

Reaction of Dehydrodithizone with Tetraphenylcyclopentadienone. X-Ray Crystal Structures of a Stable 1,5-Dipole, Azobenzene *N*-(*cis*-3a,6a-Dihydro-4-oxo-3a,5,6,6a-tetraphenyl-4*H*-cyclopentathiazol-2-yl)-imide, and of *cis*-3a,6a-Dihydro-3a,5,6,6a-tetraphenyl-2-phenylazo-4*H*-cyclopentathiazol-4-one

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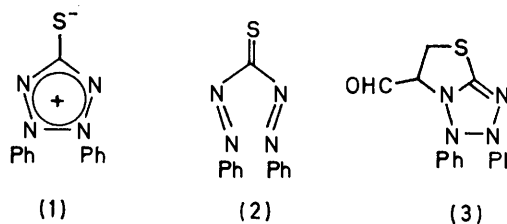
The title compounds (5) and (8) were obtained from the reaction of dehydrodithizone with tetraphenylcyclopentadienone and their structures were determined by single-crystal *X*-ray analysis by direct methods. Crystals of both compounds are triclinic, with $Z = 8$ in unit cells of dimensions: (5) $a = 19.933(6)$, $b = 9.755(3)$, $c = 36.515(12)$ Å, $\alpha = 87.429(8)$, $\beta = 102.659(6)$, $\gamma = 99.675(4)^\circ$; (8) $a = 14.855(2)$, $b = 19.816(3)$, $c = 19.335(3)$, $\alpha = 94.260(6)$, $\beta = 90.815(6)$, $\gamma = 93.041(8)^\circ$. The structures were refined to R 0.046 [(5) 2 808 observed reflections] and 0.040 [(8) 2 380 observed reflections].

DEHYDRODITHIZONE (1) reacts in an unexpected fashion with electron-rich dipolarophiles, such as enamines and ynamines: instead of 1,3-cycloadducts it yields products derived from the acyclic valence isomer (2).¹ This behaviour was rationalised by applying frontier orbital theory, which indicated that the reactions were governed by interaction of the highest occupied molecular orbital (HOMO) of the dipolarophile with the lowest unoccupied molecular orbital (LUMO) of dehydrodithizone, whose nodal properties make concerted cycloaddition 'forbidden'. In addition to electron-poor components, on the other hand, the HOMO of dehydrodithizone is involved and this has suitable symmetry for interaction with the LUMOs of the dipolarophiles; thus, acrylaldehyde should yield a 1,3-cycloadduct with the orientation shown in (3). These predictions seemed to be borne out by experiments with dimethyl acetylenedicarboxylate² and tetraphenylcyclopentadienone, both of which yielded adducts thought to correspond to (3), since their mass spectra contained signals at m/e 182, attributed to the azobenzene radical ion, which was regarded as diagnostic for the presence of an intact tetrazole ring. Further, the i.r. spectrum of the second adduct showed that it was a derivative of cyclopentenone and it was concluded that tetraphenylcyclopentadienone had functioned as a 2π -component in the dipolar cycloaddition reaction, but the exact structure of the product was not specified.¹

We now report the results of an *X*-ray analysis of the

† This finding raises the question as to whether the adduct of dimethyl acetylenedicarboxylate to dehydrodithizone is bicyclic² or monocyclic; we are currently investigating this problem.

adduct of tetraphenylcyclopentadienone to dehydrodithizone and that of a by-product. Our expectation that the adduct would have the orientation and stereochemistry (4), as required by theory, was only partially realised: the compound does not exist in this covalent tricyclic form but rather as the bicyclic 1,5-dipolar



valence tautomer (5) (Figure 1).† We suggest that the tetrazoline ring in (4) is destabilised by the presence of eight π -electrons and therefore undergoes symmetry-allowed electrocyclic opening. Indeed, Δ^4 -tetrazolines appear to be unknown and the preference for acyclic 1,5-dipolar structures over 8π cyclic forms has previously been observed³ in the case of the products of the reaction of benzocinnoline *N*-imide with imidoyl chlorides, which exist as benzaminamides (6) rather than in the cyclic form (7).

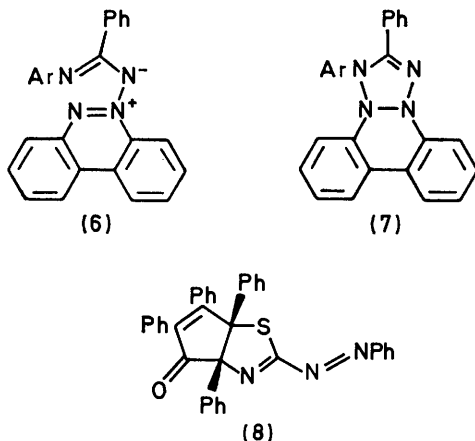
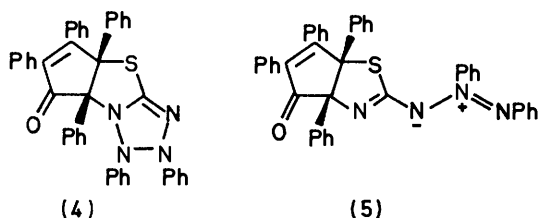
The minor product of the reaction of dehydrodithizone

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

² P. Rajagopalan and P. Penev, *Chem. Comm.*, 1971, 490.

