Structure of the Channel Inclusion Complex of 1,2,3,4-Tetrahydro-6,8-dihydroxy-1,1,7-tris(3-methylbut-2-enyl)xanthen-2,9-dione (Wightianone, Zeyloxanthonone) with Palmitic Acid

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Abstract. $C_{28}H_{34}O_5.xC_{15}H_{31}COOH$ ($x \simeq 0.2$), nominal $M_r = 450.6 + 0.2(256.4) = 501.9$, orthorhombic, *Pbca*, $a = 29.095$ (4), $b = 9.508$ (2), $c = 20.718$ (2) Å, $V = 5731.3$ Å^3, $Z = 8$, $D_m = 1.16$, $D_x = 1.163$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ(Mo $K\alpha$) = 0.70 cm^{-1}, $F(000) = 2166$, room temperature, $R_F = 0.0962$ for 1910 unique observed reflections. Somewhat different molecular structures have been proposed for the two chemically identical xanthonoid pigments 'wightianone' {isolated from the heartwood of *Calophyllum wightianum* T. Anders and characterized as a 'clathrate' by Dean, Khan, Minhaj, Prakash & Zaman [*J. Chem. Soc. Perkin Trans.* 1 (1984), pp. 1755–1759]} and 'zeyloxanthonone' {isolated as the neat material from *Calophyllum lankaensis* Kosterm by Gunasekera, Sotheeswaran & Sultanbawa [*J. Chem. Soc. Perkin Trans.* 1 (1981), pp. 1831–1835]}. Crystal structure analysis of a sample analogous to the 'clathrate' shows that the pigment is 1,2,3,4-tetrahydro-6,8-dihydroxy-1,1,7-tris(3-methylbut-2-enyl)xanthen-2,9-dione as proposed by Gunasekera *et al.* The 'clathrate' is an inclusion complex in which pigment molecules are hydrogen bonded to give a framework containing channels extended along the **b** direction, with palmitic acid molecules accommodated in these channels in a partially ordered fashion.

Introduction. Xanthonoids are widely distributed in tropical plants (Sultanbawa, 1980). For a pigment named zeyloxanthonone which they had isolated from *Calophyllum lankaensis* Kosterm, Sultanbawa and his colleagues advanced structure (1) (Karunanayake, Sotheeswaran & Sultanbawa, 1979). For a pigment then named wightianone, a component of an extractive from the heartwood of *Calophyllum wightianum* T. Anders (Guttiferae), a similar structure (2) has been proposed (Dean, Khan, Minhaj, Prakash & Zaman, 1980). It was later established that the two pigments were identical, and the only point at issue was the orientation of the hydroaromatic ring (C) with respect to the rest of the molecule (Gunasekera, Sotheeswaran & Sultanbawa, 1981; Dean, Khan, Minhaj, Prakash & Zaman, 1984). The former workers placed the carbonyl group of ring C *para* to the ring oxygen atom mainly because this orientation is typical of related xanthones. The latter preferred the *meta* orientation of oxygen atoms for ring C partly because spectroscopic evidence, though weak, was thought to support it, and partly because of the double substitution by prenyl groups (prenyl = 3-methylbut-2-enyl), all previous examples of *gem* substitution, including one recently observed in an alkaloid (Hufford, Oguntimein, Martin & Clardy, 1984), having been confined to *meta*-dioxygenated systems.

(1)   (3)

(2)   (4)
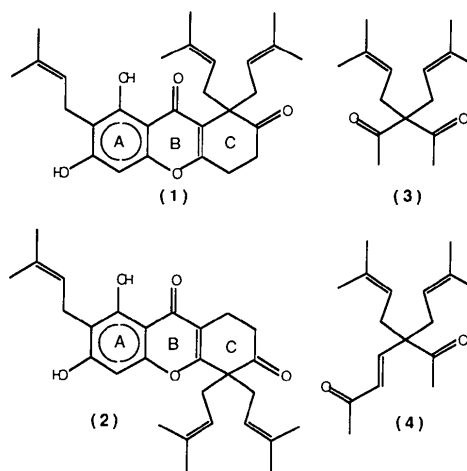
The isolate appeared as the neat compound from *Calophyllum lankaensis* but as a 'clathrate' with palmitic acid (and minor amounts of other long-chain acids) from *Calophyllum wightianum*. We do not attach importance to the fact that the Sri Lankan group appear not to have observed the formation of

$C_{28}H_{34}O_5.xC_{15}H_{31}COOH$ $(x \simeq 0.2)$

an inclusion complex with the fatty acid. It is possible that the bark they used contained no acid or too little (though they state no yields), or that the alkaline wash they included in their workup procedure removed all the fatty acid while leaving behind some of the (somewhat acidic) pigment.

