

Discussion. Bond lengths and angles and pertinent torsion angles with estimated standard deviations are shown in Fig. 1. The 'modified 9-phenylphenalenone ring system' is an acenaphthenone. Thus, while the title compound is not a classical dimer (*i.e.* with two identical fragments), the primed and unprimed segments have a common biosynthetic origin. Both ring systems are flat and non-coplanar [C(4)–C(5)–C(2')–C(1') = –75°]; they are joined at C(5) and C(2'). The phenyl rings are about –53° out of plane and the C(17) and C(16') methyl groups are nearly ($\pm 5^\circ$) in the planes of the larger aromatic systems. On the other hand, the C(16) and C(15') methyl groups are not coplanar with the larger aromatic ring systems as the result of non-bonded repulsions with C(7) and O(C4'), respectively (Fig. 2).

The bond distances and angles for the heavier atoms compare favorably with those observed in other compounds (Ruble, Hite & Soares, 1976, and previous

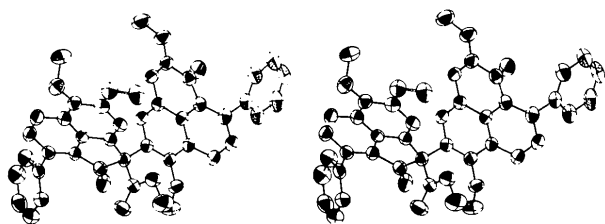


Fig. 2. Stereoprojection down the *z* axis. Atoms are represented by thermal ellipsoids including 50% probability.

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The Structure of 5,6-Dihydro-3-thiobenzoylmethylene-3*H*-thiazolo[2,3-*c*]1,2,4-thiadiazole

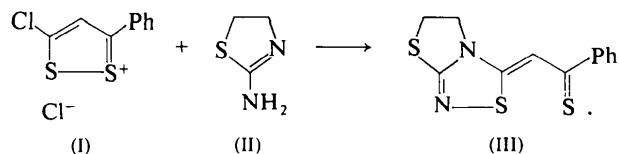
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Abstract. C₁₂H₁₀N₂S₃, monoclinic, *C*2/*c*, *a* = 23.316 (11), *b* = 8.187 (11), *c* = 13.127 (10) Å, β = 103.73 (5)°, *U* = 2434.28 Å³, *M_r* = 278.40, *D_c* = 1.519 Mg m⁻³ for *Z* = 8, *F*(000) = 1152.00, Mo *K*α radiation, λ = 0.71069 Å, μ (Mo *K*α) = 0.521 mm⁻¹; *R* = 0.088 for 1162 reflections. The title compound does not contain a hypervalent S atom.

Introduction. The title compound (III) was obtained from the reaction of 3-chloro-5-phenyl-1,2-dithiol-1-ium chloride (I) with 2-amino-4,5-dihydrothiazole (II):



Crystals suitable for X-ray investigation were provided by Professor D. H. Reid and Mr J. Mitchell.

The intensities of 1426 unique reflections in the quadrant *h*, +*k*, ±*l*, with 2° ≤ θ ≤ 30°, *k* = 0–10 (0 ≤ *μ*

papers in this series). The aromatic hydrogens (σ = 0.05 Å) are also well defined. The sums of the three associated bond angles for each H are within one estimated standard deviation of 360°, indicating that they are coplanar with the aromatic rings to which they are attached. The positions of the fifteen methyl protons are in general less adequately defined. The body of chemical and physical data now available permits unambiguous structural assignments for the parent dimeric pigment and its analogs. This will be the subject of a forthcoming publication.

We wish to thank The University of Connecticut Computer Center for a generous grant.

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$\leq 25.723^\circ$), were measured, using a Stoe STADI-2 diffractometer in the ω - 2θ scan mode, with graphite-monochromatized Mo $K\alpha$ radiation: the scan speed was $0.0167^\circ \text{ s}^{-1}$ in ω , and backgrounds were measured at each end of the peak scan for a time of (scan time/2). Standard reflections were measured every fifty reflections and showed only small random deviations from their means. Lorentz and polarization corrections were applied to the data, but no corrections for absorption were made.

