

Table 4. *Hydrogen-bond geometry*

Superscript (I) refers to equivalent position  $x, -\frac{1}{2} - y, \frac{1}{2} + z$ . E.s.d.'s for distances not involving hydrogen atoms are ca 0.01 Å.

Molecule			Molecule	Distance (Å)	Angle (°)	
N(1)	B	...O(3)	B <sup>I</sup>	2.65	H[O(3)]B <sup>I</sup> —O(3)B <sup>I</sup> ...N(1)B	17
		...H[O(3)]	B <sup>I</sup>	1.73		
O(3)	B	...O(3)	A	2.81	H[O(3)]A—O(3)A...O(3)B	21
		...H[O(3)]	A	1.80		
N(4)	B	...N(12)	A	3.03	H[N(12)]A—N(12)A...N(4)B	24
		...H[N(12)]	A	2.22		
N(4)	A	...N(12)	B	3.10	H[N(12)]B—N(12)B...N(4)A	24
		...H[N(12)]	B	2.24		

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## The Structure of (±)-Methyl 4,5-Dimethoxy-2-(2,6-dimethoxy-1-oxo-9-phenyl-5-phenalenyl)-1-oxo-8-phenyl-1,2-dihydro-2-acenaphthylenecarboxylate

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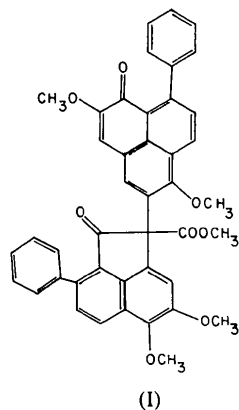
(Received 18 September 1979; accepted 14 January 1980)

**Abstract.** C<sub>43</sub>H<sub>32</sub>O<sub>8</sub>,  $M_r = 676.72$ , m.p. 447–449 K, *Pbca*,  $a = 19.874$  (5),  $b = 29.835$  (8),  $c = 11.569$  (2) Å,  $Z = 8$ ,  $D_x = 1.310$ ,  $D_m$  (flotation H<sub>2</sub>O/KI) = 1.304 Mg m<sup>-3</sup>; 4345 reflections,  $2\theta < 110^\circ$ ,  $741 < 3\sigma(F_o)$ . The structure was solved by direct methods. Full-matrix least-squares refinement converged at  $R = 0.045$ . The points of attachment of the two monomeric units were established.

**Introduction.** While the pigments of *Lachnanthes*

*tinctoria* Ell. (Haemodoraceae) contain either an intact or a modified 9-phenylphenalenone ring system (Harmon, Edwards & Hight, 1977, and previous papers in this series) one pigment isolated from the seeds of the plant appeared to contain both. Although considerable chemical and physical data have been developed for this unique, amorphous, dimeric pigment and its derivatives, the nature of the modified segment and the points of attachment of the two monomeric units remained obscure. For this reason, a permethylated, crystalline derivative, (I), was subjected to X-ray analysis.

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Photographs of a crystal (0.2 × 0.1 × 0.05 mm, from ethyl acetate) of the title compound revealed orthorhombic symmetry and led to the assignment of space group *Pbca*. Lattice parameters and intensity data were measured with Ni-filtered Cu *K*α radiation ( $\lambda = 1.5404 \text{ \AA}$ ) at 298 K using a computer-controlled Picker FACS-I four-circle diffractometer. Lattice parameters were refined by least-squares fitting of 30 automatically centered reflections ( $32^\circ < 2\theta < 50^\circ$ ). Four standard reflections remained constant  $|\pm 2\sigma(I)_{av}|$  throughout the data collection. Of 4345 independent reflections ( $2\theta < 110^\circ$ ) measured in the  $\theta/2\theta$  scan mode, 741 were considered unobserved according to the criterion  $|F_o| > 3.0\sigma$ . These were not

Table 1. *Positional parameters* ( $\times 10^4$  except hydrogens  $\times 10^3$ ) given as fractions of the lattice translations