³ J. J. Barr, R. C. Storr, and J. Rimmer, *J.C.S. Chem. Comm.*, 1974, 657.

with tetraphenylcyclopentadienone, obtained in 5% yield, was an orange-red crystalline solid, whose i.r. spectrum exhibited cyclopentenone carbonyl absorption



at 1710 cm^{-1} and whose analysis and mass spectrum indicated that it had the composition of a 1 : 1 adduct

minus $\text{C}_6\text{H}_5\text{N}$. X-Ray analysis (Figure 2) showed that it was the phenylazocyclopentathiazole derivative (8). We are investigating the possibility that this compound is formed from the adduct (5) by extrusion of phenyl-nitrene.

DISCUSSION AND DESCRIPTION OF STRUCTURES (5) AND (8)

Figures 1 and 2 are stereodrawings of the molecules of compounds (5) and (8), respectively. The labelling of the atoms in the two structures together with appropriate intramolecular bond lengths and angles are shown schematically in Figures 3 and 4. Further details of the molecular geometries are given in Tables 1 and 2.

TABLE I

Molecular geometry: torsion angles ($^\circ$) for the five-membered rings

	(5)	(8)
S(1)-C(2)-N(3)-C(4)	-2.3	-1.9
C(2)-N(3)-C(4)-C(8)	-14.4	-5.4
N(3)-C(4)-C(8)-S(1)	23.2	9.4
C(4)-C(8)-S(1)-C(2)	-20.1	-8.4
C(8)-S(1)-C(2)-N(3)	14.9	6.9
C(4)-C(5)-C(6)-C(7)	15.7	2.4
C(5)-C(6)-C(7)-C(8)	-1.6	3.5
C(6)-C(7)-C(8)-C(4)	-12.2	-7.6
C(7)-C(8)-C(4)-C(5)	19.9	8.1
C(8)-C(4)-C(5)-C(6)	-21.9	-6.7

Both structures contain a central unit consisting of a thiazole ring fused to a cyclopentenone ring. The sulphur atom and the carbonyl group are both adjacent to the ring junction but are remote from one another across this junction. The ring junction configuration is

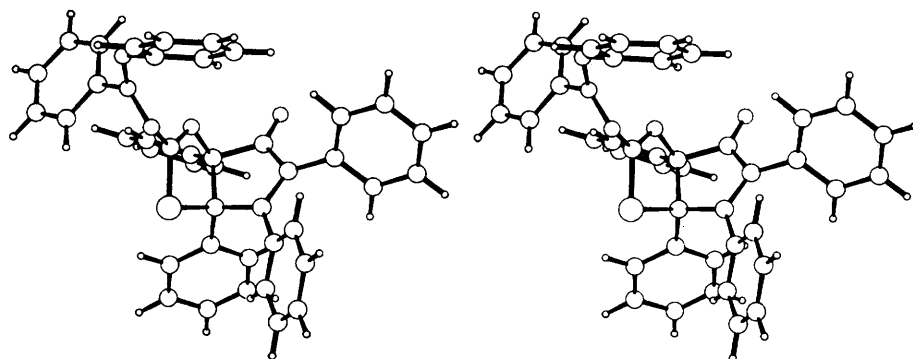


FIGURE 1 Stereodrawing of a molecule of azobenzene *N*-(*cis*-3a, 6a-dihydro-4-oxo-3a,5,6,6a-tetraphenyl-4*H*-cyclopentathiazol-2-yl)imide (5)

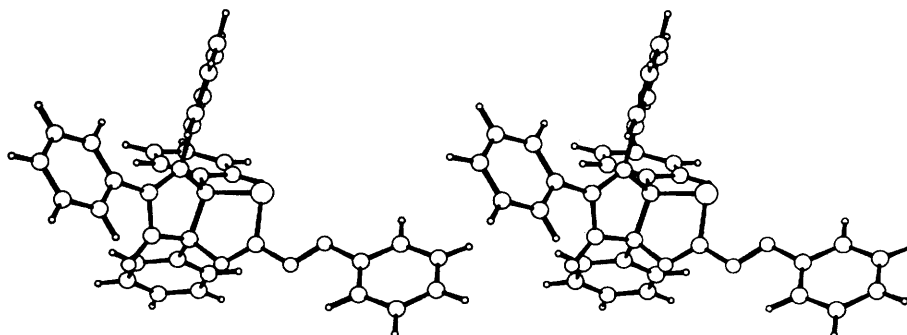


FIGURE 2 Stereodrawing of a molecule of *cis*-3a,6a-dihydro-3a,5,6,6a-tetraphenyl-2-phenylazo-4*H*-cyclopentathiazol-4-one (8)

cis and the dihedral angle between the least-squares planes defined by the respective ring atoms is 75.5° in (5) and 68.5° in (8). The bond lengths and angles in the central unit are closely similar in the two structures but the conformations of the respective rings are not identical.

conformation has partial half-chair character with $\Delta 44.4^\circ$. The conformation of the cyclopentenone ring in (5) approximates to a C(4) envelope configuration with $\Delta 24.8$ and $\phi_m -22.5$ [the torsion angle C(8)-C(4)-C(5)-C(6) is taken as ϕ_0] whereas in (8) the ring is again more