Systematic absences were: in hkl , $h + k \neq 2n$, in $h0l$, $l \neq 2n$, and in $0k0$, $k \neq 2n$, indicating Cc or $C2/c$. $C2/c$

Table 1. Fractional atomic coordinates ($\times 10^4$; for H $\times 10^3$)

	x	y	z
S(1)	9618 (1)	3616 (4)	3643 (2)
S(2)	8099 (1)	3757 (5)	4815 (2)
S(3)	773 (2)	2610 (5)	3966 (2)
N(1)	8895 (4)	4167 (13)	3572 (7)
N(2)	9210 (4)	2968 (11)	5184 (6)
C(1)	9730 (5)	2806 (13)	4887 (8)
C(2)	8757 (5)	3652 (17)	4422 (8)
C(3)	8461 (6)	3066 (21)	6115 (12)
C(4)	9055 (5)	2448 (18)	6137 (8)
C(5)	234 (5)	2117 (15)	5512 (8)
C(6)	751 (5)	1964 (14)	5163 (8)
C(7)	1278 (4)	1219 (14)	5902 (8)
C(8)	1239 (5)	181 (15)	6698 (8)
C(9)	1735 (5)	-487 (15)	7354 (9)
C(10)	2289 (5)	-56 (17)	7240 (10)
C(11)	2350 (5)	974 (17)	6451 (10)
C(12)	1851 (5)	1667 (16)	5770 (10)
H(31)	820 (1)	216 (2)	639 (1)
H(32)	852 (1)	411 (2)	663 (1)
H(41)	903 (1)	113 (2)	615 (1)
H(42)	938 (1)	287 (2)	681 (1)
H(5)	17 (7)	132 (22)	624 (13)
H(8)	84 (5)	-26 (13)	686 (8)
H(9)	174 (4)	-155 (14)	796 (8)
H(10)	273 (5)	-67 (13)	766 (8)
H(11)	266 (5)	188 (14)	641 (8)
H(12)	184 (5)	254 (14)	524 (8)

Table 2. Bond distances (Å)

S(1)-N(1)	1.727 (10)	C(8)-C(9)	1.379 (15)
S(1)-C(1)	1.723 (11)	C(9)-C(10)	1.382 (17)
S(2)-C(2)	1.734 (11)	C(10)-C(11)	1.369 (17)
S(2)-C(3)	1.806 (14)	C(11)-C(12)	1.409 (17)
S(3)-C(6)	1.670 (11)	C(3)-H(31)	1.08*
N(1)-C(2)	1.302 (13)	C(3)-H(32)	1.08*
N(2)-C(1)	1.365 (12)	C(4)-H(41)	1.08*
N(2)-C(2)	1.388 (13)	C(4)-H(42)	1.08*
N(2)-C(4)	1.447 (12)	C(5)-H(5)	1.2 (2)
C(1)-C(5)	1.384 (14)	C(8)-H(8)	1.1 (1)
C(3)-C(4)	1.467 (15)	C(9)-H(9)	1.2 (1)
C(5)-C(6)	1.393 (14)	C(10)-H(10)	1.2 (1)
C(6)-C(7)	1.503 (14)	C(11)-H(11)	1.1 (1)
C(7)-C(8)	1.367 (15)	C(12)-H(12)	1.0 (1)
C(7)-C(12)	1.433 (15)		

* H(31), H(32), H(41), and H(42) are in calculated positions.

was confirmed by the structure solution and refinement.

The structure was solved in $C2/c$ by direct methods using *SHELX* 76 (Sheldrick, 1976). The best E map gave positions for all the non-hydrogen atoms, and three cycles of full-matrix least-squares refinement gave an R ($= \sum \Delta / \sum F_o$, $\Delta = |F_o - F_c|$) of 0.2357 and an R_G [$= (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$] of 0.2625. Introduction of anisotropic temperature parameters for the S and N atoms reduced R to 0.1269 and R_G to 0.1527, and for the non-phenyl C atoms reduced R to 0.1196 and R_G to 0.1453. The unique H(5) atom and the phenyl H atoms were located by means of a difference map: introduction of these atoms, with a common isotropic temperature factor for the phenyl hydrogens and anisotropic temperature factors for all non-hydrogen atoms, reduced R to 0.0900 and R_G to 0.0958 for 1162 intensity data having $F_o \geq 6\sigma(F_o)$. The four H atoms attached to C(3) and C(4) could not be identified unambiguously in a difference map, and they were placed in calculated positions with $d(\text{C}-\text{H}) = 1.080 \text{ \AA}$ and $\angle(\text{HCH}) = 109.5^\circ$ and allocated a common isotropic temperature parameter; R was reduced to 0.0880 and R_G to 0.0916. When the constraints on the positions of these atoms were released R_G was reduced to 0.0910, but the geometrical parameters associated with these atoms were not acceptable: their positions were not well determined by the X-ray data.

