}$
1 2 1	−	−	−	−	−	−	−	−	−	−	+
9 3 2	−	−	−	−	−	−	−	−	−	−	+
8 5 3	−	−	−	−	−	−	+	+	−	−	+
6 3 1	−	−	−	−	−	−	+	−	−	−	+
2 7 3	+	+	+	+	−	+	+	+	+	+	−
2 4 2	−	−	−	+	−	−	−	−	−	−	+
6 1 5	+	−	−	−	+	+	−	−	−	−	+
5 6 7	−	−	−	−	−	−	−	−	−	−	+
4 11 1	+	+	+	−	+	+	+	+	+	+	−
9 5 2	−	−	+	−	−	+	+	+	+	+	−
5 4 3	+	+	+	+	+	+	+	+	+	+	−
7 8 3	−	+	+	−	−	−	−	−	−	−	+
8 4 7	+	+	+	+	+	+	+	+	+	+	−
6 1 9	+	+	−	−	−	−	−	−	−	−	+
7 5 8	+	−	+	+	−	+	+	+	+	+	−
9 2 4	+	+	+	+	+	+	+	+	+	+	−
8 3 1	−	−	−	−	−	−	−	−	−	−	+
6 5 3	−	+	+	+	+	+	+	+	+	+	−
6 4 1	−	−	−	−	−	−	−	−	−	−	+
5 7 8	+	+	+	+	−	+	+	+	+	+	−

* $I_{hkl}+I_{\bar{h}\bar{k}l}-I_{\bar{h}kl}-I_{h\bar{k}l}$.
† Absorption correction ratios for the average are $I_{\overline{hkl}}/I_{hkl}=(I_{\bar{h}kl}+I_{h\bar{k}l})/(I_{hkl}+I_{\bar{h}\bar{k}l})$.
‡ Calculated for the S configuration.

Table 3. *Final atomic positions and thermal parameters for the R configuration of* (+)-(I)

$T=\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\times 10^{-4}]$

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	1·3586 (2)	0·2543 (3)	0·2898 (2)	51 (3)	85 (2)	40 (2)	−3 (3)	−1 (2)	−3 (2)
C(2)	1·1961 (3)	0·2543 (3)	0·3459 (2)	57 (3)	64 (2)	43 (2)	−3 (3)	−10 (2)	−4 (2)
C(3)	1·0821 (3)	0·2861 (3)	0·2484 (3)	68 (4)	67 (3)	60 (3)	5 (2)	8 (3)	1 (2)
C(4)	1·1682 (4)	0·2216 (4)	0·1530 (3)	100 (5)	120 (4)	43 (2)	12 (3)	18 (3)	12 (2)
C(5)	1·3536 (3)	0·2442 (3)	0·1709 (2)	85 (4)	86 (3)	33 (2)	−1 (3)	−5 (2)	−2 (2)
O(6)	1·4930 (2)	0·2554 (3)	0·3431 (2)	56 (3)	170 (3)	51 (2)	−10 (3)	10 (2)	−2 (3)
C(7)	1·1695 (5)	0·1169 (3)	0·3951 (4)	107 (5)	82 (3)	74 (3)	−7 (3)	−15 (4)	−21 (3)
C(8)	1·1941 (5)	0·3604 (4)	0·4319 (3)	115 (5)	104 (4)	51 (3)	−15 (4)	−9 (3)	17 (2)
C(9)	0·9067 (3)	0·2369 (3)	0·2636 (3)	72 (4)	78 (3)	88 (3)	12 (3)	16 (3)	17 (3)
O(10)	0·8607 (3)	0·1283 (3)	0·2426 (5)	96 (4)	120 (3)	295 (7)	−21 (3)	−15 (4)	95 (4)
O(11)	0·8089 (3)	0·3236 (2)	0·3086 (2)	78 (3)	95 (2)	96 (2)	−2 (3)	−18 (2)	12 (2)
C(12)	1·4577 (5)	0·1300 (4)	0·1330 (4)	138 (6)	99 (4)	64 (4)	9 (4)	−17 (3)	7 (3)
C(13)	1·4157 (5)	0·3746 (4)	0·1235 (4)	199 (7)	99 (4)	60 (3)	9 (5)	−27 (4)	−21 (3)