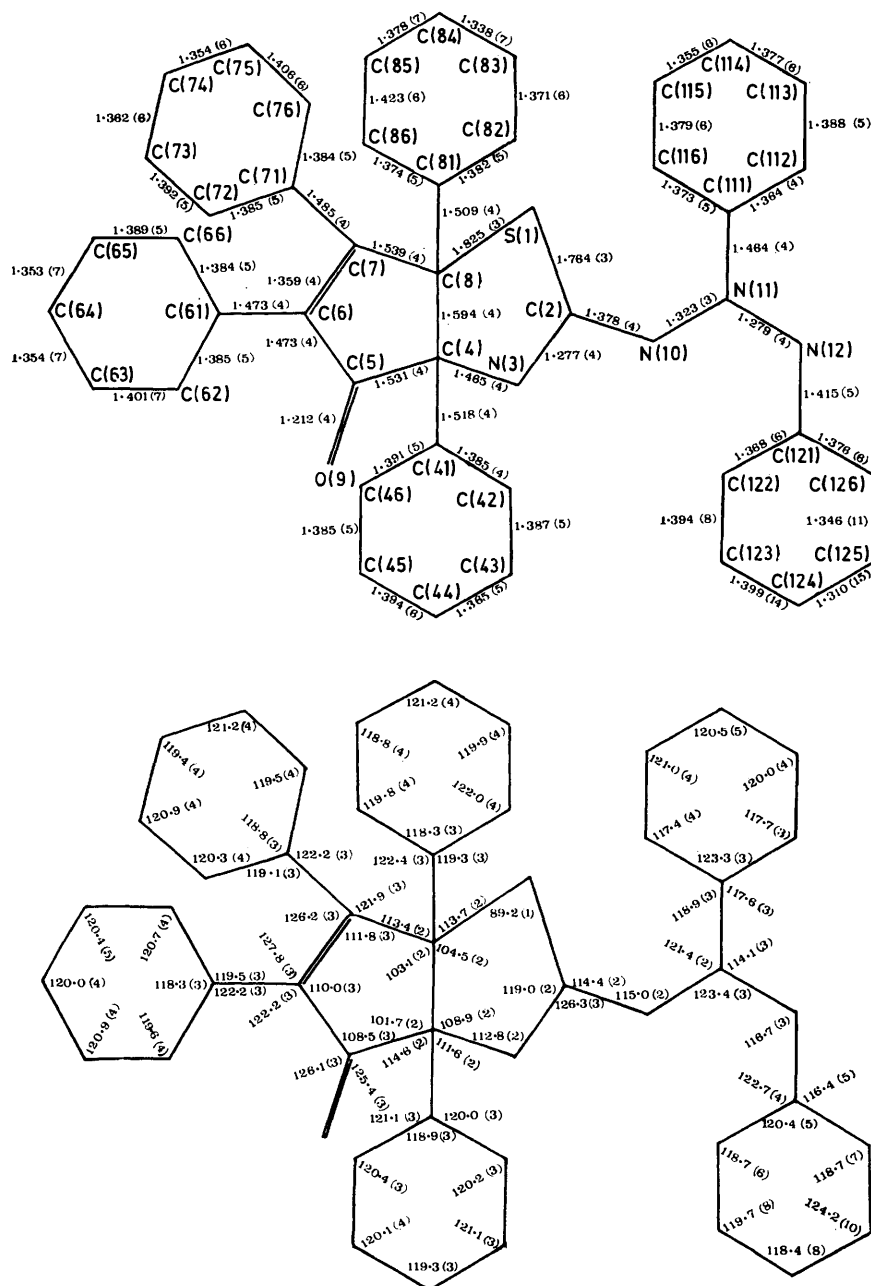


FIGURE 3 Schematic drawing of the molecule of (5) showing the atom labelling and bond lengths (Å) and angles ($^\circ$), with estimated standard deviations in parentheses. Angles not shown: N(3)-C(4)-C(5) $102.5(2)$, C(8)-C(4)-C(41) $116.2(2)$, S(1)-C(8)-C(7) $106.3(2)$, and C(4)-C(8)-C(81) $114.7(2)^\circ$

In (5) the thiazole ring adopts a C(8) envelope conformation with a pseudo-rotational phase parameter,⁴ $\Delta 35.7^\circ$ and a maximum torsional angle, $\phi_m 24.3^\circ$ [the torsion angle S(1)-C(2)-N(3)-C(4) is taken as ϕ_0] whereas in (8) this ring is considerably more planar, $\phi_m 10.2^\circ$, and the

planar, $\phi_m 8.2^\circ$, although the predominant symmetry corresponds to a half-chair configuration with $\Delta -9.0^\circ$ [C(7)-C(8)-C(4)-C(5) is ϕ_0]. The orientations of the

⁴ C. Altona, H. J. Geise, and C. Romers, *Tetrahedron*, 1968, **24**, 13.

phenyl groups attached to the central unit in both structures are such as to minimise non-bonded interactions.