A crystal structure analysis has been carried out in order to settle the disputed orientation of the substituents of ring C and to clarify the nature of the postulated 'clathrate'. The structure (1) proposed by Gunasekera et al. has been confirmed and we shall use only the name 'zeyloxanthonone' in the rest of this paper.* The 'clathrate' is shown to be a channel inclusion complex.

Experimental. The sample used was that reconstituted from a mixture of purified zeyloxanthonone and palmitic acid in molar ratio 6:1 and recrystallized from benzene–petroleum, giving yellow hexagonal prisms elongated along [001], m.p. 429–431 K [see p. 1759 of Dean et al. (1984)]. Best agreement with the chemical analysis for hydrogen was obtained for a composition $5C_{28}H_{34}O_5.C_{15}H_{31}COOH$ (see below for further discussion of the composition). Only a very small amount of material was available and our study was carried out using three crystals, one for the density measurement (by flotation), one (dimensions $0.26 \times 0.26 \times 0.43$ mm) for X-ray diffractometry (Philips PW1100; graphite-monochromated Mo $K\alpha$ radiation) and one for oscillation and Weissenberg photography (Ni-filtered Cu $K\alpha$). Unit-cell dimensions were determined by least-squares from 25 strong reflections in the range $5 \le 2\theta \le 25°$. Crystal (sealed in a capillary) and electronic stability were confirmed by the constancy of three reflections ($\bar{3}04$, 212, 12,0,0) whose intensities were monitored every 120 min (with $\sim 2.5\%$ intensity variation). $\omega/2\theta$ scan technique ($0 \le h \le 31$; $0 \le k \le 10$; $0 \le l \le 22$), scan speed $2°$ ω min^{-1}, scan width $1.2°\omega$, $5 \le 2\theta \le 46°$, 3750 unique reflections, of which 1910 with $F_o > 3\sigma(F_o)$ were used in the structure analysis and final refinement. Lorentz and polarization, but not absorption, corrections were applied. $R_{int} = 3.6\%$ for 1116 pairs of hkl and $\bar{h}kl$ reflections. Structure solved by SHELXS86 (Sheldrick, 1986) direct methods and refined by the SHELX77 (Sheldrick, 1977) system of programs. Anisotropic refinement of all the non-hydrogen atoms of the zeyloxanthonone molecule converged at $R_F = 17.4\%$, inclusion of hydrogens (apart from the methyl hydrogens) with isotropic displacement parameters reduced this to 15.5%. A difference map computed at this stage showed a continuous ridge of electron density of

height ~ 1 e Å^{-3} about the line $x = 0.25$, y, $z \simeq 0.16$, with four peaks of ~ 0.5 e Å^{-3} protruding above the ridge. We assigned this difference density to an ordered arrangement of 'carbon' atoms within the channels; their inclusion (isotropic, half-occupancy) reduced R_F to 13.0%; a further difference synthesis showed a second group of four 'carbons', again assigned half-occupancy and found to have somewhat higher isotropic displacement parameters than the first group. Five more cycles of least-squares refinement {two blocks; non-hydrogen atoms of the zeyloxanthonone molecule given anisotropic displacement parameters, isotropic refinement of all its hydrogens except for methyl hydrogens which were treated as riding atoms [$d(C—H) = 1.08$ Å, $U_{iso} = 0.05$ Å^2] and isotropic refinement of eight atoms of the guest molecule (assigned carbon scattering factors, all having occupancies of 0.5)} converged at $R_F = 9.6\%$ [$wR = 8.3\%$; $w(F_o) = 2.64/\sigma^2(F_o)$]. Maximum and minimum heights in the final difference map were 0.40 and -0.32 e Å^{-3} respectively, with $(\Delta/\sigma)_{max} = 0.37$ for the non-hydrogen atoms. Diagrams by ORTEP (Johnson, 1965). The relatively high R_F factor is presumably due to our inability to include completely the contributions of the guest molecules (see below). Atomic scattering factors were those from SHELX77.