In the final cycles of refinement, with the H atoms attached to C(3) and C(4) in calculated positions, 175 parameters were simultaneously varied, comprising 69 positional coordinates, 102 anisotropic temperature factor components, three isotropic thermal parameters, and one overall scale factor; a final difference synthesis showed no unexpected features. Complex

Table 3. Bond angles ($^\circ$)

N(1)-S(1)-C(1)	94.5 (5)	S(3)-C(6)-C(7)	122.1 (8)
C(2)-S(2)-C(3)	91.0 (5)	C(5)-C(6)-C(7)	117.7 (9)
S(1)-N(1)-C(2)	107.7 (8)	C(6)-C(7)-C(8)	123.5 (10)
C(1)-N(2)-C(2)	114.2 (8)	C(6)-C(7)-C(12)	117.5 (10)
C(2)-N(2)-C(4)	115.9 (9)	C(8)-C(7)-C(12)	119.0 (10)
S(1)-C(1)-N(2)	106.7 (7)	C(7)-C(8)-C(9)	121.7 (11)
S(1)-C(1)-C(5)	129.5 (8)	C(7)-C(8)-H(8)	126 (6)
N(2)-C(1)-C(5)	123.8 (9)	C(9)-C(8)-H(8)	113 (6)
S(2)-C(2)-N(2)	112.4 (8)	C(8)-C(9)-C(10)	119.8 (12)
N(1)-C(2)-N(2)	116.6 (9)	C(8)-C(9)-H(9)	126 (5)
S(2)-C(3)-C(4)	110.7 (9)	C(10)-C(9)-H(9)	114 (5)
S(2)-C(3)-H(31)	111.3*	C(9)-C(10)-C(11)	120.5 (12)
S(2)-C(3)-H(32)	107.9*	C(9)-C(10)-H(10)	126 (5)
N(2)-C(4)-C(3)	108.1 (10)	C(11)-C(10)-H(10)	113 (5)
N(2)-C(4)-H(41)	109.5*	C(10)-C(11)-C(12)	120.6 (12)
N(2)-C(4)-H(42)	109.6*	C(10)-C(11)-H(11)	132 (6)
C(1)-C(5)-C(6)	121.4 (10)	C(12)-C(11)-H(11)	99 (6)
C(1)-C(5)-H(5)	117 (8)	C(7)-C(12)-C(11)	118.3 (11)
C(6)-C(5)-H(5)	120 (8)	C(7)-C(12)-H(12)	113 (7)
S(3)-C(6)-C(5)	120.2 (9)	C(11)-C(12)-H(12)	128 (7)

* H(31), H(32), H(41), and H(42) are in calculated positions.

Table 4. *Least-squares planes*Planes are defined in orthogonal ångström coordinates by the equation: $Ax + By + Cz + 1 = 0$.

Plane	Atoms	A	B	C	Atom distances from plane ($\text{Å} \times 10^{-3}$)
1	S(1), N(1), N(2), C(1), C(2)	-0.0226	-0.1029	-0.0459	S(1), 14; N(1), -27; N(2), -15; C(1), -16; C(2), 32; S(2), 80; S(3), 78; C(5), -8; C(6), 24
2	C(7), C(8), C(9), C(10), C(11), C(12)	+0.0480	-0.3075	-0.2476	C(7), 8; C(8), -7; C(9), 10; C(10), -12; C(11), 9; C(12), -4; C(6), 3

The dihedral angle between the planes is 23.5° .

neutral-atom scattering factors were used for all atoms (Cromer & Mann, 1968; Doyle & Turner, 1968; Cromer & Liberman, 1970). The reduction in R_G was significant at the 99.5% level (Hamilton, 1965) for each stage of the refinement, except for the removal of the constraints on the H atoms on C(3) and C(4).

The final atomic coordinates are in Table 1, bond distances in Table 2, bond angles in Table 3, and

least-squares planes in Table 4. Fig. 1 shows the molecule and the numbering scheme, and Fig. 2 the unit-cell contents; the atom numbering in Fig. 1 is non-standard.*

Discussion. The structure determination shows that the compound should be represented as (III) rather than (IV) as the S-N distance is $1.727(10)$ Å and S-S $2.750(5)$ Å. In the compounds (V)-(VII), containing hypervalent S atoms at the centres of NSS chains, the

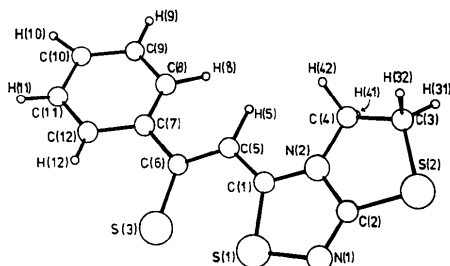


Fig. 1. The molecule showing the atom-numbering scheme.

