ag^-g^+, in the above list contain one exception each from the preferred conformation, *i.e.* g^+ instead of *a*. These occur around bonds O4—C13 and O15—C44 and are responsible for a moderate bending (Dale, 1980) in the cyclic structure at O4 and O15. The unusual conformation in this region of the macroring is also responsible for positioning O3 and O16 (Fig. 1) in between the two side arms enabling them to hydrogen bond across the two faces of the ring (see above).

The bond distances and bond angles in the 18-crown-6 ring are quite similar to those observed in the unsubstituted 18-crown-6 (Dunitz & Seiler, 1974; Maverick, Seiler, Schweizer & Dunitz, 1980). There are significant differences, however, owing to the side-chain substitution and a change in symmetry from C_i to pseudo C_2. For example, the mean C—C and C—O bond distances, 1·507 and 1·422 Å, respectively, Table 2, happen to be exactly the same as those observed for the unsubstituted crown (Dunitz & Seiler, 1974), but the individual variations, especially in the C—O bond distances, are much more pronounced in the substituted crown than in the unsubstituted. Also, as pointed out in Table 2, the variations in bond distances as well as bond angles are consistent with the presence of the approximate C_2 symmetry. The six C—O—C bond angles in the crown ring vary from 112·9 to 114·8° with a mean of 113·9° (113·5° for the unsubstituted crown; Dunitz & Seiler, 1974) and ten of the twelve O—C—C bond angles vary from 107·9 to 109·7° with a mean of 108·6°. The two exceptions, at C13 and C44, have identical values of 114·7°, and are much larger than other O—C—C angles cited above. The larger O—C—C bond angles at C13 and C44 together with somewhat larger C—O—C bond angles at O4 and O15, Table 2, seem to be related to the anomalous g^+ conformation around O4—C13 and O15—C44 (see above) and may be a result of the *gauche* effect (Bartell, 1959) proposed by Dunitz & Seiler (1974).

The bond distances and bond angles in the four identical side chains are all normal with the following average values: ester moiety, $COOCH_3$: C=O 1·193 (8), C—OCH_3 1·303 (8), O—CH_3 1·449 (9) Å; peptide moiety, CONHCH: C=O 1·233 (5), CO—N 1·331 (5), NH—CH 1·443 (5) Å.

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Structure of Elsinochrome A*

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Abstract. $C_{30}H_{24}O_{10}$, $M_r = 554·49$, orthorhombic, $P2_12_12_1$, $a = 12·439$ (4), $b = 13·001$ (7), $c = 14·957$ (6) Å, $V = 2418$ (1) Å^3, $Z = 4$, $D_x = 1·49$ g cm^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, $\mu = 8·48$ cm^{-1}, $F(000) = 1136$, $T = 293$ (2) K, $R = 0·054$ for 2037 observed independent reflections with $I > 3\sigma(I)$. The molecule is X-shaped, with the two acetyl groups pointing outwards, perpendicular to the average

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* *trans*-1,2-Diacetyl-1,2-dihydro-5,10-dihydroxy-3,7,8,12-tetramethoxybenzo[*ghi*]perylene-4,11-dione.

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molecular plane. There is strong intramolecular hydrogen bonding between the hydroxy groups and their β-keto groups. No intermolecular hydrogen bonds are observed. Arguments are given for the existence of a fixed asymmetric non-planar shape of the molecule in solution, which contributes to the high optical activity.

Introduction. The title compound (Fig. 1) was studied by NMR methods in solution (Lousberg, Salemink, Weiss & Batterham, 1969; Lousberg, Paolillo, Kon, Weiss & Salemink, 1970). Solutions of elsinochrome A exhibit high optical activity (Lousberg *et al.*, 1970), which has been ascribed to two chiral centres only. There were indications, based on the coupling constant between the two H atoms attached to the optically active centres, for fast conformational interchange (Lousberg *et al.*, 1970); this would exclude any contribution from the non-planarity of the molecule to the optical activity. The present structure determination was undertaken to obtain further evidence for this assertion.

Experimental. The optically pure compound was isolated from moulds of the fungus *Sphaceloma randii* (Hackeng, 1963; Lousberg *et al.*, 1969). Dark-red bipyramidal crystal 0·3 × 0·3 × 0·4 mm, D_m not measured (highly soluble in all solvents), Enraf–Nonius CAD-4F diffractometer, Ni-filtered Cu $K\alpha$ radiation, unit-cell parameters from 72 equivalent angular settings of 12 reflections (with $40 < \theta < 45°$). Intensity data of 2594 unique reflections were collected within one octant of the reflection sphere ($0 \le h \le 16$, $0 \le k \le 17$, $0 \le l \le 19$, $0·1 < \theta < 70°$), ω–2θ scan mode with $\Delta\omega = (1·10 + 0·14\tan\theta)°$, 2037 observed reflections with $I > 3\sigma(I)$. Three control reflections ($\bar{2}23$, $2\bar{2}3$ and $22\bar{3}$) measured every hour showed a linear decay of 2·0% during the 141 h of X-ray exposure time. The intensity data were corrected for this and for Lorentz and polarization effects but not for absorption.