Table 3 (*cont.*)

	x/a	y/b	z/c	B(Å^2)
H(3)	1·0801 (44)	0·3796 (40)	0·2420 (35)	1·5 (0·7)
H(4*A*)	1·1383 (53)	0·1308 (46)	0·1523 (37)	2·1 (0·8)
H(4*B*)	1·1413 (62)	0·2653 (48)	0·0875 (48)	3·4 (1·0)
H(7*A*)	1·1703 (47)	0·0497 (33)	0·3364 (32)	1·0 (0·6)
H(7*B*)	1·2499 (94)	0·0862 (59)	0·4353 (64)	5·7 (1·5)
H(7*C*)	1·0808 (59)	0·1161 (39)	0·4376 (41)	2·0 (0·8)
H(8*A*)	1·2889 (85)	0·3287 (51)	0·4779 (51)	4·4 (1·1)
H(8*B*)	1·0965 (60)	0·3692 (41)	0·4672 (42)	2·3 (0·8)
H(8*C*)	1·2219 (55)	0·4492 (38)	0·3997 (37)	2·2 (0·8)
H(11)	0·7139 (66)	0·2813 (41)	0·3116 (39)	2·5 (0·9)
H(12*A*)	1·4327 (57)	0·0584 (43)	0·1660 (39)	2·0 (0·8)
H(12*B*)	1·4290 (64)	0·1269 (46)	0·0572 (56)	3·4 (1·0)
H(12*C*)	1·5854 (64)	0·1587 (46)	0·1386 (46)	3·4 (1·0)
H(13*A*)	1·4075 (46)	0·3620 (35)	0·0381 (41)	1·7 (0·7)
H(13*B*)	1·5556 (69)	0·3977 (48)	0·1523 (48)	3·7 (1·0)
H(13*C*)	1·3550 (59)	0·4465 (42)	0·1430 (38)	2·5 (0·9)

cording to a suitability parameter $\mathscr{P}=I_c\times\mathrm{IDEL}^2$. Reflections with an l index greater than 10 were rejected because of the difficulty with crystal alignment at high values of μ. A list of absorption-correction reflections having I_c greater than 1·0, IDEL less than 1·0% and located within a range $\Delta\mu=0{\cdot}0°$, $\Delta\varphi=\pm15°$, $\Delta\gamma=\pm15°$ was compiled for each of the enantiomer-sensitive reflections. From the set of enantiomer-sensitive reflections having at least one absorption-correction reflection, the twenty reflections with the greatest values of $\mathscr{P}$ were selected for measurement of Bijvoet pairs.

A crystal mounted on the c axis was used for the intensity measurements. For each of the enantiomer-sensitive reflections values of I_{hkl}, $I_{\bar{h}kl}$, $I_{h\bar{k}l}$, and $I_{\bar{h}\bar{k}l}$ were manually measured four times and the replicates aver-

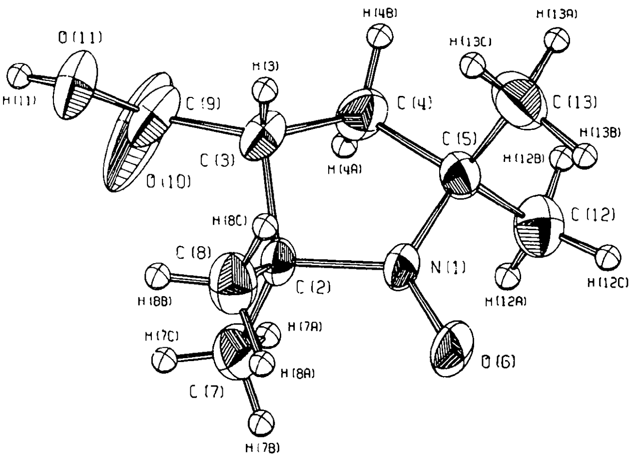


Fig. 1. An *ORTEP* II (Johnson, 1970) drawing of the *R* configuration of (+)-(I) with thermal ellipsoids representing 50% probability.