Estimated standard deviations in the last figure are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
O(C1)	6178 (1)	3545 (1)	-2515 (2)	O(C1')	8944 (1)	1745 (1)	-1187 (2)
O(C2)	5624 (1)	2829 (1)	-3417 (2)	O(C4')	6110 (1)	330 (1)	251 (2)
O(C6)	8241 (1)	2278 (1)	1372 (2)	O(C5')	6599 (1)	-59 (1)	-1669 (2)
C(1)	6293 (1)	3189 (1)	-2028 (2)	O(C17'a)	8940 (1)	1313 (1)	1184 (2)
C(2)	6071 (1)	2764 (1)	-2552 (2)	O(C17'b)	7924 (1)	1384 (1)	1977 (2)
C(3)	6339 (1)	2373 (1)	-2222 (2)	C(1')	8519 (1)	1457 (1)	-1034 (2)
C(3a)	6826 (1)	2351 (1)	-1301 (2)	C(2')	7990 (1)	1476 (1)	-30 (2)
C(4)	7132 (1)	1957 (1)	-1011 (2)	C(2'a)	7546 (1)	1073 (1)	-303 (2)
C(5)	7621 (1)	1922 (1)	-130 (2)	C(3')	6988 (1)	904 (1)	248 (2)
C(6)	7779 (1)	2298 (1)	491 (2)	C(4')	6667 (1)	526 (1)	-229 (2)
C(6a)	7442 (1)	2713 (1)	276 (2)	C(5')	6897 (1)	326 (1)	-1244 (2)
C(7)	7543 (1)	3092 (1)	970 (2)	C(5'a)	7462 (1)	496 (1)	-1819 (2)
C(8)	7194 (1)	3482 (1)	759 (2)	C(6')	7753 (1)	337 (1)	-2858 (2)
C(9)	6750 (1)	3524 (1)	-187 (2)	C(7')	8320 (1)	535 (1)	-3311 (2)
C(9a)	6667 (1)	3157 (1)	-920 (2)	C(8')	8652 (1)	905 (1)	-2773 (2)
C(9b)	6981 (1)	2745 (1)	-649 (2)	C(8'a)	8638 (1)	1066 (1)	-1764 (2)
C(10)	6378 (1)	3955 (1)	-333 (2)	C(8'b)	7784 (1)	866 (1)	-1314 (2)
C(11)	5685 (1)	3959 (1)	-437 (3)	C(9')	9279 (1)	1088 (1)	-3287 (2)
C(12)	5337 (2)	4353 (1)	-589 (3)	C(10')	9861 (1)	1123 (1)	-2659 (3)
C(13)	5692 (2)	4753 (1)	-632 (3)	C(11')	10450 (1)	1287 (1)	-3179 (3)
C(14)	6372 (2)	4761 (1)	-499 (3)	C(12')	10433 (2)	1428 (1)	-4310 (3)
C(15)	6720 (1)	4356 (1)	-343 (3)	C(13')	9853 (2)	1393 (1)	-4939 (3)
C(16)	8893 (2)	2474 (1)	1105 (3)	C(14')	9277 (2)	1220 (1)	-4439 (3)
C(17)	5370 (2)	2435 (1)	-3982 (3)	C(15')	5946 (2)	8 (1)	-2188 (4)
				C(16')	5884 (2)	493 (1)	1349 (3)
				C(17')	8347 (1)	1393 (1)	1105 (2)
				C(18')	8226 (2)	1304 (1)	3109 (3)
H(C3)	621 (1)	208 (1)	-265 (2)	H(C3')	680 (1)	102 (1)	100 (2)
H(C4)	700 (1)	168 (1)	-146 (2)	H(C6')	754 (1)	7 (1)	-326 (2)
H(C7)	787 (1)	307 (1)	160 (2)	H(C7')	848 (1)	41 (1)	-407 (2)
H(C8)	724 (1)	373 (1)	130 (2)	H(C10')	990 (1)	104 (1)	-181 (2)
H(C11)	546 (1)	367 (1)	-34 (3)	H(C11')	1091 (1)	134 (1)	-267 (3)
H(C12)	480 (2)	437 (1)	-68 (3)	H(C12')	1083 (1)	153 (1)	-470 (2)
H(C13)	543 (1)	503 (1)	-80 (2)	H(C13')	983 (2)	148 (1)	-579 (3)
H(C14)	666 (1)	506 (1)	-48 (2)	H(C14')	884 (1)	119 (1)	-490 (3)
H(C15)	725 (1)	437 (1)	-29 (3)	H(C15'a)	79 (2)	530 (1)	250 (4)
H(C16a)	929 (2)	234 (2)	167 (4)	H(C15'b)	160 (3)	506 (2)	167 (4)
H(C16b)	889 (2)	269 (1)	50 (4)	H(C15'c)	102 (3)	488 (2)	290 (4)
H(C16c)	900 (3)	262 (1)	183 (6)	H(C16'a)	573 (1)	82 (1)	128 (2)
H(C17a)	515 (1)	224 (1)	-335 (3)	H(C16'b)	633 (2)	51 (1)	194 (3)
H(C17b)	575 (1)	225 (1)	-437 (3)	H(C16'c)	554 (2)	30 (1)	150 (3)
H(C17c)	505 (2)	257 (1)	-452 (3)	H(C18'a)	857 (2)	152 (2)	323 (4)
				H(C18'b)	889 (3)	121 (2)	280 (5)
				H(C18'c)	791 (4)	129 (2)	358 (5)