In the $-(N-NPh-NPh)$ unit of (5), N(11) is within 0.085 Å of the plane defined by the atoms N(10), N(12),

N(11)-N(12) [1.279(4) Å] and the C(2)-N(3) bonds [1.277(4) Å] suggest that both linkages have considerable double-bond character. In (8) the N(10)-N(11) bond distance is 1.252(4) Å, but in (5) has a significantly larger value, [1.323(3) Å]. This implies in terms

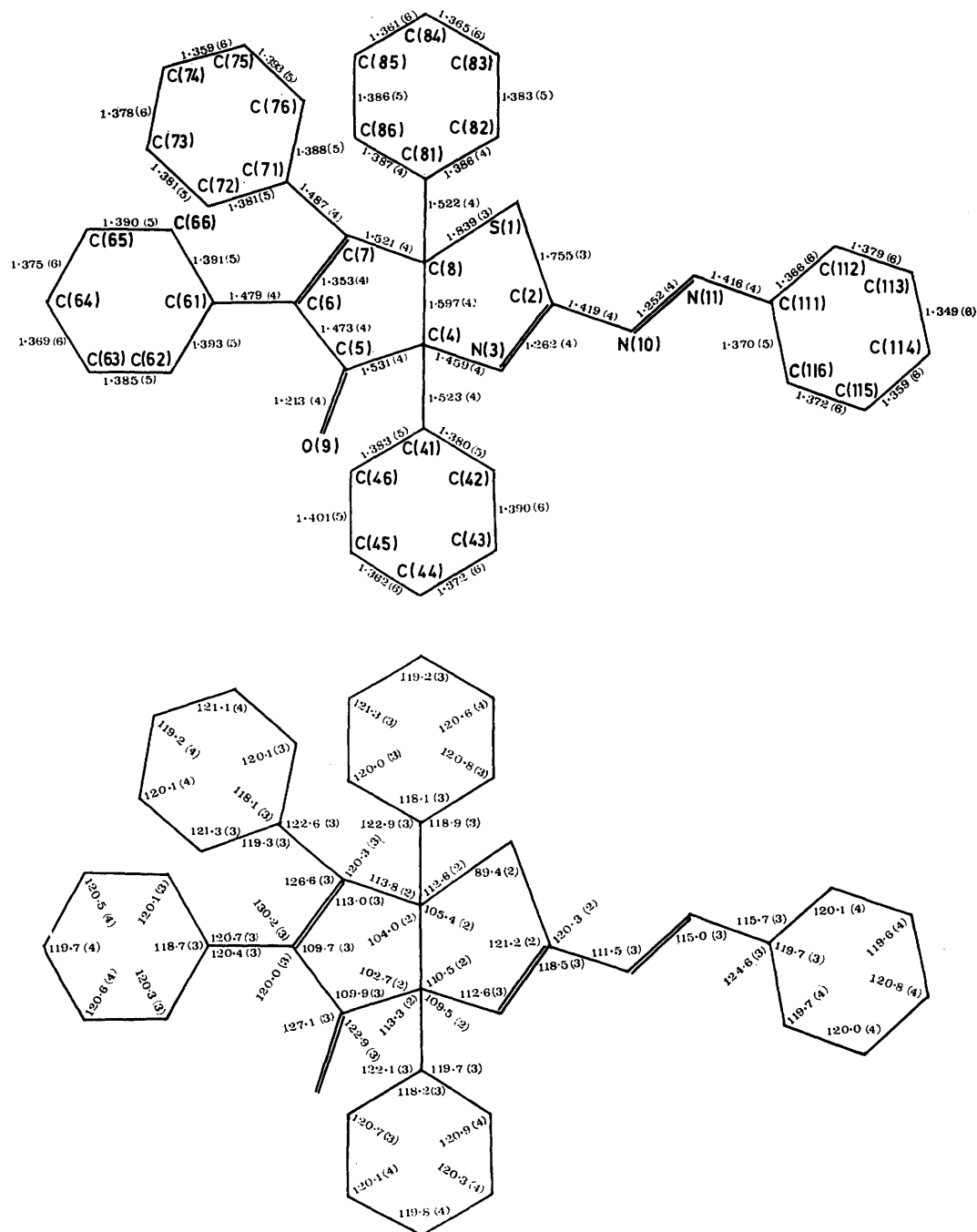


FIGURE 4 Schematic drawing of the molecule of (8), showing the atom labelling and bond lengths (Å) and angles ($^{\circ}$), with estimated standard deviations in parentheses. Angles not shown: N(3)-C(4)-C(5) 104.9(2), C(8)-C(4)-C(41) 115.4(2), S(1)-C(8)-C(7) 107.3(2), and C(4)-C(8)-C(81) 113.0(2) $^{\circ}$

and C(111), and makes dihedral angles of 67.9 $^{\circ}$ with the least-squares plane defined by the atoms in the thiazole ring and 52.8 and 57.9 $^{\circ}$ with the phenyl rings attached to N(11) and N(12) respectively. The magnitudes of the

of valence-bond theory that the predominant canonical form corresponds to one in which N(11) has a formal positive charge and N(10) a formal negative charge, as expressed in formula (5). The lengthening of the N(11)-

C(111) bond distance in (8) to 1.464(4) Å, compared with both the N(12)–C(121) bond length of 1.415(5) Å in (5) and the N(11)–C(111) bond length of 1.416(4) Å in (8) and the shortening of the C(2)–N(10) distance to 1.378(4) Å compared with the corresponding value of 1.419(4) Å in (8) are in agreement with this charge distribution.

In the phenyl ring involving atoms C(121)–(126) the significant departures from regular geometry are associated with unusually large values in the anisotropic thermal vibration parameters (see Supplementary Publication). A tensor analysis of these parameters shows that the direction of maximum anisotropy of the thermal vibration ellipsoids for atoms C(123)–(125) lies approximately in the plane of the ring and also approximately perpendicular to the C(121)···C(124) vector corresponding to a liberation of this phenyl group in its own plane.