Table 4. *Observed and calculated structure factors and phases* (°) *for* (+)-(I)

An asterisk (*) indicates an unobserved reflection.

H	K	L	|FO|	|FC|	φ
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

aged. For the absorption-correction reflections the ratios $I_{\bar{h}kl}/I_{hkl}$, $I_{h\bar{k}l}/I_{hkl}$, $I_{\bar{h}kl}/I_{h\bar{k}\bar{l}}$ and $I_{h\bar{k}l}/I_{\bar{h}\bar{k}l}$ were computed and applied as absorption-correction factors to the appropriate member of the enantiomer-sensitive Bijvoet pairs. Table 2 is a comparison of the signs of the observed differences before and after absorption corrections with those calculated for the *S* configuration. The consistent disagreement between the observed signs and those calculated for the *S* configuration establishes the absolute configuration of (+)-(I) as *R*.

Engel (1972) has determined the absolute configuration of seven compounds containing only C, H and O in order to compare the principal methods currently used for light-atom structures. His findings indicate that methods involving the direct measurement of enantiomer-sensitive Bijvoet pairs are superior to methods based solely on the comparison of weighted *R* values calculated from enantiomer-sensitive reflections representing single members of the Bijvoet pairs.

Final values of the atomic positional and thermal parameters for the *R* configuration of (+)-(I) are given in Table 3. Observed and calculated structure factors and computed phases appear in Table 4.

Discussion

Fig. 1 is an *ORTEP* II (Johnson, 1970) drawing of the *R* configuration of (+)-(I). Interatomic distances and angles and their estimated standard errors [*ORFFE*, (Busing, Martin & Levy, 1964)] are given in Tables 5 and 6. The N(1)–O(6) bond distance and the angles C(2)–N(1)–C(5), C(2)–N(1)–O(6) and C(5)–N(1)–O(6) are in close agreement with the values observed in the two pyrrolinyl nitroxides (II) and (III) (Boeyens & Kruger, 1970; Turley & Boer, 1972). The –C(NO)C– group is nearly planar, with the N–O bond making an angle of 3·3° with the plane C(2), N(1), C(5). Planarity of the –C(NO)C– group was also observed in (II) and (III) but in the structures of four piperdinyl nitroxides (Berliner, 1970; Capiomont, Chion & Lajzérowicz, 1971; Capiomont, 1972, 1973) angles of 15·8, 30·5, 18·2, and 24·9° were observed between the N–O bond and the C–N–C plane. The five-membered ring exists in the envelope conformation with a C(3) displacement of 0·57 Å from the best least-squares plane N(1), C(2), C(4), C(5). The angle between normals to the

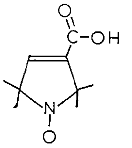
Table 5. *Interatomic distances and estimated standard errors for* (+)-(I)

