Reactions of Dehydrodithizone with Dimethyl Acetylenedicarboxylate and with Benzyne. *X*-Ray Crystal Structure of Azobenzene *N*-(4,5-Bismethoxycarbonylthiazol-2-yl)imide, a Stable Dipole

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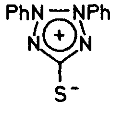
Dehydrodithizone adds dimethyl acetylenedicarboxylate to yield the title compound (7), whose structure was determined by single-crystal *X*-ray analysis. 2-Phenylazobenzothiazole and azobenzene were obtained from dehydrodithizone and benzyne. These products are thought to be formed by the decomposition of initial 1,3-cycloadducts.

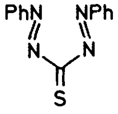
DEHYDRODITHIZONE (1) reacts with enamines and ynamines to give products derived from the acyclic valence isomer (2).[1] In contrast, the electron-deficient tetraphenylcyclopentadienone forms the azobenzene *N*-imide (4) by ring opening of the intermediate 1,3-dipolar cycloadduct (3). A minor product, the phenylazothiazoline (5), is derived from the *N*-imide by formal loss of phenylnitrene.[2] The different behaviour of electron-rich and electron-poor components was rationalised [1] by frontier-orbital theory, which indicated that only the latter could undergo a concerted 1,3-cycloaddition to yield compounds of type (3). The reaction of dehydrodithizone with dimethyl acetylenedicarboxylate, another electrophilic dipolarophile, was reported [3] to yield compound (6); the formation of such a 1,3-cycloadduct would be in accord with theory, and its mass spectrum, which contained a signal attributable to the azobenzene radical ion, seemed to confirm the proposed constitution.[1] However, in view of our experience with the adduct of tetraphenylcyclopentadienone we thought it desirable to establish whether the adduct to the acetylenic ester does, in fact, exist in this bicyclic form or as the monocyclic valence isomer (7).

The compound was subjected to *X*-ray analysis, which showed that it had the dipolar structure (7) (see Figure 1); the bond lengths in the triazene chain (Figure 2) indicate that the molecule is best represented by this canonical form. We propose that the reaction of dehydrodithizone with dimethyl acetylenedicarboxylate is an exact analogue of that with tetraphenylcyclopentadienone: initial 1,3-dipolar cycloaddition to give (6), followed by fission of the tetrazoline ring, which is destabilised by its antiaromatic character, *i.e.* the presence of eight π-electrons.

The reaction of dehydrodithizone with benzyne, generated from anthranilic acid and isopentyl nitrite,[4] led to a complex mixture, from which azobenzene and a dark orange compound, $C_{13}H_9N_3S$, were isolated. I.r. data and the n.m.r. spectrum (which showed only aromatic protons) of the latter were not informative. The



(1)



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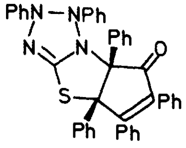

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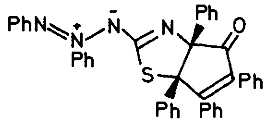

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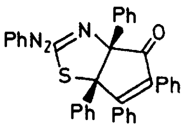

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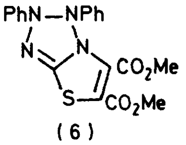

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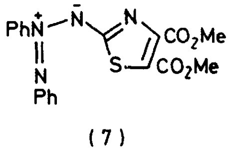

(7)

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[1] G. V. Boyd, T. Norris, and P. F. Lindley, *J.C.S. Perkin I*, 1976, 1673.

[2] G. V. Boyd, T. Norris, and P. F. Lindley, *J.C.S. Perkin I*, 1977, 965.

[3] P. Rajagopalan and P. Penev, *Chem. Comm.*, 1971, 490.

[4] L. Friedman and F. M. Logullo, *J. Org. Chem.*, 1969, **34**, 3089.

mass spectrum showed the molecular ion peak at *m/e* 239; other fragment ions were assigned as $C_6H_5N_2^{+\cdot}$ (105), $C_7H_4NS^{+\cdot}$ (134), and $C_6H_4S^{+\cdot}$ (104). The signal at *m/e* 105 apparently indicated the presence of a phenylazo-group, and the peak at *m/e* 134 a benzothiazole residue. These conclusions, together with consideration of a likely reaction path, suggested that the compound might be 2-phenylazobenzothiazole (**9**), and this was confirmed by comparison with an authentic specimen, prepared[5] from 2-aminobenzothiazole and nitrosobenzene. The formation of compound (**9**) is analogous to the production of the phenylazothiazoline (**5**); it is therefore reasonable to postulate a corresponding dipolar precursor, the azo-imide (**8**).