In (8) the geometry and orientation of the phenylazo-unit at C(2) are closely similar to those found in 4a,5,6,7-, 8,8a-hexahydro-6-methyl-8a-morpholino-1-phenyl-3-

TABLE 2

Least-squares planes * defined by atomic positions and, in square brackets, distances (Å) of atoms from the planes.

(a) In $C_{12}H_{10}N_3OS$, compound (5)

Plane (i): S(1), C(2), N(3), C(4), and C(8)

$$0.387\ 0X + 0.530\ 0Y - 0.754\ 6Z = -2.274\ 0$$

$$[S(1)\ 0.125, C(2)\ -0.077, N(3)\ -0.031, C(4)\ 0.140, C(8)\ -0.156, N(10)\ -0.396, N(11)\ 0.150]$$

Plane (ii): C(4)–(8)

$$0.726\ 0X - 0.638\ 1Y + 0.256\ 5Z = -1.709\ 2$$

$$[C(4)\ 0.138, C(5)\ -0.123, C(6)\ 0.052, C(7)\ 0.042, C(8)\ -0.108, O(9)\ -0.379, C(61)\ 0.216, C(71)\ 0.224]$$

Plane (iii): C(41)–(46)

$$0.250\ 1X + 0.893\ 4Y + 0.373\ 1Z = 2.846\ 8$$

$$[C(41)\ 0.005, C(42)\ -0.007, C(43)\ 0.005, C(44)\ -0.002, C(45)\ 0.000, C(46)\ -0.002, C(4)\ 0.020]$$

Plane (iv): C(61)–(66)

$$0.626\ 7X + 0.151\ 9Y + 0.764\ 4Z = 2.499\ 4$$

$$[C(61)\ 0.009, C(62)\ -0.002, C(63)\ -0.005, C(64)\ 0.005, C(65)\ 0.003, C(66)\ -0.010, C(6)\ 0.074]$$

Plane (v): C(71)–(76)

$$0.991\ 4X + 0.043\ 6Y - 0.123\ 8Z = -2.775\ 2$$

$$[C(71)\ -0.008, C(72)\ -0.002, C(73)\ 0.009, C(74)\ -0.006, C(75)\ -0.005, C(76)\ 0.012, C(7)\ 0.010]$$

Plane (vi): C(81)–(86)

$$0.140\ 8X + 0.294\ 6Y + 0.945\ 2Z = 5.291\ 5$$

$$[C(81)\ -0.002, C(82)\ 0.000, C(83)\ 0.002, C(84)\ -0.002, C(85)\ 0.000, C(86)\ 0.002, C(8)\ -0.052]$$

Plane (vii): C(111)–(116)

$$0.907\ 0X - 0.416\ 9Y + 0.060\ 3Z = 2.035\ 4$$

$$[C(111)\ 0.002, C(112)\ -0.008, C(113)\ 0.002, C(114)\ 0.010, C(115)\ -0.017, C(116)\ 0.010, N(10)\ -0.655, N(11)\ 0.106, N(12)\ 0.130]$$

Plane (viii): C(121)–(126)

$$0.019\ 4X + 0.826\ 8Y + 0.562\ 2Z = 1.665\ 3$$

$$[C(121)\ -0.001, C(122)\ 0.009, C(123)\ -0.009, C(124)\ -0.001, C(125)\ 0.009, C(126)\ -0.008, N(12)\ -0.185]$$

Plane (ix): N(10), N(12), and C(111)

$$0.856\ 5X + 0.448\ 7Y + 0.255\ 2Z = 2.895\ 2$$

$$[N(11)\ -0.085, C(2)\ -0.664, C(121)\ -0.179]$$

TABLE 2 (Continued)

(b) In $C_{36}H_{25}N_3OS$, compound (8)

Plane (i): S(1), C(2), N(3), C(4), and C(8)

$$0.436\ 6X - 0.870\ 1Y + 0.228\ 9Z = -2.573\ 5$$

$$[S(1)\ -0.054, C(2)\ 0.037, N(3)\ 0.009, C(4)\ -0.057, C(8)\ 0.064, N(10)\ 0.129, N(11)\ -0.020]$$

Plane (ii): C(4)–(8)

$$0.083\ 6X - 0.119\ 0Y + 0.989\ 4Z = 2.897\ 9$$

$$[C(4)\ 0.049, C(5)\ -0.033, C(6)\ -0.002, C(7)\ 0.036, C(8)\ -0.050, O(9)\ -0.066, C(61)\ -0.088, C(71)\ 0.246]$$

Plane (iii): C(41)–(46)

$$0.827\ 2X + 0.329\ 7Y + 0.455\ 1Z = 6.921\ 1$$

$$[C(41)\ -0.002, C(42)\ 0.005, C(43)\ -0.005, C(44)\ 0.003, C(45)\ 0.000, C(46)\ 0.000, C(4)\ -0.045]$$

Plane (iv): C(61)–(66)

$$0.352\ 9X + 0.548\ 5Y - 0.758\ 1Z = 1.177\ 2$$

$$[C(61)\ 0.005, C(62)\ -0.003, C(63)\ -0.003, C(64)\ 0.006, C(65)\ -0.004, C(66)\ -0.002, C(6)\ 0.133]$$

Plane (v): C(71)–(76)

$$0.377\ 1X - 0.478\ 4Y - 0.793\ 1Z = -3.000\ 5$$

$$[C(71)\ 0.011, C(72)\ 0.003, C(73)\ -0.015, C(74)\ 0.014, C(75)\ -0.001, C(76)\ -0.012, C(7)\ -0.035]$$

Plane (vi): C(81)–(86)

$$0.613\ 0X + 0.785\ 7Y - 0.083\ 6Z = 5.312\ 7$$

$$[C(81)\ 0.008, C(82)\ -0.008, C(83)\ 0.003, C(84)\ 0.002, C(85)\ -0.002, C(86)\ -0.002, C(8)\ 0.115]$$

Plane (vii): C(111)–(116)

$$0.000\ 6X + 0.990\ 4Y - 0.138\ 1Z = 5.176\ 3$$

$$[C(111)\ -0.012, C(112)\ 0.006, C(113)\ 0.006, C(114)\ -0.012, C(115)\ 0.006, C(116)\ 0.006, N(10)\ 0.210, N(11)\ -0.077]$$