included in the refinement. Integrated intensities were corrected for Lorentz and polarization effects but no absorption correction was applied. The structure was solved by direct methods using the program *MULTAN*, with magic integers (Declercq, Germain & Woolson, 1975). This revealed the positions of all 51 heavy atoms. Full-matrix least-squares refinement (Busing, Martin & Levy, 1962), with a  $1/\sigma^2$  weighting scheme, zerovalent scattering factors (*International Tables for X-ray Crystallography*, 1974) isotropic temperature factors and corrections for secondary extinction, was followed by anisotropic refinement. This was carried out by repeatedly refining the primed then the unprimed atom parameters until convergence at  $R = 0.087$ . The function minimized was  $\sum w (|F_o| - |F_c|)^2$ . A difference Fourier map revealed acceptable positions for all

32 H atoms from among the 40 strongest peaks. Refinement of the H atom parameters, including isotropic thermal parameters which were initially assigned values of  $5.0 \text{ \AA}^2$ , was followed by refinement of the structure in three segments, the primed, the unprimed and the H atom parameters. Refinement converged at  $R = 0.045^*$  at which point parameter shifts were less than  $0.5\sigma$ . Final atomic positional parameters with estimated standard deviations (Busing, Martin & Levy, 1964) are in Table 1.

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34980 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