The reactions of dehydrodithizone with tetraphenylcyclopentadienone, dimethyl acetylenedicarboxylate, and benzyne thus all follow the same pattern: 1,3-dipolar cycloaddition to form an unstable tetrazoline, followed by ring opening to an azo-imide, which may then fragment into a phenylazo-compound and phenylnitrene. The intermediacy of phenylnitrene is strongly suggested by the isolation of azobenzene in the last reaction. Azobenzene is frequently observed when phenylnitrene is generated but its formation by dimerisation of the nitrene is unlikely; it is usually thought to arise by attack of phenylnitrene on some other species.[6] In the present case, azobenzene may well be produced by the reaction of phenylnitrene with the azo-imide (**8**), as shown.

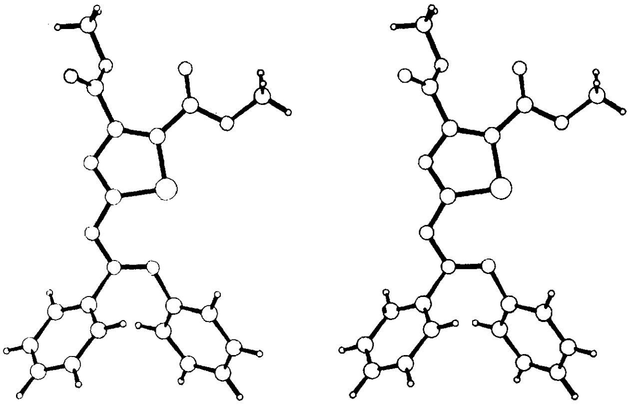


FIGURE 1 A stereodrawing of the molecule (7) viewed along the normal to the plane defined by S(1), N(3), and C(5)

Structure of the Azo-imide (**7**).—Figure 1 is a stereoscopic drawing of the molecule (**7**) as viewed along the normal to the plane defined by the atoms S(1), N(3), and C(5). The atom labelling scheme for the molecule, together with appropriate intramolecular bond lengths and angles, is shown schematically in Figure 2. Further details of the molecular geometry are given in Table 2.

The molecule is monocyclic, containing a thiazole ring which is planar within experimental error. The geometry of the –N–NPh–NPh moiety at C(2) is closely similar to that found in azobenzene *N*-(*cis*-3a,6a-dihydro-4-oxo-3a,5,6,6a-tetraphenyl-4*H*-cyclopentathiazol-2-yl)imide.[2] The atom N(15) lies within 0.047 Å of the plane defined by N(14), C(151), and N(16), and the phenyl rings attached to N(15) and N(16) make dihedral angles of 55.2 and 120.6°, respectively, with this plane. The N(15)–N(16) distance, 1.288(3)Å, is indicative of considerable double-bond character, suggesting a dipolar structure in which N(14) and N(15) have formal negative and positive charges, respectively. The long N(15)–C(151) bond distance, 1.466(3) Å, in comparison with the N(16)–C(161) distance of 1.417(3) Å, and the short C(2)–N(14) distance, 1.375(3) Å, are in agreement with this charge distribution.*