(c) Dihedral angles (°) between normals to planes; values for (8) follow those for (5): (i)–(ii) 104.5, 68.5; (i)–(iii) 73.2, 79.7; (i)–(vi) 120.2, 115.8; (i)–(vii) 153.3 (8); (i)–(ix) 67.9 (5); (ii)–(iii) 107.0, 61.3; (ii)–(iv) 56.4, 141.8; (ii)–(v) 48.7, 134.1; (ii)–(vi) 81.0, 97.2; (vii)–(ix) 52.8 (5); (viii)–(ix) 57.9 (5).

* X, Y and Z refer to orthogonal co-ordinates obtained by the transformation:

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

phenylazo-1*H*-pyrido[4,3-*e*][1,3,4]thiadiazine.¹ The torsion angles N(3)–C(2)–N(10)–N(11), C(2)–N(10)–N(11)–C(111), and N(10)–N(11)–C(111)–C(116) are 171.8, 178.2, and –16.8° and the phenyl ring, C(111)–(116) inclusive makes a dihedral angle of 26.7° with the least-squares plane defined by thiazole ring atoms. The opening out of the N(11)–C(111)–C(116) angle to 124.6(3)° and the twist of the phenyl ring with respect to the plane defined by N(10), N(11), and C(111) may be associated with steric hindrance between N(10) and H(116); the N(10)···H(116) separation is 2.49 Å. The S···N(11) separation (2.79 Å) compares with a value (3.35 Å) for the sum of the respective van der Waals radii⁵ and is probably indicative of weak interaction between these two atoms.

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

⁵ L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 260.

EXPERIMENTAL

cis-3a,6a-Dihydro-3a,5,6,6a-tetraphenyl-2-phenylazo-4H-cyclopentathiazol-4-one (8).—The reaction of dehydrotithizone with tetraphenylcyclopentadienone and the properties

TABLE 3

Positional parameters for non-hydrogen atoms in (5), with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
S	0.019 98(4)	0.324 45(8)	0.141 50(2)
C(2)	0.025 3(2)	0.164 5(3)	0.122 5(1)
N(3)	-0.023 5(1)	0.111 9(2)	0.095 6(1)
C(4)	-0.079 7(1)	0.195 0(3)	0.085 5(1)
C(5)	-0.143 5(2)	0.091 5(3)	0.091 2(1)
C(6)	-0.151 4(2)	0.103 3(3)	0.130 0(1)
C(7)	-0.112 8(2)	0.222 2(3)	0.145 3(1)
C(8)	-0.071 9(1)	0.304 1(3)	0.118 0(1)
O(9)	-0.179 5(1)	0.010 2(2)	0.067 9(1)
N(10)	0.080 4(1)	0.102 6(3)	0.141 3(1)
N(11)	0.019 9(1)	0.037 2(3)	0.119 7(1)
N(12)	0.141 6(2)	-0.065 6(3)	0.131 0(1)
C(41)	-0.085 1(2)	0.254 2(3)	0.046 0(1)
C(42)	-0.027 2(2)	0.275 2(3)	0.030 0(1)
C(43)	-0.031 6(2)	0.331 8(4)	-0.005 9(1)
C(44)	-0.092 9(2)	0.364 8(4)	-0.026 3(1)
C(45)	-0.151 6(2)	0.343 2(4)	-0.010 6(1)
C(46)	-0.147 6(2)	0.287 7(4)	-0.025 3(1)
C(61)	-0.195 7(2)	-0.004 1(4)	0.147 7(1)
C(62)	-0.250 9(2)	0.025 3(5)	0.161 6(1)
C(63)	-0.289 3(2)	-0.079 7(7)	0.179 6(1)
C(64)	-0.273 0(3)	-0.209 6(7)	0.183 6(1)
C(65)	-0.219 6(3)	-0.239 9(5)	0.169 8(1)
C(66)	-0.181 1(2)	-0.138 5(4)	0.151 5(1)
C(71)	-0.105 5(2)	0.269 7(3)	0.184 3(1)
C(72)	-0.096 6(2)	0.174 6(4)	0.213 6(1)
C(73)	-0.088 2(2)	0.216 8(5)	0.250 4(1)
C(74)	-0.089 7(2)	0.351 2(5)	0.258 3(1)
C(75)	-0.098 1(2)	0.445 3(5)	0.230 0(1)
C(76)	-0.105 2(2)	0.406 9(4)	0.192 5(1)
C(81)	-0.096 5(2)	0.439 7(3)	0.104 8(1)
C(82)	-0.166 6(2)	0.447 8(4)	0.099 3(1)
C(83)	-0.192 3(3)	0.566 7(6)	0.086 3(1)
C(84)	-0.149 2(3)	0.679 3(6)	0.078 4(1)
C(85)	-0.078 7(3)	0.678 7(4)	0.083 4(1)
C(86)	-0.052 0(2)	0.555 3(4)	0.097 0(1)
C(111)	0.121 4(2)	0.095 7(3)	0.083 5(1)
C(112)	0.150 8(2)	0.232 3(4)	0.082 5(1)
C(113)	0.166 9(2)	0.285 0(4)	0.049 0(1)
C(114)	0.152 5(2)	0.200 4(6)	0.018 1(1)
C(115)	0.121 5(3)	0.066 4(6)	0.020 0(1)
C(116)	0.106 6(2)	0.009 5(4)	0.053 1(1)
C(121)	0.128 2(3)	-0.133 4(4)	0.164 4(1)
C(122)	0.062 3(3)	-0.181 8(5)	0.169 4(1)
C(123)	0.054 2(5)	-0.265 6(6)	0.200 5(2)
C(124)	0.113 1(9)	-0.295 3(7)	0.226 4(2)
C(125)	0.174 7(7)	-0.243 9(11)	0.220 2(2)
C(126)	0.185 2(3)	-0.165 5(6)	0.190 0(2)