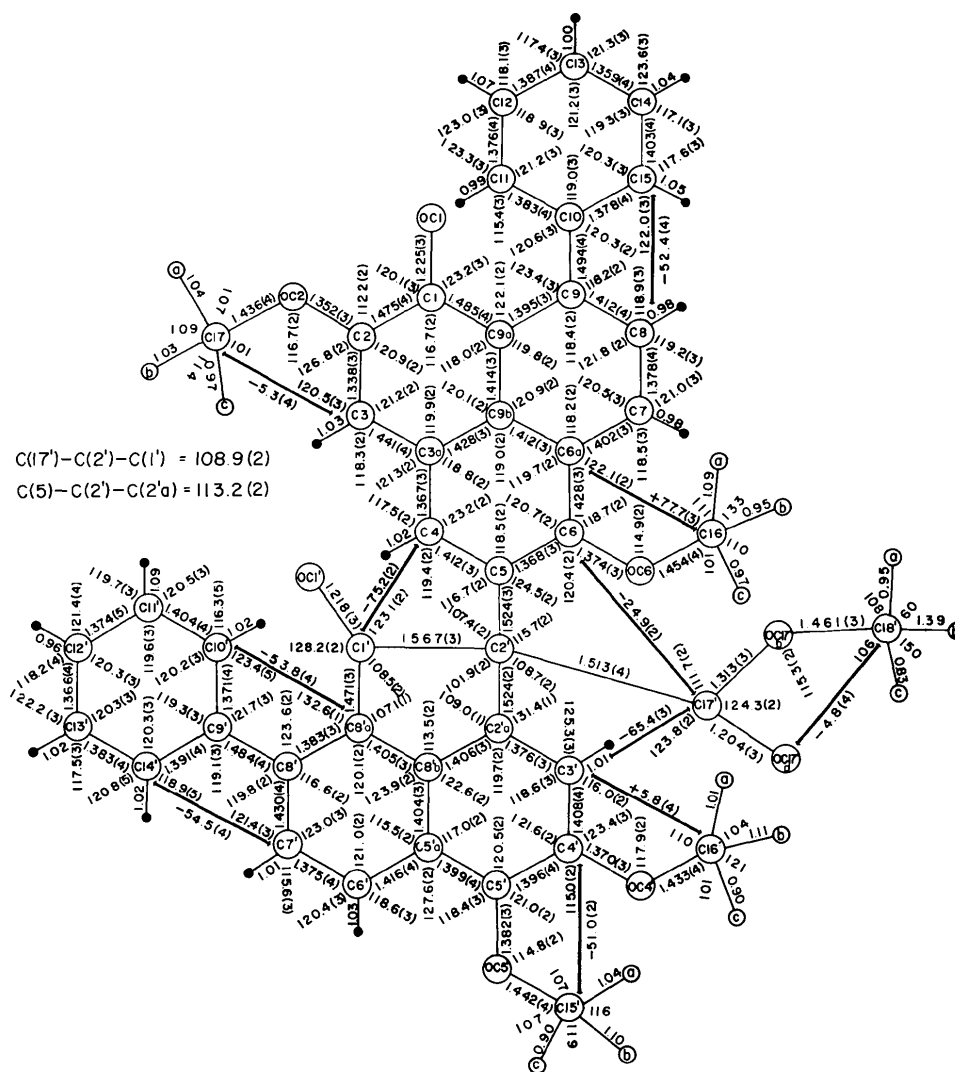


Fig. 1. Bond lengths (Å) and bond and torsion angles (°). Estimated standard deviations (except hydrogen =  $0.05 \text{ \AA}$ ) in the last figures are given in parentheses.

**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

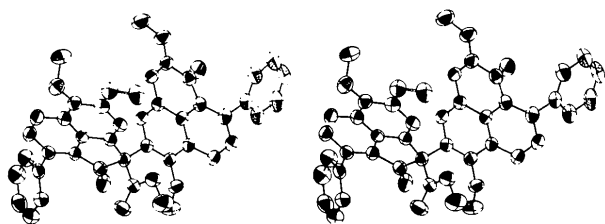


Fig. 2. Stereoprojection down the *z* axis. Atoms are represented by thermal ellipsoids including 50% probability.

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

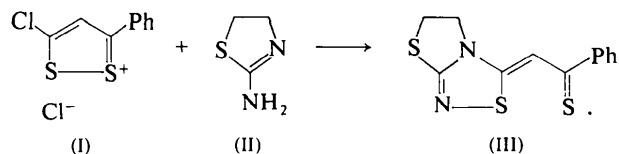
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**Abstract.** C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>S<sub>3</sub>, monoclinic, *C*2/*c*, *a* = 23.316 (11), *b* = 8.187 (11), *c* = 13.127 (10) Å,  $\beta$  = 103.73 (5)°, *U* = 2434.28 Å<sup>3</sup>, *M<sub>r</sub>* = 278.40, *D<sub>c</sub>* = 1.519 Mg m<sup>-3</sup> for *Z* = 8, *F*(000) = 1152.00, Mo *K*α radiation,  $\lambda$  = 0.71069 Å,  $\mu$ (Mo *K*α) = 0.521 mm<sup>-1</sup>; *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° ≤  $\theta$  ≤ 30°, *k* = 0–10 (0 ≤ *μ*

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papers in this series). The aromatic hydrogens ( $\sigma$  = 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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