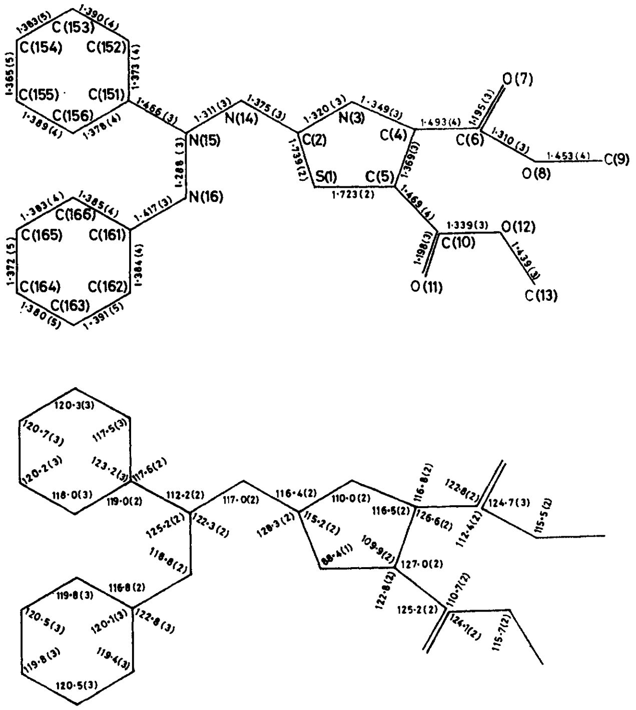
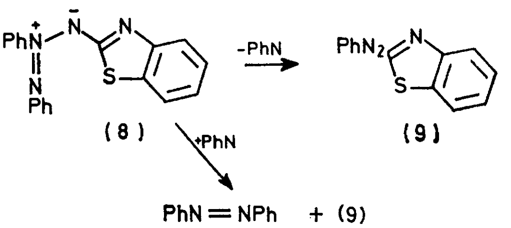


FIGURE 2 A schematic drawing of the molecule (7) showing the atom labelling, together with intramolecular bond lengths and angles and their associated estimated standard deviations



However, in contrast to the structure of azobenzene *N*-(*cis*-3a,6a-dihydro-4-oxo-3a,5,6,6a-tetraphenyl-4*H*-cyclopentathiazol-2-yl)imide, the three nitrogen atoms

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* We thank a referee for drawing our attention to the structure of tetramethyl 3,8a-dimethylpyrido[2,1-*b*]thiazole-5,6,7,8-tetracarboxylate (P. J. Abbott, R. M. Acheson, U. Eisner, D. J. Watkin, and J. R. Carruthers, *J.C.S. Perkin I*, 1976, 1269), in which the difference in the geometries of the carboxylate groups has been ascribed to the contribution of a resonance structure in which the negative charge is located on the carbonyl oxygen atom of one of the ester groups. An analogous canonical form may make a minor contribution to the structure of compound (7).

[5] L. Pontinally and L. Greci, *Gazzetta*, 1968, **98**, 1369.

[6] See *e.g.* P. Walker and W. A. Waters, *J. Chem. Soc.*, 1962, 1632; R. K. Smalley and H. Suschitzky, *Chem. and Ind.*, 1970, 1338 and references cited therein.

N(14), N(15), and N(16) lie very close to the plane of the thiazole ring; the displacements are —0.067, —0.048, and 0.040 Å, respectively. The N(16)–S(1) separation of 2.56 Å is significantly greater than the single-bond value of 1.772(1) Å found in sulphamic acid,[7] but significantly shorter than the value of 3.35 Å for the sum of the respective van der Waals radii.[8] This implies weak interaction between these two atoms, which may lead to further resonance stabilisation in the molecule. Other short S–N separations of 2.79 Å have been found in 4a,5,6,7,8,8a-hexahydro-6-methyl-8a-morpholino-1-phenyl-3-phenylazo-1*H*-pyrido[4,3-*e*][1,3,4]thiadiazine,[1] 3′-phenyl-5′-phenylazo-2-pyrrolidinospiro-[1*H*-indene-1,2′(3′*H*)-[1,3,4]thiadiazole],[1] and *cis*-3a,6a-dihydro-3a,5,6,6a-tetraphenyl-2-phenylazo-4*H*-cyclopentathiazol-4-one,[1] whereas several structures of heterocyclic compounds displaying analogous S–O interactions have been reported; *e.g.* 2.67 Å in 2-benzoylimino-3-methylthiazolidin-5-one.[9] In the structure of azobenzene *N*-(*cis*-3a,6a-dihydro-4-oxo-3a,5,6,6a-tetraphenyl-4*H*-cyclopentathiazol-2-yl)imide[2] the rotation of the –N–NPh–NPh– moiety out of the plane of the thiazole ring is presumably caused by steric hindrance between phenyl groups.