of the adduct (5) have been described.¹ The orange-red minor product, the cyclopentathiazolone (8), had m.p. 241–242 °C; ν_{\max} (Nujol) 1 710, 1 600, 1 565w, 1 485, 1 465, and 1 445 cm^{-1} , τ (CDCl_3) 1.80–3.40 (m, Ar); m/e 547 (M^+ , 5.5%), 519(39), 442(55), 414(100), 178(72), 105(19), and 77(70) (Found: C, 78.5; H, 4.65; N, 7.5. $\text{C}_{36}\text{H}_{25}\text{N}_3\text{OS}$ requires C, 78.9; H, 4.6; N, 7.7%).

Crystal Data.—*Compound* (5), $\text{C}_{42}\text{H}_{30}\text{N}_4\text{OS}$. Triclinic, $M = 638.8$, $a = 19.933(6)$, $b = 9.755(3)$, $c = 36.515(12)$ Å, $\alpha = 87.429(8)$, $\beta = 102.659(6)$, $\gamma = 99.675(4)^\circ$, $U = 6 828.3$ Å³, $Z = 8$, $D_c = 1.242$ g cm^{-3} , $F(000) = 2 672$. Space group $F\bar{1}$, $\mu(\text{Cu}-K\alpha) = 11.25$ cm^{-1} .

Compound (8), $\text{C}_{36}\text{H}_{25}\text{N}_3\text{OS}$. Triclinic, $M = 547.7$, $a = 14.855(2)$, $b = 19.816(3)$, $c = 19.335(3)$ Å, $\alpha = 94.260(6)$, $\beta = 90.815(6)$, $\gamma = 93.041(8)^\circ$, $U = 5 667.1$ Å³, $Z = 8$, $D_c = 1.283$ g cm^{-3} , $F(000) = 2 288$. Space group $F\bar{1}$, $\mu(\text{Cu}-K\alpha) = 12.52$ cm^{-1} .

Both compounds form red lath-shaped crystals elongated about b for (5) and a for (8). Preliminary cell dimensions and space-group information were obtained from Weissenberg and precession photographs using suitable crystal fragments mounted about these respective axes; Ni-filtered copper radiation was used throughout data collection. Accurate cell dimensions were obtained by the least-squares refinement of the θ values of the $\text{Cu}-K\alpha_1$ components ($\lambda = 1.540 5$ Å) of 20 reflections measured on a Hilger and Watts Y 290 automated four-circle diffractometer.

Intensity data were measured on a Y 290 diffractometer in the ranges $0 \leq \theta \leq 50$ for (5) and for (8) by use of the ω - 2θ step scanning technique with an ω step size of 0.01° and a counting time of 1 s per step. The width of scan for

