

Fig. 2. A stereoview showing the intertwining of the major and minor tetramers in Ph_3COH . The view is such that the orientation of the major isomer is the same as in Fig. 1. For clarity, the atoms of the minor tetramer are shown as spheres of arbitrary size.

of the structural coordinates with *PLATON* (Spek, 1991) shows that there are no voids in the lattice which could have contained solvent.

This analysis completes the series for the group 14 Ph_3MOH molecules ($M = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$). Ph_3SiOH (Puff, Braun & Reuter, 1991) is isomorphous with Ph_3GeOH (Puff *et al.*, 1991; Ferguson, Gallagher, Murphy, Spalding, Glidewell & Holden, 1992) and the structures consist of hydrogen-bonded tetramers with the O atoms in a flattened tetrahedral arrangement. Both Ph_3SnOH and Ph_3PbOH have structures consisting of zigzag chains of planar Ph_3M ($M = \text{Sn}, \text{Pb}$) groups joined by OH groups giving trigonal bipyramidal geometry at M (Glidewell & Liles, 1978). The molecular volumes (U/Z) for

Ph_3MOH show an increase from $M = \text{C}$ to Pb with C 360, Si 381, Ge 385, Sn 389 and Pb 394 \AA^3 . The unique nature of the pyramidal hydrogen-bonded tetramer in Ph_3COH probably accounts for its relatively low molecular volume compared with the other molecules of the series.

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trans-5-(*n*-Heptyl)-4-(1-iodovinyl)-2-oxazolidinone and *syn*-[4-Cyclohexyl-2-iodo-3-(*N*-tosylamino)-1-buten-4-yl] Acetate

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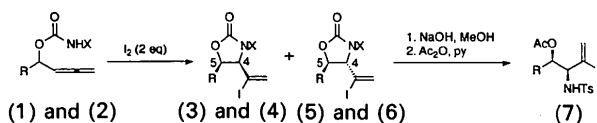
Abstract. *trans*-5-(*n*-Heptyl)-4-(1-iodovinyl)-2-oxazolidinone, (6), $\text{C}_{12}\text{H}_{20}\text{INO}_2$, $M_r = 337.2$, monoclinic, $P2_1/a$, $a = 13.820$ (2), $b = 6.205$ (1), $c = 17.550$ (3) \AA , $\beta = 106.06$ (1) $^\circ$, $V = 1446.2$ (4) \AA^3 , $Z = 4$, $D_x = 1.55$ g cm^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71073$ \AA , $\mu = 21.8$ cm^{-1} , $F(000) = 672$, room temperature, $R = 0.037$ for 2679 observed reflections. *syn*-[4-Cyclohexyl-2-iodo-3-(*N*-tosylamino)-1-buten-4-yl]

acetate, (7), $\text{C}_{19}\text{H}_{26}\text{INO}_4\text{S}$, $M_r = 491.4$, monoclinic, $P2_1/a$, $a = 12.233$ (3), $b = 13.733$ (3), $c = 14.169$ (6) \AA , $\beta = 112.75$ (3) $^\circ$, $V = 2213.1$ \AA^3 , $Z = 4$, $D_x = 1.49$ g cm^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71073$ \AA , $\mu = 15.5$ cm^{-1} , $F(000) = 992$, room temperature, $R = 0.047$ for 1311 observed reflections. The tentative assignments of the relative stereochemistries of compounds (6) and (7) were confirmed by the structure determinations. Molecules of (6) form hydrogen-bonded chains [$\text{N}(\text{—H})\cdots\text{O}$ 2.975 (4) \AA] while in (7) pairs of molecules form hydrogen-bonded centro-

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symmetric dimers [N(—H)···O 2.989 (10) Å]. In (7) the vinyl iodide group is disordered over two sites.