The bond lengths and angles in the two carboxylate groups are normal. The carboxylate group at C(4) is inclined at a dihedral angle of 57.4° with respect to the plane of the thiazole ring, whereas the group at C(5) lies close to this plane, the dihedral angle being 168.3°.

There are no intermolecular separations significantly less than the sum of the respective van der Waals radii.

EXPERIMENTAL

Azobenzene N-(*4,5-Bismethoxycarbonylthiazol-2-yl*)*imide* (7).—The reaction of dehydrodithizone with dimethyl acetylenedicarboxylate has been described;[1] a more convenient procedure follows. A mixture of dehydrodithizone (1.25 g), dimethyl acetylenedicarboxylate (1 ml), and dry dimethyl sulphoxide (25 ml) was stirred at 80 °C for 45 min and then poured into water (300 ml), whereupon an orange solid was precipitated. It was collected and dissolved in ethyl acetate (100 ml); the dried ($MgSO_4$) solution was concentrated and adsorbed on Florisil (*ca.* 30 g). Elution with ethyl acetate gave the *product* (0.45 g, 23%), amber crystals (from ethanol), m.p. 178—180 °C, identical with the previously described sample.[1]

Reaction of Dehydrodithizone with Benzyne.—A mixture of dehydrodithizone (1.07 g), isopentyl nitrite (0.54 g), and 1,2-dichloroethane (120 ml) was heated under reflux with stirring while a solution of anthranilic acid (0.6 g) in diethylene glycol dimethyl ether (20 ml) was added during 40 min. After a further 1 h reflux, the solvents were distilled off until the temperature at the stillhead reached 150 °C. The residue was poured into ice–water (200 ml) and the precipitated black tar was dissolved in a small volume of chloroform; the dried ($MgSO_4$) solution was subjected to column chromatography on alumina (Type 0; 60 g) with light petroleum (b.p. 40—60 °C) containing increasing amounts of ethyl acetate (5—25%) as eluant. Two crystalline products were isolated: (*a*) azobenzene (0.03 g, 9%), m.p. 68—69 °C, identified by analysis and direct comparison with an authentic sample, and (*b*) 2-phenylazobenzothiazole (9) (0.10 g, 11%), dark orange, m.p. 144—146 °C (lit.,[5] 142 °C), $\nu_{max.}$ (KBr) 1 580w, 1 460, 1 320, 1 145, 1 070, 890, 760, 728, and 680 cm^{-1}, $\nu_{max.}$ (Nujol) 1 580w, 1 320, 1 145, 1 070, 890, 760, 725, and 680 cm^{-1}, δ ($CDCl_3$) 7.46 and 8.10 (m, Ar), *m/e* 239 (M^+, 43%), 211 (48), 210 (78), 134 (20), 108 (36), 105 (74), and 77 (100) (Found: C, 65.4; H, 3.75; N, 17.7; S, 13.2. Calc. for $C_{13}H_9N_3S$: C, 65.25; H, 3.8; N, 17.55; S, 13.4%), identified by comparison with an authentic specimen.

Structure of the Azo-imide (7).—*Crystal data.* $C_{19}H_{16}N_4O_4S$, *M* 396.3. Monoclinic, $a = 16.300(6)$, $b = 16.896(6)$, $c = 6.996(2)$ Å, $\beta = 95.33(1)°$, $U = 1918$ Å^3, $D_c = 1.37$ g cm^{-3}, $Z = 4$, $F(000) = 824$. Cu-K_α radiation, μ(Cu-K_α) 17.1 cm^{-1}. The conditions limiting possible reflection, $0k0$, $k = 2n$, and $h0l$, $h + l = 2n$, uniquely determine the space group as $P2_1/n$ (alternative orientation of $P2_1/c$, No.14).

The compound forms red lath-shaped crystals elongated along the *b* axis. Preliminary cell dimensions and space group information were obtained from Weissenberg and precession photographs. Refined cell parameters were obtained by least-squares refinement of the θ values of the Cu-K_{α_1} components [$\lambda(K_{\alpha_1}) = 1.5405$ Å] of 19 reflections measured on a Hilger–Watts Y290 automated four-circle diffractometer. Intensity data were also collected on this instrument using Ni-filtered copper radiation and the ω–2θ step scanning technique. The scan width was 0.90° plus a dispersion correction and stationary background counts were taken at either side of each peak. Three reference reflections were measured after every 50 reflections and the intensity sums of the reference reflections were used to scale the observed intensities by interpolation between groups of references. The overall variation in the intensities of the reference reflections during data collection was 3.3%.