Discussion. The parameters of the non-hydrogen atoms of the zeyloxanthonone molecule and the 'atoms' of the guest are listed in Table 1,* with the crystallographic numbering of the atoms defined in Fig. 1. Bond lengths and angles are in Table 2; the e.s.d.'s of C—C and C—O bond lengths are $\simeq 0.01$ Å, but presumably have been underestimated by $\sim 50\%$ (Taylor & Kennard, 1986). The 1,4-benzopyrone ring skeleton is approximately planar with deviations from the mean plane given in Table 2(c). The cyclohex-3-enone ring has puckering parameters $Q = 0.41$ Å, $\varphi = 199.5°$, $\theta = 64.1°$, from analysis by the method of Cremer & Pople (1975) using Cremer's (1979) program RING. Reference to Boeyens' (1978) diagram indicates that the conformation is approximately screw boat, torsion angles being given in Table 2(d). The gem-diprenyl groups at C(6) and the prenyl group at C(1) are extended roughly normal to the mean plane of the xanthonone ring system. The torsion angles about the 1–2 bonds of the prenyl groups (Table 2e) show that one of the C(6) prenyls and the C(1) prenyl have very similar gauche conformations while the second C(6) prenyl

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* The chemical numbering in the title and elsewhere follows Gunasekera et al., while the crystallographic numbering [atoms denoted as $C(n)$ etc.] used throughout the rest of this paper (apart from chemical names) is defined in the Discussion.

Table 1. *Final fractional coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* (U_{eq}, $\mathrm{\AA}^2 \times 10^3$) *for atoms of the zeyloxanthonone molecule, and isotropic displacement parameters* (U_{iso}, $\mathrm{\AA}^2 \times 10^3$) *for the guest 'atoms'*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}
C(1)	1245 (3)	−1912 (8)	7474 (4)	47 (2)
C(2)	1258 (3)	−1763 (8)	6805 (4)	47 (2)
C(3)	1264 (3)	−446 (8)	6499 (3)	40 (2)
C(4)	1249 (3)	−317 (7)	5798 (3)	42 (2)
C(5)	1230 (3)	1115 (8)	5538 (3)	43 (2)
C(6)	1159 (3)	1374 (8)	4823 (3)	44 (2)
C(7)	1217 (3)	2915 (8)	4631 (3)	53 (2)
C(8)	1387 (3)	3959 (8)	5112 (4)	61 (3)
C(9)	1202 (3)	3714 (8)	5784 (4)	55 (2)
C(10)	1234 (3)	2217 (8)	5957 (3)	48 (2)
C(11)	1258 (3)	724 (7)	6893 (4)	46 (2)
C(12)	1261 (3)	672 (8)	7556 (4)	50 (3)
C(13)	1246 (3)	−654 (9)	7837 (4)	53 (2)
C(14)	1215 (3)	−3300 (8)	7809 (4)	60 (2)
C(15)	701 (4)	−3531 (11)	8007 (5)	87 (3)
C(16)	433 (4)	−4551 (10)	7796 (5)	74 (3)
C(17)	554 (5)	−5769 (12)	7379 (6)	155 (6)
C(18)	−60 (4)	−4516 (13)	8026 (6)	148 (5)
C(19)	1518 (3)	570 (9)	4395 (4)	56 (2)
C(20)	2003 (3)	913 (9)	4587 (4)	60 (3)
C(21)	2325 (3)	1587 (11)	4258 (5)	78 (3)
C(22)	2802 (3)	1878 (10)	4523 (5)	109 (4)
C(23)	2244 (4)	2243 (16)	3601 (5)	163 (6)
C(24)	672 (3)	910 (8)	4625 (4)	59 (3)
C(25)	302 (3)	1700 (10)	4962 (4)	51 (2)
C(26)	−6 (3)	2615 (10)	4730 (5)	68 (3)
C(27)	−364 (3)	3287 (10)	5170 (5)	94 (3)
C(28)	−13 (3)	3065 (11)	4025 (4)	100 (3)
O(1)	1260 (2)	−2952 (5)	6441 (2)	59 (1)
O(2)	1253 (2)	−1371 (5)	5444 (2)	59 (2)
O(3)	1132 (2)	3276 (5)	4083 (2)	70 (2)
O(4)	1257 (2)	2060 (5)	6619 (2)	52 (1)
O(5)	1229 (2)	−793 (6)	8491 (2)	74 (2)
C(1)GA	2482 (8)	328 (39)	1879 (14)	110 (8)
C(2)GA	2500 (7)	2063 (38)	1387 (12)	94 (7)
C(3)GA	2502 (7)	2760 (35)	1869 (13)	103 (7)
C(4)GA	2536 (7)	4588 (33)	1455 (12)	81 (6)
C(1)GB	2484 (11)	675 (54)	1258 (15)	184 (14)
C(2)GB	2469 (8)	1342 (40)	1801 (15)	113 (9)
C(3)GB	2489 (9)	3355 (43)	1424 (14)	129 (9)
C(4)GB	2528 (10)	3928 (46)	1929 (16)	143 (10)