N(1)–C(2)	1·487 (3) Å	C(7)—H(7*A*)	0·996 (38) Å
N(1)–C(5)	1·479 (4)	C(7)—H(7*B*)	0·876 (79)
N(1)–O(6)	1·272 (3)	C(7)—H(7*C*)	0·890 (51)
C(2)–C(3)	1·554 (4)	C(8)—H(8*A*)	1·007 (67)
C(2)–C(7)	1·531 (4)	C(8)—H(8*B*)	0·907 (50)
C(2)–C(8)	1·512 (4)	C(8)—H(8*C*)	1·007 (41)
C(3)–C(4)	1·520 (5)	O(11)–H(11)	0·880 (53)
C(3)–C(9)	1·515 (4)	C(12)–H(12*A*)	0·855 (47)
C(4)–C(5)	1·533 (4)	C(12)–H(12*B*)	0·969 (68)
C(5)–C(12)	1·504 (5)	C(12)–H(12*C*)	1·075 (51)
C(5)–C(13)	1·527 (5)	C(13)–H(13*A*)	1·069 (50)
C(9)–O(10)	1·187 (4)	C(13)–H(13*B*)	1·209 (56)
C(9)–O(11)	1·305 (4)	C(13)–H(13*C*)	0·909 (45)
C(3)–H(3)	0·947 (40)		
C(4)–H(4*A*)	0·949 (46)	O(11)···O(6)′	2·681 (3)
C(4)–H(4*B*)	0·950 (59)	H(11)···O(6)′	1·848 (54)

Table 6. *Interatomic angles and estimated standard errors for* (+)-(I)

C(2)—N(1)–C(5)	116·2 (2)°	C(2)—C(7)—H(7*A*)	109·0 (1·4)°
C(2)—N(1)–O(6)	120·8 (2)	C(2)—C(7)—H(7*B*)	116·3 (4·1)
C(5)—N(1)–O(6)	122·8 (2)	C(2)—C(7)—H(7*C*)	111·0 (2·6)
N(1)—C(2)–C(3)	99·3 (2)	H(7*A*)—C(7)—H(7*B*)	99·8 (4·7)
N(1)—C(2)–C(7)	108·1 (2)	H(7*A*)—C(7)—H(7*C*)	115·5 (3·5)
N(1)—C(2)–C(8)	109·8 (2)	H(7*B*)—C(7)—H(7*C*)	104·9 (5·4)
C(3)—C(2)–C(7)	114·5 (3)	C(2)—C(8)—H(8*A*)	99·6 (3·1)
C(3)—C(2)–C(8)	113·4 (3)	C(2)—C(8)—H(8*B*)	114·7 (2·9)
C(7)—C(2)–C(8)	111·0 (3)	C(2)—C(8)—H(8*C*)	110·4 (2·5)
C(2)—C(3)–C(4)	104·2 (2)	H(8*A*)—C(8)—H(8*B*)	114·8 (4·6)
C(2)—C(3)–C(9)	113·0 (3)	H(8*A*)—C(8)—H(8*C*)	109·8 (4·2)
C(4)—C(3)–C(9)	112·7 (3)	H(8*B*)—C(8)—H(8*C*)	107·3 (3·6)
C(3)—C(4)–C(5)	105·8 (2)	C(9)—O(11)–H(11)	102·8 (2·8)
N(1)—C(5)–C(4)	100·4 (2)	C(5)—C(12)–H(12*A*)	111·4 (3·0)
N(1)—C(5)–C(12)	110·5 (3)	C(5)—C(12)–H(12*B*)	101·1 (3·0)
N(1)—C(5)–C(13)	108·4 (3)	C(5)—C(12)–H(12*C*)	108·1 (2·5)
C(4)—C(5)–C(12)	112·9 (3)	H(12*A*)–C(12)–H(12*B*)	112·4 (4·4)
C(4)—C(5)–C(13)	113·2 (3)	H(12*A*)–C(12)–H(12*C*)	115·2 (4·5)
C(3)—C(9)–O(10)	124·7 (3)	H(12*B*)–C(12)–H(12*C*)	107·6 (4·3)
C(3)—C(9)–O(11)	113·6 (3)	C(5)—C(13)–H(13*A*)	105·0 (1·9)
C(10)–C(9)–O(11)	121·6 (3)	C(5)—C(13)–H(13*B*)	111·1 (2·5)
		C(5)—C(13)–H(13*C*)	114·1 (2·8)
C(2)—C(3)–H(3)	106·3 (2·4)	H(13*A*)–C(13)–H(13*B*)	112·0 (3·5)
C(4)—C(3)–H(3)	111·7 (2·5)	H(13*A*)–C(13)–H(13*C*)	108·9 (3·6)
C(9)—C(3)–H(3)	108·7 (2·2)	H(13*B*)–C(13)–H(13*C*)	105·9 (3·7)
C(3)—C(4)–H(4*A*)	107·7 (2·7)		
C(5)—C(4)–H(4*A*)	113·2 (2·6)	N(1)—O(6)····O(11)′	137·2 (2)
C(3)—C(4)–H(4*B*)	111·2 (3·0)	N(1)—O(6)····H(11)′	135·9 (1·5)
C(5)—C(4)–H(4*B*)	106·2 (3·0)	C(9)—O(11)···O(6)′	118·2 (2)
H(4*A*)–C(4)–H(4*B*)	112·5 (4·0)	O(11)–H(11)···O(6)′	157·3 (3·9)