Intensity data were collected for the $\bar{h}kl$ and $\bar{h}\bar{k}l$ reflections over the range $0 \leqslant \theta \leqslant 70°$. A second set of data was collected for the $h\bar{k}l$ and $h\bar{k}l$ reflections over the range $0 \leqslant \theta \leqslant 34°$. Averaging of the two sets of data gave 3 502 independent reflections of which 2 799 had $I/\sigma(I) \geqslant 3.0$ and were thereby classified as significant. The overall residual for the 917 reflections measured more than once was 0.047. Lorentz and polarisations corrections were applied to all reflections but no corrections were made for absorption.

Structure solution and refinement. The sulphur atom was located from a three-dimensional Patterson synthesis. The positions of the remaining non-hydrogen atoms were then determined by using the iterative Fourier synthesis technique to give a residual of 0.235.

The structure was refined by the full-matrix least-squares technique, using only the significant reflections and initially with all atoms treated isotropically. Hydrogen atoms were placed in calculated positions assuming a C–H bond length of 1.0 Å but no attempt was made to refine their positional or thermal parameters. Refinement with all non-hydrogen atoms treated anisotropically yielded final residuals of 0.042 (R) and 0.059 [$R' = (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$]. The weighting scheme $w = a_0$ if $|F_o| \leqslant 30.0$ otherwise, $w = [1 - \exp(-a_1 \sin^2\theta/\lambda^2)]/(a_2 + |F_o| + a_3|F_o|^2)$ was used to make the average values of $\Sigma w\Delta^2$ constant when analysed in terms of batches of increasing $\sin\theta/\lambda$ and $|F_o|$. Values of $a_0 = 0.01$,

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[7] A. F. Cameron and F. D. Duncanson, unpublished results cited in *Acta Cryst.*, 1976, **B32**, 1987.

[8] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Oxford University Press, 1960, p. 260.

[9] H. Steeple, *Acta Cryst.*, 1961, **14**, 847.

$a_1 = 30.0$, $a_2 = 20.0$, and $a_3 = 0.002$ were used in the final cycle.

A difference Fourier synthesis computed after the final refinement cycle confirmed the correctness of the refinement, and structure factor calculations for the insignificant reflections showed no outstanding discrepancies. Throughout the structure factor calculations the atomic scattering factors listed by Hanson *et al.*[10] were used. All computations were performed on the CDC 6600 computer at the University of London Computer Centre.

TABLE 1

Refined positional parameters for the non-hydrogen atoms with e.s.d.s in parentheses

Atom	*X*	*Y*	*Z*
S(1)	0.073 56(4)	−0.008 46(3)	0.258 05(8)
C(2)	0.101 8(1)	0.088 8(1)	0.215 8(3)
N(3)	0.040 4(1)	0.140 1(1)	0.198 0(3)
C(4)	−0.031 5(1)	0.102 9(2)	0.218 4(3)
C(5)	−0.027 4(2)	0.022 9(1)	0.249 2(3)
C(6)	−0.107 7(2)	0.152 4(2)	0.198 5(4)
O(7)	−0.127 2(1)	0.191 6(2)	0.059 5(3)
O(8)	−0.148 8(1)	0.148 9(1)	0.350 7(3)
C(9)	−0.225 5(2)	0.193 2(3)	0.338 7(6)
C(10)	−0.097 0(2)	−0.032 1(2)	0.254 6(4)
O(11)	−0.167 9(1)	−0.015 5(1)	0.213 8(3)
O(12)	−0.070 2(1)	−0.104 8(1)	0.304 3(3)
C(13)	−0.132 3(2)	−0.165 6(2)	0.297 2(5)
N(14)	0.178 8(1)	0.118 0(1)	0.190 1(3)
N(15)	0.240 5(1)	0.067 9(1)	0.210 1(3)
C(151)	0.317 3(2)	0.102 8(2)	0.155 8(4)
C(152)	0.354 4(2)	0.067 5(2)	0.009 0(4)
C(153)	0.424 2(2)	0.103 7(2)	−0.050 7(5)
C(154)	0.453 8(2)	0.173 0(2)	0.035 4(5)
C(155)	0.415 7(2)	0.206 5(2)	0.181 4(5)
C(156)	0.346 1(2)	0.171 5(2)	0.244 6(4)
N(16)	0.230 7(1)	−0.005 4(1)	0.253 6(3)
C(161)	0.301 4(2)	−0.052 4(2)	0.304 3(4)
C(162)	0.362 7(2)	−0.030 1(2)	0.444 4(5)
C(163)	0.426 1(2)	−0.082 8(2)	0.499 6(6)
C(164)	0.427 9(2)	−0.156 8(2)	0.416 3(6)
C(165)	0.366 7(2)	−0.178 5(2)	0.278 2(5)
C(166)	0.302 9(2)	−0.127 0(2)	0.222 4(4)