TABLE 4

Positional parameters for non-hydrogen atoms in (8), with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
S	0.131 61(5)	0.273 14(4)	0.276 42(4)
C(2)	0.229 8(2)	0.316 7(2)	0.311 4(2)
N(3)	0.293 4(2)	0.334 5(1)	0.273 0(1)
C(4)	0.276 1(2)	0.312 8(2)	0.200 0(2)
C(5)	0.348 3(2)	0.262 4(2)	0.181 5(2)
C(6)	0.306 6(2)	0.193 2(1)	0.171 8(1)
C(7)	0.216 4(2)	0.194 9(1)	0.179 4(1)
C(8)	0.184 8(2)	0.266 5(2)	0.191 0(2)
O(9)	0.427 7(2)	0.279 2(1)	0.178 4(1)
N(10)	0.238 6(2)	0.333 4(1)	0.383 9(1)
N(11)	0.166 6(2)	0.320 2(1)	0.414 3(1)
C(41)	0.281 2(2)	0.374 4(2)	0.157 3(2)
C(42)	0.237 3(2)	0.431 5(2)	0.179 3(2)
C(43)	0.238 0(3)	0.487 5(2)	0.140 1(3)
C(44)	0.284 0(3)	0.487 2(2)	0.079 0(3)
C(45)	0.327 9(3)	0.431 4(2)	0.056 3(2)
C(46)	0.326 8(2)	0.374 7(2)	0.095 4(2)
C(61)	0.362 9(2)	0.135 6(2)	0.152 5(2)
C(62)	0.449 4(2)	0.133 6(2)	0.180 6(2)
C(63)	0.504 9(2)	0.082 8(2)	0.158 0(2)
C(64)	0.475 7(3)	0.033 9(2)	0.107 6(2)
C(65)	0.390 0(3)	0.034 7(2)	0.080 0(2)
C(66)	0.333 3(2)	0.085 3(2)	0.102 0(2)
C(71)	0.151 4(2)	0.135 5(2)	0.182 4(2)
C(72)	0.173 8(2)	0.082 4(2)	0.220 6(2)
C(73)	0.114 0(3)	0.027 7(2)	0.227 4(2)
C(74)	0.031 0(3)	0.024 1(2)	0.194 2(3)
C(75)	0.007 4(3)	0.076 4(2)	0.157 4(3)
C(76)	0.066 3(2)	0.132 6(2)	0.151 4(2)
C(81)	0.123 4(2)	0.286 9(1)	0.133 3(2)
C(82)	0.143 6(2)	0.268 0(2)	0.065 1(2)
C(83)	0.093 9(3)	0.290 0(2)	0.010 8(2)
C(84)	0.022 8(3)	0.329 7(2)	0.023 5(2)
C(85)	0.001 5(2)	0.347 9(2)	0.090 4(2)
C(86)	0.050 7(2)	0.326 9(2)	0.145 6(2)
C(111)	0.170 5(2)	0.333 5(2)	0.487 3(2)
C(112)	0.089 3(3)	0.335 6(3)	0.519 3(2)
C(113)	0.085 9(3)	0.345 1(4)	0.590 6(2)
C(114)	0.163 2(3)	0.352 3(3)	0.628 5(2)
C(115)	0.244 5(3)	0.352 1(3)	0.597 1(2)
C(116)	0.248 6(3)	0.342 7(2)	0.526 2(2)

each reflection was evaluated as an integral number of steps from the expression $(A + B \cdot \tan\theta)$ where A was 80 steps for (5) and 85 steps for (8) and B is a dispersion constant for $\text{Cu}-K\alpha$ radiation (0.142°). A background count was taken at both ends of each scan for 0.1 of the total time taken for the scan. The intensities of three reference reflections measured after every 50 reflections were used to scale the observed intensities by interpolation between groups of references. 3 528 Independent reflections were obtained for (5) of which 2 808 were considered significant, having $I \leq 3\sigma(I)$; values for (8) are 2 911 and 2 380. Symmetry-related reflections [787 for (5), 902 for (8)] were

collected over the low-angle ranges to check for internal consistency and weighted averages for these reflections were incorporated in the sets of independent reflections. Lorentz and polarisation corrections were applied to all reflections but no corrections were made for absorption. For both compounds a set of normalised structure factors, $|E_h|$, was computed from the observed structure factors using the *K*-curve method of Karle and Karle.⁶

Structure Solution and Refinement.—Details of the solution and refinement of both structures are given in the Supplementary Publication. In both cases a weighted multi-solution tangent formula refinement⁷ was used to determine an initial set of phases leading to a partial structure and from which the complete structure was determined using the iterative Fourier-synthesis technique.

Refinement of both structures was carried out using a full-matrix least-squares technique and initially all non-hydrogen atoms were treated isotropically. Most of the hydrogen atoms were located from difference-Fourier syntheses but in subsequent calculations these atoms were placed in calculated positions assuming C-H 1.0 Å; no attempts were made to refine the positional or thermal parameters of the hydrogen atoms. Further refinement with the non-hydrogen atoms treated anisotropically proceeded by a partial full-matrix technique in which no more than 21 atoms (189 parameters) were permitted to vary in any one cycle although an overall scale factor was always refined.

The weighting scheme $w = a_3$ for $|F_o| < F_{\min}$, else $w =$

* See Notice to Authors No. 7 in *J.C.S. Perkin I*, 1976, Index issue.

$[1 - \exp(-a_0 \sin^2\theta/\lambda^2)]/(a_1 + |F_o| + a_2|F_o|^2)$ was used to make the average values of $w\Delta^2$ uniform when analysed in terms of batches of increasing $|F_o|$ and $\sin\theta/\lambda$. The final unweighted residuals *R* are 0.046 for (5) and 0.040 for (8); the corresponding weighted residuals *R'* are 0.051 and 0.054.

Difference-Fourier syntheses computed after the final refinement cycles showed no significant details and structure-factor calculations for the insignificant reflections showed no outstanding discrepancies. Throughout structure-factor calculations atomic scattering factors listed in ref. 8 were used and all computations were performed on a CDC 6 600 computer at the University of London Computer Centre.

Final atomic co-ordinates for (5) and (8) are given in Tables 3 and 4. Satisfactory tensor analyses of the anisotropic thermal vibration parameters were obtained in all cases.

Observed and calculated structure factors, details of the solution and refinement of the structures, anisotropic thermal parameters and calculated positional parameters for the hydrogen atoms, are contained in Supplementary Publication No. SUP 21944 (29 pp., 1 microfiche).*

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⁶ J. Karle and I. L. Karle, in 'Computing Methods in Crystallography,' ed. J. S. Rollett, Pergamon, Oxford, 1965, p. 151.

⁷ G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

⁸ H. P. Hanson, F. Herman, J. D. Lea, and S. Skilman, *Acta Cryst.*, 1964, **17**, 1044.