Introduction. The reactions of allylic alcohol derivatives with electrophiles have received much attention recently, both from the synthetic and mechanistic point of view (Chamberlain, Mulholland, Kahn & Hehre, 1987). In connection with a project exploring the reactions of the analogous α -allenic alcohol derivatives, we have prepared several *N*-tosyl-*O*-carbamate and *N*-trichloroacetyl-*O*-carbamate derivatives and have studied their reactions with iodine (Friesen, 1990; Friesen & Kolaczewska, 1991). In all cases that were examined using the *N*-tosyl carbamates, cyclization proceeded to provide two diastereomeric cyclic carbamates (30:1) as illustrated by the conversion of (1) to (3) and (5) (see the scheme below). Similarly, the iodocyclizations of the



- (1), (3) and (5) X = Ts, R = cyclohexyl; (2) X = COCCl₃;
 (4) and (6) X = H; (2), (4) and (6) R = *n*-heptyl;
 (7) R = cyclohexyl.

N-trichloroacetyl derivatives (2) were highly stereoselective and provided, in ratios of >98: <2, the deacetylated 2-oxazolidinones (4) and (6). It was imperative that we be able to establish the relative stereochemistry at the two asymmetric C atoms (C4 and C5) in order to make definitive structural assignments and to make a rational argument regarding the reaction mechanism. On the basis of ¹H NMR data, the major isomers were tentatively assigned as the *trans* diastereomers (5) and (6) [*J*_{4,5} = 6.6 and 7.8 Hz for (3) and (4), respectively; *J*_{4,5} = 2.7 and 4.5 Hz for (5) and (6), respectively] (Cardillo, Orena & Sandri, 1986). However, owing to the highly substituted nature of the five-membered rings, there was a certain amount of doubt as to the validity of these assignments. Thus, the 2-oxazolidinone (5) was converted into the acyclic acetate (7) since (3) and (5) were inseparable by chromatography column (Friesen, 1990). The structures of (6) and (7) were determined by X-ray crystallographic methods.

Experimental. Compound (6): Crystals (m.p. 333–334 K) from hexane/ethyl acetate/ether. Accurate cell dimensions and crystal-orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range 17 < θ < 20°. Crystal dimensions 0.20 × 0.15 × 0.15 mm; intensities of reflections with

indices $h = 17$ to 16, $k = 0$ to 10, $l = 0$ to 20, with $2 < 2\theta < 50^\circ$ measured, ω - 2θ scans, ω -scan width (0.6 + 0.35tan θ)°; graphite-monochromated Mo *K* α radiation; intensities of three reflections (35 $\bar{1}$, 121 and 12 $\bar{3}$) measured every 2 h showed no evidence of crystal decay. 3548 reflections measured, 3146 with non-zero F_o and unique ($R_{\text{int}} = 0.015$), and 2679 with $I > 3\sigma(I)$ labelled observed and used in the structure solution and refinement. Data corrected for Lorentz and polarization effects. Empirical absorption correction (Walker, 1983), maximum and minimum corrections 1.324 and 0.605. No correction for extinction. Space group $P2_1/a$ was determined uniquely by systematic absences ($h0l$ absent if $h = 2n + 1$; $0k0$ absent if $k = 2n + 1$). The position of the heavy atom (I) was solved from a Patterson map and other non-H atoms were located from subsequent Fourier and difference Fourier maps. Refinement was by full-matrix least-squares calculations to minimize $\sum w(F_o - F_c)^2$, initially with isotropic and then with anisotropic thermal parameters for non-H atoms. The H atom bonded to N was located from a difference map and refined with an isotropic thermal parameter. Other H atoms were positioned on geometric grounds (C—H 0.95 Å) and included (as riding atoms) in the structure factor calculation. H atoms were assigned a common isotropic thermal parameter which refined to a value U_{iso} of 0.1233 (8) Å². Final cycle of least-squares refinement included 150 parameters, $R = 0.0374$, $wR = 0.0493$, goodness of fit 1.607, $w = 1/[\sigma^2(F_o) + 0.00139(F_o)^2]$. Maximum shift/e.s.d. in final refinement cycle 0.05; the ten largest density peaks in final difference map were in the vicinity of the I atom and in the range 0.77–0.30 e Å⁻³; there were no chemically significant features.