Fig. 1. Perspective view of the zeyloxanthonone molecule together with the crystallographic numbering.

Table 2. *Geometry of the zeyloxanthonone molecule*

(a) Bond lengths (Å)

C(1)—C(2)	1·393 (10)	C(13)—O(5)	1·363 (9)
C(2)—C(3)	1·405 (10)	C(13)—C(1)	1·412 (11)
C(2)—O(1)	1·368 (10)	C(1)—C(14)	1·494 (11)
C(3)—C(4)	1·457 (10)	C(14)—C(15)	1·565 (14)
C(4)—C(5)	1·465 (10)	C(15)—C(16)	1·320 (14)
C(4)—O(2)	1·242 (8)	C(16)—C(17)	1·488 (15)
C(5)—C(6)	1·515 (10)	C(16)—C(18)	1·512 (15)
C(6)—C(7)	1·527 (11)	C(6)—C(19)	1·558 (11)
C(7)—C(8)	1·491 (11)	C(19)—C(20)	1·502 (13)
C(7)—O(3)	1·212 (8)	C(20)—C(21)	1·325 (13)
C(8)—C(9)	1·510 (11)	C(21)—C(22)	1·517 (14)
C(9)—C(10)	1·470 (11)	C(21)—C(23)	1·514 (15)
C(10)—C(5)	1·361 (10)	C(6)—C(24)	1·540 (12)
C(10)—O(4)	1·381 (8)	C(24)—C(25)	1·487 (12)
O(4)—C(11)	1·374 (9)	C(25)—C(26)	1·337 (13)
C(3)—C(11)	1·381 (10)	C(26)—C(27)	1·525 (13)
C(11)—C(12)	1·373 (11)	C(26)—C(28)	1·522 (14)
C(12)—C(13)	1·390 (11)		

(b) Bond angles (°)