plane of the carboxy group C(3), C(9) O(10), O(11), and the plane N(1), C(2), C(4), C(5), O(6) is 114·7°. The equations of and the atomic displacements from several calculated least squares planes are given in Table 7.


(II)

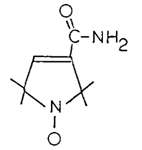

(III)

Fig. 2 is a stereoscopic drawing (Johnson, 1970) of the contents of the unit cell illustrating the molecular packing and hydrogen bonding. Molecules of (+)-(I) are linked translationally parallel to x by hydrogen bonds between the oxygen of the *N*-oxide and the carboxy hydroxyl group with an O(11)···O(6) distance of 2·681 Å. Distances and angles involving the hydrogen bond are included in Tables 5 and 6. The e.s.r. spectrum of a 10^{-4} *M* aqueous solution of (+)-(I) consists of the three lines expected for a monomeric nitroxide species, indicating that no such intermolecular hydrogen bonds occur in dilute aqueous solution (Kaiser, 1973).

The support of this research by a grant from the National Science Foundation, an Alfred P. Sloan Foundation Fellowship (JWM), a NDEA Fellowship (JBW) and the assistance of the Emory University Computer Center and Professor E. T. Kaiser are gratefully acknowledged.

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Table 7. *Equations of calculated least-squares planes and atomic displacements for* (+)-(I)

Equations of least squares planes (Cartesian coordinates)

(*a*) $0{\cdot}0360X-0{\cdot}9970Y+0{\cdot}0679Z=-1{\cdot}921$
(*b*) $0{\cdot}0058X-0{\cdot}9987Y+0{\cdot}0501Z=-2{\cdot}300$
(*c*) $0{\cdot}0449X-0{\cdot}9949Y+0{\cdot}0907Z=-1{\cdot}706$
(*d*) $0{\cdot}0051X-0{\cdot}9987Y+0{\cdot}0498Z=-2{\cdot}301$
(*e*) $0{\cdot}2521X-0{\cdot}3253Y+0{\cdot}9114Z=4{\cdot}070$
(*f*) $0{\cdot}1007X-0{\cdot}9888Y+0{\cdot}1104Z=-1{\cdot}070$

Atomic deviations from least-squares planes (Å)

	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)
N(1)	0·000*	0·021*	0·035*	0·028		−0·034*
C(2)	0·000*	−0·006*	0·030*	0·000*		0·021*
C(3)	0·435	0·380	0·500	0·386	−0·005*	0·565
C(4)	−0·159	−0·215	−0·071*	−0·210		−0·019*
C(5)	0·000*	−0·007*	0·069*	0·000*		0·032*
O(6)	−0·074	−0·008*	−0·063*	0·000*		−0·206
C(9)					0·019*	
O(10)					−0·007*	
O(11)					−0·006*	

* Atoms defining least-squares planes.