Compound (7): Diffractometer measurements and structure determination as for compound (6) except: crystals (m.p. 423–424 K) obtained from benzene. θ for cell refinement 11–15°. Crystal dimensions 0.20 × 0.16 × 0.05 mm; index range $h = 0$ to 14, $k = 0$ to 16, $l = -16$ to 15; indices of standard reflections were $\bar{1}0, 0, 12, 528$ and 446. 4230 reflections measured, 3675 unique ($R_{\text{int}} = 0.022$) and 1311 with $I > 3\sigma(I)$ labelled observed. Numerical absorption correction, maximum and minimum transmission coefficients 0.910 and 0.639. When all the non-H atoms (corresponding to the molecular formula) had been located, a calculated difference map showed a density peak (~ 6.0 e Å⁻³) in the vicinity of the —C(CH₂)I group. The presence of this peak and an unusually high thermal parameter ($U_{\text{iso}} = 0.12$ Å²) associated with the full occupancy I atom suggested that the I atom could be disordered over two sites. The peak was included in the refinement as a partial occupancy (25%) I atom (I*) and the occupancies of I and I* were tied to give a combined value of 1.00; final values 0.775 (2) and 0.225 (2). All non-H atoms were

refined with anisotropic thermal parameters (except for the C atom of the CH₂ group which was refined with an isotropic thermal parameter). The H atoms were positioned on geometric grounds (C—H, N—H 0.95 Å) and included (as riding atoms) in the structure factor calculation. A difference map showed a torus of electron density in the locations expected for methyl H atoms. The methyl H atoms for each group were included as six 0.5 occupancy atoms and refined as two staggered rigid bodies. U_{iso} for H atoms 0.100 (8) Å². Final cycle of least-squares refinement included 283 parameters, $R = 0.047$, $wR = 0.046$, goodness of fit 1.990, $w = 1/[\sigma^2(F_o) + 0.00028(F_o)^2]$. Maximum shift/e.s.d. in final refinement cycle 0.12; density in final difference map in the range -0.37 – 0.32 e Å⁻³; there were no chemically significant features. Atomic scattering factors and anomalous scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were carried out on a PDP 11/23 computer using *SDP* (Frenz, 1982), a MicroVAX II using *NRCVAX* (Larson, Lee, Le Page, Webster, Charland & Gabe, 1990) and an Apollo computer using *SHELX76* and *SHELXS86* (Sheldrick, 1976, 1986). Atomic coordinates* are given in Table 1.

Discussion. Bond lengths and angles for compounds (6) and (7) are listed in Table 2. Figs. 1 and 2 are views of the molecules prepared using *ORTEPII* (Johnson, 1976).

The X-ray structure of compound (6) (Fig. 1) demonstrates that the substituents at C atoms C4 and C5 and have a *trans* arrangement with respect to one another. The analysis of compound (7) reveals that the O and N moieties (O3 and N) have a *syn* relationship (Fig. 2), indicating that this material originated from the *trans* cyclic carbamate (5). In (6), molecules are linked by hydrogen bonds [N3...O6 ($-0.5 - x$, $0.5 + y$, $1 - x$), 2.975 (4) Å] through 2₁ screw axes, to form infinite chains. In (7), pairs of molecules are connected by hydrogen bonds [N...O2 ($-x$, $1 - y$, $-z$), 2.989 (10) Å] to form centrosymmetric dimers.

In (6), the geometry of the substituted oxazolidinone ring is similar to that in molecules of unsubstituted 2-oxazolidinone (which are also connected by intermolecular hydrogen bonds) (Turley, 1972). Two other compounds which contain the oxazolidinone moiety (Durant, Lefevre, Evrard & Michel, 1982; Durant, Lefevre, Norberg & Evrard,

* Lists of structure factors, anisotropic thermal parameters, calculated H-atom coordinates, mean-planes data, and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54903 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD0061]

Table 1. *Positional and thermal parameters (Å²) with e.s.d.'s in parentheses*

Equivalent isotropic thermal parameters for all non-H atoms, except for the C atom C(1) of the CH₂ group in compound (7) which was refined with an isotropic thermal parameter; $U_{eq} = (U_{11} + U_{22} + U_{33})/3$. I and I* in compound (7) are disorder sites with occupancies of 0.775 and 0.225 respectively.