C(2)—C(1)—C(13)	116·3 (7)	C(9)—C(10)—C(5)	126·1 (6)
C(2)—C(1)—C(14)	123·6 (7)	C(9)—C(10)—O(4)	110·4 (7)
C(13)—C(1)—C(14)	120·1 (7)	C(5)—C(10)—O(4)	123·4 (7)
C(1)—C(2)—C(3)	122·7 (7)	C(10)—O(4)—C(11)	120·3 (5)
C(1)—C(2)—O(1)	117·9 (6)	O(4)—C(11)—C(3)	119·6 (7)
C(3)—C(2)—O(1)	119·3 (6)	C(3)—C(11)—C(12)	124·3 (7)
C(2)—C(3)—C(4)	121·7 (7)	O(4)—C(11)—C(12)	116·1 (6)
C(2)—C(3)—C(11)	116·7 (6)	C(11)—C(12)—C(13)	116·8 (7)
C(4)—C(3)—C(11)	121·5 (7)	C(12)—C(13)—C(1)	123·1 (7)
C(3)—C(4)—C(5)	116·5 (6)	C(12)—C(13)—O(5)	120·4 (7)
C(3)—C(4)—O(2)	121·3 (6)	O(5)—C(13)—C(1)	116·5 (7)
C(5)—C(4)—O(2)	122·2 (6)	C(1)—C(14)—C(15)	107·6 (7)
C(4)—C(5)—C(6)	121·0 (6)	C(14)—C(15)—C(16)	125·6 (9)
C(4)—C(5)—C(10)	118·7 (6)	C(15)—C(16)—C(17)	128·7 (10)
C(6)—C(5)—C(10)	120·0 (7)	C(15)—C(16)—C(18)	116·1 (9)
C(5)—C(6)—C(7)	113·3 (6)	C(17)—C(16)—C(18)	115·2 (10)
C(5)—C(6)—C(19)	112·6 (6)	C(6)—C(19)—C(20)	111·7 (7)
C(5)—C(6)—C(24)	107·6 (6)	C(19)—C(20)—C(21)	129·4 (8)
C(7)—C(6)—C(24)	107·9 (6)	C(20)—C(21)—C(22)	123·3 (9)
C(19)—C(6)—C(24)	108·8 (6)	C(20)—C(21)—C(23)	123·4 (9)
C(7)—C(6)—C(19)	104·3 (6)	C(22)—C(21)—C(23)	113·1 (9)
C(6)—C(7)—C(8)	120·1 (6)	C(6)—C(24)—C(25)	113·4 (7)
C(6)—C(7)—O(3)	119·5 (7)	C(24)—C(25)—C(26)	130·1 (8)
C(8)—C(7)—O(3)	120·4 (7)	C(25)—C(26)—C(27)	120·9 (8)
C(7)—C(8)—C(9)	113·3 (6)	C(25)—C(26)—C(28)	122·6 (8)
C(8)—C(9)—C(10)	110·6 (6)	C(27)—C(26)—C(28)	116·5 (8)

(c) Deviations (Å) of atoms from the best plane defined by the 1,4-benzopyrone ring (atoms in first column on left)

This plane is given by $x + 0.0016y - 0.0087z = 3.516$ Å, where x, y, z are atomic coordinates in Å.

C(1)	−0·03	C(6)	−0·23	C(21)	3·17
C(2)	0·02	C(7)	−0·05	C(22)	4·56
C(3)	0·04	C(8)	0·43	C(23)	2·95
C(4)	0·01	C(9)	−0·12	C(24)	−1·64
C(5)	−0·04	C(14)	−0·13	C(25)	−2·73
C(10)	−0·03	C(15)	−1·62	C(26)	−3·61
C(11)	0·02	C(16)	−2·41	C(27)	−4·66
C(12)	0·02	C(17)	−2·05	C(28)	−3·62
C(13)	−0·03	C(18)	−3·84	O(1)	0·03
O(4)	0·02	C(19)	0·82	O(2)	0·03
		C(20)	2·23	O(3)	−0·29
				O(5)	−0·10

(d) Torsion angles (°) in the cyclohex-3-enone ring

C(5)—C(6)—C(7)—C(8)	7·4	C(6)—C(7)—C(8)—C(9)	−38·0
C(7)—C(8)—C(9)—C(10)	45·8	C(8)—C(9)—C(10)—C(5)	−27·2
C(9)—C(10)—C(5)—C(6)	−3·7	C(10)—C(5)—C(6)—C(7)	14·2

(e) Torsion angles (°) in the prenyl groups

C(6)—C(19)—C(20)—C(21)	−114·0	C(1)—C(14)—C(15)—C(16)	112·5
C(6)—C(24)—C(25)—C(26)	117·1		

has the opposite conformation. The hydroxyl at C(2) and the carbonyl at C(4) are linked by an intramolecular hydrogen bond; the distance between the oxygens is 2·55 (2) Å, and the hydroxyl hydrogen has

been located between them, albeit with limited precision.

With the structure (1) proposed by Sultanbawa and colleagues beyond doubt, the *gem*-substitution in ring *C* arouses interest. Conventionally, this grouping would be thought to indicate that an arrange-

ment (3) had been formed at some stage in the biosynthesis and then modified. Arrangement (3) accounts for the 1,3-dioxygenation pattern associated with *gem* groupings and is the one readily obtained *in vitro* (Helboe & Arends, 1973*a,b*; Shimizu, Ohashi & Tsuji, 1983). But such an arrangement cannot be fitted into any reasonble xanthone structure, while if the vinylogous arrangement (4) is postulated a fitting can be achieved only by making use of a xanthone oxygenation pattern at variance with those in recognized sequences. It seems simpler to assume that, not withstanding the chemical and phytochemical preponderance of grouping (3), only one carbonyl group is absolutely essential to *gem*-disubstitution.