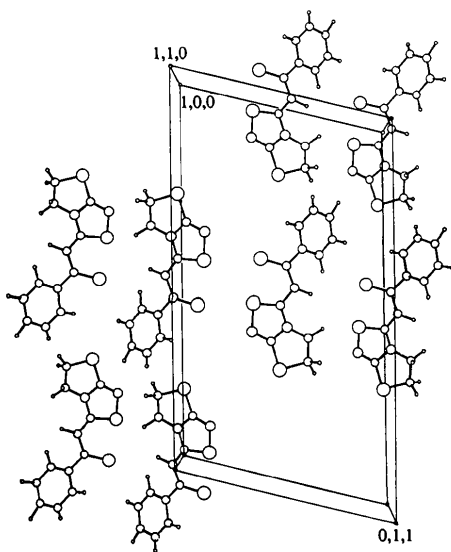
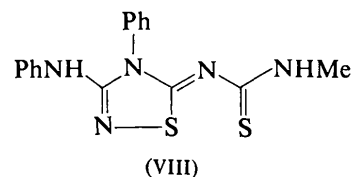
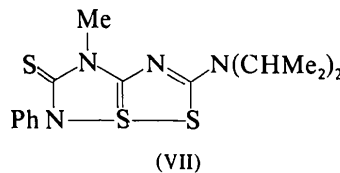
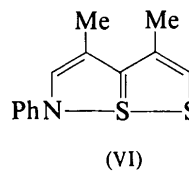
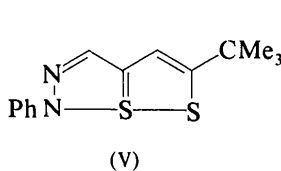
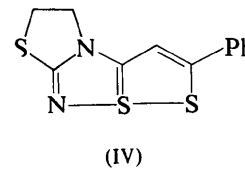
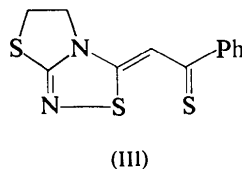


Fig. 2. The contents of the unit cell.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35035 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

N—S distances are 1.849 Å (Hansen & Tomren, 1977) in (V), 1.779 Å (Darmo & Hansen, 1977) in (VI) and 1.863 Å (Hansen, 1977) in (VII), all much longer than the 1.727 Å in (III), while the S—S distances in (V), (VI) and (VII) are 2.435, 2.493, and 2.447 Å respectively, all shorter than the 2.750 Å in (III). The overall N...S distances in (V), (VI) and (VII), 4.273, 4.267, and 4.290 Å respectively, are also rather shorter than the 4.471 Å in (III).

It is interesting that (VIII), the adduct of Hector's base and methyl isothiocyanate, has a skeleton very similar to that of (III) with S—N 1.705 Å, and S—S 2.808 Å (Cuthbertson, Glidewell & Holden, 1980).

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Arsatriptycene and Phosphatriptycene

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Abstract. C₁₉H₁₃As, monoclinic, *Cc*, $a = 15.316$ (5), $b = 8.310$ (2), $c = 13.305$ (3) Å, $\beta = 121.02$ (1)°, $Z = 4$. C₁₉H₁₃P, monoclinic, *Cc*, $a = 15.074$ (2), $b = 8.210$ (1), $c = 13.207$ (2) Å, $\beta = 120.53$ (2)°, $Z = 4$. The two compounds are isostructural and consist of densely packed layers parallel to (10 $\bar{1}$) in which the molecular quasi-threefold axes are nearly perpendicular to the layers. Both structures show the same kind of disorder in which a fraction of the molecules have As(P) and the bridgehead C atom interchanged. Phosphatriptycene shows twinning on (10 $\bar{1}$).

Introduction. The aim of the investigation was to obtain information about the geometry around As and P.

Arsatriptycene (AT) was prepared by Vermeer, Kevenaar & Bickelhaupt (1972). 1119 reflexions with $I > 2\sigma(I)$ were collected on a Nonius CAD-3 diffractometer with Cu $K\alpha$ radiation. The structure was obtained from a Patterson minimum function based on the positions of the two translation-independent As atoms in the unit cell. During the refinement a ΔF synthesis showed the As atom to be electron deficient, whilst a prominent peak appeared near the bridgehead C(19).

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(For the atomic numbering see Fig. 1.) This was interpreted as being due to disorder, some of the molecules being in an alternative orientation with As and C(19) interchanged. A peak corresponding to the vector between the two partially occupied As positions was indeed present in the Patterson synthesis. The ring planes in the two orientations more or less coincide but not so the individual atoms. The situation is indicated in Fig. 2. The ring atoms are at most 0.3 Å from their counterparts and could not be refined separately. Anisotropic block-diagonal least-squares refinement of As(I), As(II), C(19)(I), C(19)(II) and average positions for the ring atoms converged to $R = 0.066$. The population parameters for the two positions of As and C(19) refined to 0.65 and 0.35. The H atoms were introduced and kept fixed at calculated positions. Introduction of an absorption correction and an extinction parameter resulted in a final R of 0.041. The final parameters are listed in Table 1.†

† Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35041 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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