	x	y	z	U_{eq}/U_{iso}
Compound (6)				
I	0.08644 (2)	0.10489 (4)	0.61369 (2)	0.05653 (17)
O1	-0.16399 (23)	-0.0467 (4)	0.69280 (15)	0.0616 (7)
C2	-0.20227 (26)	-0.0688 (5)	0.61277 (20)	0.0472 (7)
N3	-0.17301 (23)	0.0922 (4)	0.57671 (18)	0.0464 (7)
HN	-0.2082 (8)	0.1141 (8)	0.5386 (8)	0.0173 (8)
C4	-0.12002 (24)	0.2595 (5)	0.62894 (20)	0.0453 (7)
C5	-0.10363 (27)	0.1500 (5)	0.71040 (21)	0.0501 (7)
O6	-0.25279 (22)	-0.2249 (5)	0.58576 (17)	0.0643 (7)
C7	-0.02607 (14)	0.33616 (20)	0.61070 (23)	0.0522 (7)
C8	-0.01098 (13)	0.53641 (29)	0.5917 (3)	0.0864 (8)
C9	-0.1340 (3)	0.2844 (6)	0.77102 (22)	0.0636 (8)
C10	-0.1000 (3)	0.1908 (7)	0.85341 (25)	0.0765 (8)
C11	-0.1392 (4)	0.3132 (7)	0.91339 (26)	0.0888 (8)
C12	-0.1026 (4)	0.2316 (7)	0.99677 (27)	0.0908 (8)
C13	-0.1451 (5)	0.3495 (7)	1.0564 (3)	0.1068 (8)
C14	-0.1067 (5)	0.2556 (7)	1.1397 (3)	0.1164 (8)
C15	-0.1477 (6)	0.3683 (7)	1.1993 (4)	0.1621 (8)
Compound (7)				
I	0.23372 (11)	0.20237 (7)	0.33993 (9)	0.1111 (9)
S	0.16675 (23)	0.41379 (17)	0.02767 (20)	0.0557 (17)
O1	0.2919 (5)	0.3988 (4)	0.0611 (4)	0.065 (4)
O2	0.1110 (5)	0.4900 (4)	-0.0448 (4)	0.063 (4)
O3	0.0919 (7)	0.4977 (5)	0.2896 (5)	0.076 (5)
O4	0.1034 (11)	0.4499 (8)	0.4394 (9)	0.181 (11)
N	0.1392 (6)	0.4384 (4)	0.1273 (5)	0.053 (5)
C1	0.0221 (14)	0.2794 (15)	0.1890 (14)	0.074 (8)
C2	0.1343 (14)	0.2976 (8)	0.2368 (8)	0.107 (10)
C3	0.2008 (8)	0.3928 (6)	0.2255 (7)	0.062 (7)
C4	0.2106 (9)	0.4672 (7)	0.3101 (7)	0.064 (7)
C5	0.2842 (10)	0.5582 (8)	0.3132 (8)	0.075 (8)
C6	0.2737 (11)	0.6334 (8)	0.3857 (9)	0.117 (11)
C7	0.3495 (15)	0.7222 (9)	0.3947 (11)	0.144 (14)
C8	0.4766 (15)	0.6944 (12)	0.4275 (11)	0.145 (15)
C9	0.4901 (13)	0.6216 (12)	0.3565 (13)	0.158 (16)
C10	0.4117 (11)	0.5323 (9)	0.3416 (9)	0.114 (11)
C11	0.0403 (13)	0.4864 (11)	0.3582 (14)	0.119 (14)
C12	-0.0692 (12)	0.5212 (9)	0.3270 (11)	0.156 (14)
C21	0.0955 (8)	0.3040 (6)	-0.0250 (6)	0.051 (6)
C22	-0.025 (9)	0.3020 (7)	-0.0740 (8)	0.073 (8)
C23	-0.0815 (8)	0.2150 (8)	-0.1112 (7)	0.075 (8)
C24	-0.0199 (11)	0.1305 (7)	-0.1013 (8)	0.075 (8)
C25	0.1022 (11)	0.1338 (7)	-0.0553 (9)	0.094 (9)
C26	0.1587 (9)	0.2204 (7)	-0.0146 (7)	0.070 (7)
C27	-0.0786 (9)	0.0383 (7)	-0.1433 (9)	0.128 (11)
I*	0.0167 (4)	0.2593 (4)	0.2257 (5)	0.103 (4)