The molecular packing is shown in Fig. 2. The 1,4-benzopyrone rings of the zeyloxanthonone molecules lie essentially parallel to (100) and are hydrogen bonded head-to-tail through hydroxyl O(5) [55407] to carbonyl O(3) [55501] [$d = 2.70$ (2) Å; *ORTEP* numbering used for molecules]; the hydroxyl hydrogen has been located between these oxygens, again with limited precision. The consequent zigzag chains of molecules extending along [001] are lined up in sheets parallel to (100) and located at $x \simeq \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$ and $\frac{7}{8}$. The slabs of crystal between the pairs of sheets at $x \simeq \pm \frac{1}{8}$ and between the pairs of sheets at $x \simeq \frac{3}{8}$ and $\frac{5}{8}$ contain a hydrophobic filling comprised of the C(1)-prenyl group and *one* of the two *gem*-diprenyl groups. The other C(6)-prenyl group, which is approximately normal to the ring plane, forms together with the rings the walls of channels of rectangular cross-section, which contain the guest molecules. These channels are located in the slabs between $x = \frac{1}{8}$ and $\frac{3}{8}$, and between $x = \frac{5}{8}$ and $\frac{7}{8}$. Thus the host molecules are hydrogen bonded in the [001] direction but there are only dispersion interactions in the other two directions.
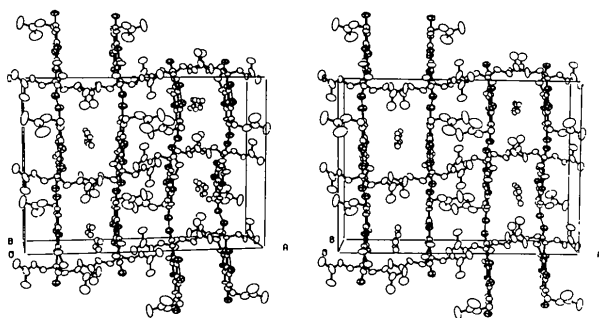

Fig. 2. *ORTEP* stereodiagram (50% probability ellipsoids) of the host and guest arrangement in the unit cell. The inter- and intramolecular hydrogen bonds are shown by thin lines. The atoms of the guest molecule in the channels have been inserted in schematic form only.

The Bragg diffraction pattern of the crystals suggests the presence of two groups of four 'carbon' atoms in the channels [atoms C(1–4)*GA* and C(1–4)*GB* in Table 1]. As these atoms have x coordinates indistinguishable from $\frac{1}{4}$, they lie in the *b* glide plane (at $\frac{1}{4}$, y, z) and are propagated along the **b** direction. Thus each group of four is the repeat unit of a zigzag infinite polymer chain extending along the **b** direction; the two crystallographically independent chains are related by a non-crystallographic mirror plane parallel to (001) at $z \simeq 0.16$. The distances between the 'carbons' within each of the chains range from 1.3 to 1.9 Å. Any particular channel will, of course, contain only one of the two types of crystallographically independent chains.

That the guest molecules are palmitic acid is shown by the method of preparation of the reconstituted sample used in our structure analysis and by its NMR analysis [see Dean *et al.* (1984), p. 1755], which also gave an approximate host:guest ratio of 4:1, the precision being limited by the small amount of sample available. The measured density gives a unit-cell content of $4C_{28}H_{34}O_5.0.8C_{15}H_{31}COOH$, which agrees with the chemical analysis for hydrogen (but note that this analysis was for the natural material and not the reconstituted sample) and with the occupancy factors derived for the guest atoms from the least-squares refinement. Palmitic acid in the extended monomeric conformation has a length of about 21 Å (Laves, Nicolaides & Peng, 1965), which is $\sim 2.2b$; this suggests that only $\sim 90\%$ occupancy of the channels is possible. Furthermore (incommensurable) diffuse scattering might be expected in oscillation photographs about [010], as is indeed found in many channel inclusion complexes of urea and thiourea (Nicolaides & Laves, 1963) and also in trimesic acid monohydrate. 2/9 (picric acid) (Herbstein & Marsh, 1977) which shows somewhat similar partial ordering of guest molecules in channels. However, no diffuse scattering was found in well-exposed [010] oscillation and *h0l* and *h1l* Weissenberg photographs (Cu $K\alpha$) from a crystal at room temperature. The problem that remains unsolved is how to reconcile the apparently linear polymeric guest shown by the structure analyses with the presence of discrete palmitic acid molecules.