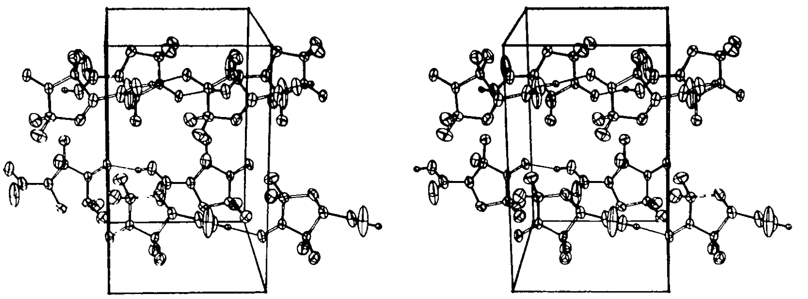

Fig. 2. A stereoscopic drawing (Johnson, 1970) of the contents of the unit cell of (+)-(I). Hydrogen bonds are drawn with thinner, solid lines. The horizontal axis is *a* and the vertical axis is *c*.

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Structure and Packing Arrangement of Molecular Compounds. V.* Constrained Refinement of a Disordered (1:1) Tetracyanoethylene–Naphthalene Structure†

By Uri Shmueli‡ and Israel Goldberg

Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

(*Received* 30 *July* 1973; *accepted* 20 *September* 1973)

The previously made suggestion that the apparent thermal motion of naphthalene in the (1:1) naphthalene–tetracyanoethylene complex conceals orientational disorder has been confirmed by a constrained refinement based on the published data. It appears that the disorder in the above structure, at room temperature, is due mainly to usual van der Waals interactions.

Introduction

A well known feature of molecular complexes is the fact that the environments of the constituent molecules are in general dissimilar. It follows, in the case of π-molecular compounds, that the forces experienced by the donor and by the acceptor may be rather different and hence a different pattern of thermal motion of such molecules is hardly surprising. However, the disparity of the thermal parameters of naphthalene and tetracyanoethylene in their 1:1 complex (Williams & Wallwork, 1967; hereafter referred to as WW) required further investigation as it is unusually large (Fig. 1). Thus, WW suggested in the original paper that a small contribution of disordered orientations may explain the observed peaks in their difference map of naphthalene. The in-plane libration, however, was considered to be genuine. Herbstein & Snyman (1969) studied this problem with the aid of electron density and difference density maps as well as by examining the thermal parameters of the naphthalene carbon atoms. They concluded that a minor orientational disorder is in fact present in this complex and that the published structure of naphthalene (WW) corresponds to a superposition of two orientations in which the molecules are rotated in a plane by $\pm 7{\cdot}5^\circ$ away from the published orientation. We have arrived at a qualitatively similar conclusion (Shmueli & Goldberg, 1973) which differs from that of Herbstein & Snyman (1969) in the angular deviation from the published orientation. The results of our approach, illustrated in Fig. 2, are based on evaluating a potential curve corresponding to the motion of naphthalene about a direction associated with the suspiciously large libration amplitude. The method is easy to apply but like other approaches it may only generate a hypothesis that still needs to be tested.

As far as we know, cases of minor orientational disorder were, so far, not confronted directly with observed structure amplitudes, although the constrained refinement that makes such a confrontation possible was long since recognized (Pawley, 1963) as an appropriate method in cases of disorder.

Following the results obtained in our study of disorder *via* potential calculations we decided to investigate this problem with the aid of constrained refinement techniques and thereby to assess the applicability of these methods to cases of apparently false thermal motion. In this communication we report our results on the π-molecular compound (1:1) tetracyanoethylene (TCNE)–naphthalene. Apart from naphthalene, the TCNE molecule in this complex was also of interest

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* Part IV: *Acta Cryst.* B**29**, 2466–2471.

† A preliminary report on this work was presented at the annual meeting of the Israel Crystallography Society in Tel-Aviv on May 31, 1973.

‡ On leave at the Department of Structural Chemistry, University of Groningen, Zemikelaan, Paddepoel, Groningen, The Netherlands.