1982), but in which molecules are not hydrogen bonded, also have ring geometries close to that of (6). In (6), the sum of the three angles at N3 is 348.4 (5)° indicating that the geometry at the N centre is not exactly planar. The atoms O1–C2–N3–C5 form a plane [maximum deviation 0.001 (4) Å for C2] with C4 0.158 (3) Å, and HN 0.30 (1) Å from the plane. The *n*-heptyl substituent has a fully extended conformation with torsion angles in the chain close to 180°.

In compound (7) possible intramolecular nonbonded interactions between O4 and H4 [2.51 (1) Å] and O1 and H3 [2.32 (1) Å] are worthy of note. In (7), the C2—I bond length is 1.987 (12) Å and the angle C3—C2—I is 115.2 (9)°. The equivalent values in (6) are 2.106 (2) Å and 118.76 (18)° and in the compound bromo(4-iodo-1,2,3,4-tetraphenyl-1,3-butadienyl)diphenyltin(IV) (Muchmore & Heeg, 1990) values of 2.136 (4) Å and 120.1 (3)° have been

Table 2. *Interatomic distances (Å) and angles (°) with e.s.d.'s in parentheses*

Compound (6)			
I—C7	2.1058 (19)	C7—C8	1.318 (3)
O1—C2	1.364 (4)	C9—C10	1.508 (6)
O1—C5	1.462 (4)	C10—C11	1.514 (6)
C2—N3	1.305 (4)	C11—C12	1.498 (6)
C2—O6	1.211 (4)	C12—C13	1.521 (7)
N3—HN	0.722 (13)	C13—C14	1.525 (7)
N3—C4	1.443 (4)	C14—C15	1.494 (9)
C4—C5	1.542 (5)	N3...O6 ⁱ	2.975 (4)
C4—C7	1.498 (4)	HN...O6 ⁱ	2.324 (12)
C5—C9	1.500 (5)		
C4—C7—I	117.12 (14)	C7—C4—N3	114.21 (28)
C8—C7—I	118.76 (18)	C7—C4—C5	115.11 (29)
C5—O1—C2	109.74 (26)	C9—C5—C4	114.46 (27)
N3—C2—O1	109.77 (29)	C8—C7—C4	124.10 (21)
O6—C2—O1	120.1 (3)	C10—C9—C5	113.1 (3)
C4—C5—O1	104.07 (26)	C11—C10—C9	113.4 (4)
C9—C5—O1	111.0 (3)	C12—C11—C10	114.9 (4)
O6—C2—N3	130.1 (3)	C13—C12—C11	114.8 (4)
HN—N3—C2	111.9 (7)	C14—C13—C12	112.2 (4)
C4—N3—C2	114.42 (29)	C15—C14—C13	113.2 (5)
C4—N3—HN	123.1 (5)	O6 ⁱ ...HN—N3	150.7 (10)
C5—C4—N3	100.97 (25)		
Compound (7)			
I—C2	1.987 (12)	C5—C10	1.495 (19)
S—O1	1.432 (7)	C6—C7	1.507 (20)
S—O2	1.440 (6)	C7—C8	1.489 (26)
S—N	1.609 (8)	C8—C9	1.473 (23)
S—C21	1.757 (9)	C9—C10	1.521 (21)
O3—C4	1.428 (15)	C11—C12	1.326 (23)
O3—C11	1.357 (20)	C21—C22	1.371 (15)
O4—C11	1.218 (21)	C21—C26	1.360 (14)
N—C3	1.444 (11)	C22—C23	1.376 (15)
C1—C2	1.299 (24)	C23—C24	1.361 (16)
C2—C3	1.581 (16)	C24—C25	1.380 (20)
C2—I*	1.483 (18)	C24—C27	1.464 (14)
C3—C4	1.544 (13)	C25—C26	1.385 (15)
C4—C5	1.532 (15)	N...O2 ⁱⁱ	2.989 (10)
C5—C6	1.497 (16)	HN...O2 ⁱⁱ	2.18
C1—C2—I	118.6 (12)	I*—C2—C3	143.0 (10)
C3—C2—I	115.2 (9)	C4—C3—C2	110.9 (9)
O2—S—O1	119.5 (4)	C5—C4—C3	115.4 (9)
N—S—O1	107.4 (4)	C6—C5—C4	112.1 (10)
C21—S—O1	108.0 (4)	C10—C5—C4	110.7 (9)
N—S—O2	105.7 (4)	C10—C5—C6	109.7 (10)
C21—S—O2	107.5 (4)	C7—C6—C5	113.7 (12)
C21—S—N	108.4 (4)	C9—C10—C5	112.4 (11)
C3—N—S	123.1 (6)	C8—C7—C6	110.7 (12)
C22—C21—S	119.6 (7)	C9—C8—C7	109.9 (13)
C26—C21—S	120.7 (8)	C10—C9—C8	114.3 (14)
C11—O3—C4	122.6 (10)	C26—C21—C22	119.7 (9)
C3—C4—O3	105.6 (8)	C23—C22—C21	119.4 (9)
C5—C4—O3	107.9 (8)	C25—C26—C21	120.6 (10)
O4—C11—O3	115.0 (15)	C24—C23—C22	121.8 (11)
C12—C11—O3	114.1 (14)	C25—C24—C23	118.4 (10)
C12—C11—O4	130.8 (17)	C27—C24—C23	122.9 (12)
C2—C3—N	111.0 (8)	C27—C24—C25	119.5 (10)
C4—C3—N	108.4 (7)	C26—C25—C24	120.0 (10)
C3—C2—C1	126.1 (12)	N—HN—O2 ⁱⁱ	142