The final atomic co-ordinates of the non-hydrogen atoms are listed in Table 1. Anisotropic thermal parameters for the non-hydrogen atoms, hydrogen atom co-ordinates, and observed and calculated structure factors are available as Supplementary Publication No. SUP 22047 (21 pp.).*

We thank Mr. S. K.-P. Lam for experimental assistance, May & Baker Ltd. for their interest, the Ministry of Higher Education and Scientific Research of the Government of Iraq for a research scholarship (to M. M. M.), and the S.R.C. for a research studentship (to T. N.).

TABLE 2

Molecular geometry

Least-squares planes defined by atomic positions and, in parentheses, distances of atoms (Å) from these planes; *X*, *Y*, and *Z* refer to orthonormal co-ordinates obtained by the transformation:

$$\begin{vmatrix} X \\ Y \\ Z \end{vmatrix} = \begin{vmatrix} a \sin\beta & 0 & 0 \\ 0 & b & 0 \\ a \cos\beta & 0 & c \end{vmatrix} \begin{vmatrix} x \\ y \\ z \end{vmatrix}$$

Plane (1): S(1), C(2), N(3), C(4), C(5)

$$0.114\,3X + 0.166\,8Y + 0.979\,3Z = 1.766\,8$$

[S(1) 0.004, C(2) −0.002, N(3) −0.002, C(4) 0.006, C(5) −0.006, N(14) −0.067, N(15) −0.048, N(16) 0.040, C(6) −0.019, C(10) −0.149]

Plane (2): N(14), C(151), N(16)

$$0.217\,5X + 0.253\,6Y + 0.942\,5Z = 2.132\,9$$

[N(15) 0.047, C(2) −0.117, C(161) 0.282]

Plane (3): C(151) to C(156)

$$0.578\,3X - 0.535\,6Y + 0.615\,4Z = 2.420\,4$$

[C(151) −0.002, C(152) −0.001, C(153) 0.004, C(154) −0.003, C(155) 0.000, C(156) 0.002, N(14) −1.161, N(15) −0.100, N(16) 0.667]

Plane (4): C(161) to C(166)

$$0.533\,0X + 0.366\,7Y - 0.762\,5Z = 1.002\,5$$

[C(161) 0.006, C(162) −0.002, C(163) −0.002, C(164) 0.001, C(165) 0.002, C(166) −0.006, N(16) −0.126]

Plane (5): C(4), C(6), O(7), O(8)

$$0.523\,0X + 0.773\,6Y + 0.357\,9Z = 1.638\,5$$

[C(4) 0.002, C(6) −0.006, O(7) 0.002, O(8) 0.002, C(9) −0.059]

Plane (6): C(5), C(10), O(11), O(12)

$$0.078\,9X - 0.228\,5Y - 0.970\,3Z = -1.857\,8$$

[C(5) 0.004, C(10) −0.013, O(11) 0.005, O(12) 0.004, C(13) 0.115]

Dihedral angles (°) between planes

Plane A	Plane B	Angle
(1)	(2)	8.0
(1)	(5)	57.4
(1)	(6)	168.3
(2)	(3)	55.2
(2)	(4)	120.6

[6/2355 *Received*, 30*th December*, 1976]

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* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1976, Index issue.

[10] H. P. Hanson, F. Herman, J. D. Lea, and S. Skilman, *Acta Cryst.*, 1964, **17**, 1040.