Long-chain paraffin hydrocarbons and derivatives with extended conformations are guests in three types of channel inclusion molecular complex, exemplified by those in which urea, deoxycholeic acid and perhydrotriphenylene are hosts. Zeyloxanthonone is thus a new type of host molecule for such guests, and its arrangement (with both hydrogen bonding and dispersion interactions) can be considered to be intermediate in nature between the fully hydrogen-bonded host matrix formed by urea (Takemoto & Sonoda, 1984) and the fully van-

der-Waals-bonded matrices formed by deoxycholeic acid (Giglio, 1984) and perhydrotriphenylene (Farina, 1984).

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Geometry of the Iminium Moiety. I. Structure of Pyrazolinium Salts and an N-Isopropylidene Derivative

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Abstract. Compound (I; PYCL), 4,5-dihydro-3,5,5-trimethylpyrazolium chloride, $C_6H_{13}N_2^+.Cl^-$, $M_r = 148.64$, orthorhombic, $P2_12_12_1$, $a = 8.324$ (1), $b = 8.381$ (1), $c = 12.121$ (1) Å, $V = 845.60$ (16) Å^3, $Z = 4$, $D_m = 1.17$ (1), $D_x = 1.167$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 3.31$ cm^{-1}, $F(000) = 320$, $T = 294$ K, $R = 0.030$ for 782 observed reflections. Compound (II; PYRA), bis(4,5-dihydro-3,5,5-trimethylpyrazolium) hexachlorostannate monohydrate, $2C_6H_{13}N_2^+.SnCl_6^{2-}.H_2O$, $M_r = 575.8$, orthorhombic, $Fdd2$, $a = 16.975$ (2), $b = 30.729$ (4), $c = 8.987$ (10) Å, $V = 4687.8$ (27) Å^3, $Z = 8$, $D_m = 1.62$ (1), $D_x = 1.631$ g cm^{-3}, $\mu = 16.5$ cm^{-1}, $F(000) = 2304$, $R = 0.021$ for 1927 observed reflections. Compound (III; PYCS), bis(4,5-dihydro-3,5,5-trimethyl-1-isopropylidenepyrazolium) hexachlorostannate, $2C_9H_{17}N_2^+.SnCl_6^{2-}$, $M_r = 637.9$, monoclinic, $C2/c$, $a = 14.145$ (1), $b = 11.630$ (1), $c = 17.054$ (6) Å, $\beta = 98.71$ (4)°, $V = 2773.1$ (10) Å^3, $Z = 4$, $D_m = 1.52$ (1), $D_x = 1.528$ g cm^{-3}, $\mu = 15.2$ cm^{-1}, $F(000) = 1288$, $R = 0.027$ for 1930 observed reflections. Compound (IV; MONS), $M_r = 654.8$, cubic, $Im3$, $a = 17.886$ (4) Å, $V = 5721.9$ (42) Å^3, $Z = 8$, $D_m = 1.52$ (1), $D_x = 1.520$ g cm^{-3}, $\mu = 14.9$ cm^{-1}, $F(000) = 2400$, $R = 0.069$ for 644 observed reflections. The four structures arise from the condensation of hydrazine compounds with acetone. In (III) and (IV) the existence of the ternary iminium ion was confirmed. Strong hydrogen bonds exist in (I) and (II). (IV) is structurally disordered, containing an equal proportion of (II) and (III) and constraints were applied to several bond lengths of the rings during the final stages of refinement.

Introduction. The condensation product (Pugh, 1954) of hydrazine dihydrochloride with acetone, namely

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