Symmetry code: (i) $-0.5 - x, 0.5 + y, 1 - z$; (ii) $-x, 1 - y, -z$.

recorded in this type of group. In (7), the I atom is disordered over two sites. The components of disorder could be the result of two different orientations of the vinyl iodide group which have arisen from rotation about the C2—C3 bond. In this case C1 will also be disordered, but only one site (defining the major component, 78%) for the —CH₂ group was determined. One would expect that the position of I* (as its population amounts to approximately 12 electrons) could be determined quite accurately, but the geometry in compound (7) of the minor component of disorder (C2—I* 1.483 (18) Å and C3—C2—I*

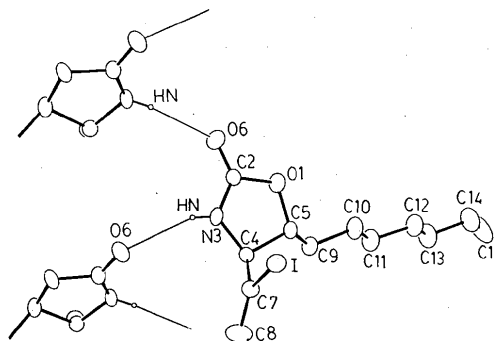


Fig. 1. View of compound (6) indicating atomic labelling scheme and hydrogen-bonded atoms. Thermal ellipsoids are drawn at the 25% probability level.

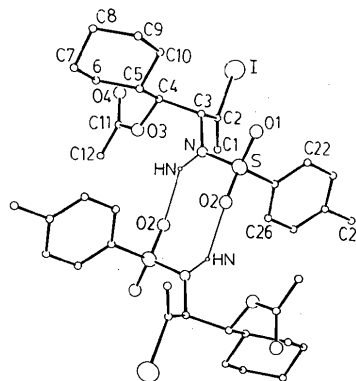


Fig. 2. View of the hydrogen-bonded dimer of compound (7) indicating atomic labelling scheme. Thermal ellipsoids of I and S atoms are drawn at the 25% probability level. C, O and N atoms are drawn as spheres of arbitrary radii.

143.0 (10)°] is not comparable to that of the major component. No constraints were applied to the disordered group during the refinement to attempt to define the geometry of the minor component. ¹H and ¹³C NMR experiments (Friesen & Kolaczewska, 1991) confirm that the sample of compound (7) is not a mixture of more than one compound, therefore we are fairly certain that the crystal structure contains a disordered pure compound. We have not been able to accurately define the geometry of the minor disorder component but the final model used gave the best agreement with the observed data and also the cleanest difference Fourier map.

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Structures of Complexes of 2,3,3a,5,6,6a-Hexahydro-3,6-diphenyl-1*H*,4*H*-pyrrolo-[3,4-*c*]pyrrole-1,4-dithione with *N*-Methyl-2-pyrrolidone and Dimethyl Sulfoxide

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Abstract. Two complexes of the title compound (DPPT) have been formed with *N*-methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide (Me₂SO): DPPT/(NMP)₂ and DPPT/(Me₂SO)₂. The crystal data for DPPT/(NMP)₂ are: C₁₈H₁₂N₂S₂·2C₅H₉NO, *M_r* = 518.6907, triclinic, *P* $\bar{1}$, *a* = 7.527 (1), *b* = 9.157 (1), *c* = 9.988 (1) Å, α = 96.39 (1), β = 110.40 (1), γ = 93.24 (1)°, *V* = 637.9 (3) Å³, *Z* = 1, *D_m* = 1.345, *D_x* = 1.350 Mg m⁻³, graphite-monochromated Mo *K*α radiation, λ = 0.70926 Å, μ = 2.32 mm⁻¹, *F*(000) = 274, *T* = 193 K, *R* = 0.077 for 1822 reflections. The crystal data for DPPT/(Me₂SO)₂ are: C₁₈H₁₂N₂S₂·2C₂H₆OS, *M_r* = 476.6838, monoclinic, *P*2₁/*c*, *a* = 12.674 (1), *b* = 10.318 (1), *c* = 8.761 (1) Å, β = 100.32 (1)°, *V* = 1127.1 (4) Å³, *Z* = 2, *D_m* = 1.398, *D_x* = 1.404 Mg m⁻³, graphite-monochromated Mo *K*α radiation, λ = 0.70926 Å, μ = 4.25 mm⁻¹, *F*(000) = 500, *T* = 188 K, *R* = 0.052 for 2146 reflections. In both complexes, two solvent molecules are bonded to one DPPT molecule through intermolecular hydrogen bonds between the NH group of DPPT and the O atom of the solvent. Both complexes belong to point group *C_i*. The phenyl rings of DPPT are twisted in the same direction out of plane of the heterocyclic system by 24.7 (4)° in DPPT/(NMP)₂ and by 21.2 (5)° in DPPT/(Me₂SO)₂. The DPPT molecule is entirely enclosed by six solvent molecules in DPPT/(NMP)₂,

whereas the environment is quite different in DPPT/(Me₂SO)₂.

Introduction. The optical properties of 3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dithione (DPPT) have been extensively studied in connection with applications to electrophotographic photoreceptors for laser printers (Mizuguchi & Rochat, 1988; Mizuguchi & Homma, 1989; Mizuguchi, 1989) and to optical information storage (Mizuguchi & Rochat, 1991). Both of the applications are based on the near-IR optical absorption of DPPT.

We have previously reported that there are three crystal modifications, (I), (II) and (III), of DPPT, all of which are monoclinic. Single crystals have been grown from the vapor phase (Mizuguchi, Rochat & Rihs, 1990; Mizuguchi, Arita & Rihs, 1991). Electronic properties of DPPT have been systematically studied in solution and in the solid state from the standpoint of deprotonation and intermolecular hydrogen bonding (Mizuguchi, Rochat & Rihs, 1992). The polarization experiments using single crystals have shown that the near-IR optical absorption is attainable only with modification (III). The optical transition is interpreted as being due to π - π interactions between neighboring molecules along the stacking axis, although a weak charge-transfer interaction is also partly operative.