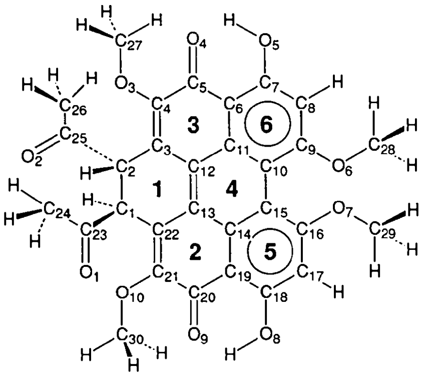

Fig. 1. Elsinochrome A; atom- and ring-numbering scheme.

The structure was solved by direct methods (*REDUC*, Pontenagel, 1983) and subsequent difference Fourier methods. Anisotropic block-diagonal refinement – $(\Delta F)^2$ minimized – of the non-H atoms resulted in $R = 0·066$. Six protons were located from the difference Fourier map (those in the methyl and methoxy groups showed rotational disorder). Refinement for the six located H atoms in riding mode, isotropic group refinement for the C and H atoms in the methyl and methoxy groups (C—H = 1·09 Å), and anisotropic block-diagonal refinement for other atoms led to a final R_f of 0·054 with $S = 3·15$. The average and maximum shift/e.s.d. for non-methyl-group atoms are 0·16, 0·88 and for methyl-group atoms 0·34, 1·29. The larger shift/e.s.d. for the methyl-group atoms is easily understood from their rotational disorder. The maximum and minimum electron densities in the final difference Fourier map are 0·37 and −0·29 e Å^{-3} respectively. The scattering factors are taken from Stewart, Davidson & Simpson (1965) and Cromer & Mann (1968). Programs used: *XRAY76* (Stewart, Machin, Dickinson, Amman, Heck & Fleck, 1976), *PLATO* (Spek, 1982) and *ORTEP* (Johnson, 1965) on the CDC Cyber-855 of the University of Utrecht.

Discussion. Refined atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, selected bond lengths and angles in Table 2.* The molecular conformation is shown in Fig. 2. The perylene part of the elsinochrome A molecule is X-shaped, in contrast to the bow-shaped perylene itself (Camerman & Trotter, 1964). The naphthalene nuclei 2,5 and 3,6 (see Fig. 1) form an angle of 16·1 (1)°. These ring systems are fairly flat [maximum deviation 0·081 (1) Å for 2,5 and 0·11 (1) Å for 3,6] when three atoms are omitted from the calculation of the least-squares planes: C(8), C(9) and C(15) with their respective deviations 0·11 (1), 0·21 (1) and 0·22 (1) Å. The ring puckering parameters determined by the method of Cremer & Pople (1975) showed that ring 1 is in a skew-boat and ring 4 is in a twist-boat conformation [ring 1: $Q = 0·470$ (5) Å, $\varphi = 32·7$ (7)° and $\theta = 60·6$ (6)°; ring 4: $Q = 0·160$ (5) Å, $\varphi = 152$ (2)° and $\theta = 96$ (2)° (Boeyens, 1978)]. Differences in bond length are sufficiently large to assign C(7)—O(5) and C(18)—O(8) as single bonds and C(5)—O(4) and C(20)—O(9) as double bonds (Stezowksi, 1976). The five neutral and 96 biradical resonance structures based on this assignment lead to

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths, bond and torsion angles, and methyl-group positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52183 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and equivalent isotropic thermal parameters for the non-*H *atoms with e.s.d.'s in parentheses*

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

	x	y	z	$U_{\rm eq}$(Å^2)
O(1)	0·4410 (3)	0·0300 (3)	0·6828 (3)	0·063 (2)
O(2)	0·2398 (4)	−0·0786 (3)	0·9637 (3)	0·083 (2)
O(3)	0·3287 (3)	0·2728 (3)	0·8930 (2)	0·052 (1)
O(4)	0·2225 (3)	0·4074 (3)	0·7805 (3)	0·056 (1)
O(5)	0·0867 (4)	0·4423 (3)	0·6597 (3)	0·062 (1)
O(6)	−0·0222 (3)	0·1651 (3)	0·4791 (2)	0·054 (1)
O(7)	−0·1359 (3)	0·0288 (3)	0·5520 (3)	0·054 (1)
O(8)	0·0204 (4)	−0·2996 (3)	0·5796 (3)	0·067 (2)
O(9)	0·1826 (4)	−0·3215 (3)	0·6734 (3)	0·066 (2)
O(10)	0·3424 (3)	−0·2423 (3)	0·7791 (3)	0·053 (1)
C(1)	0·3551 (4)	−0·0305 (4)	0·8151 (3)	0·045 (2)
C(2)	0·3099 (4)	0·0570 (4)	0·8719 (3)	0·044 (2)
C(3)	0·2538 (4)	0·1340 (4)	0·8122 (3)	0·041 (2)
C(4)	0·2660 (4)	0·2366 (4)	0·8242 (3)	0·047 (2)
C(5)	0·2090 (4)	0·3109 (4)	0·7686 (3)	0·044 (2)
C(6)	0·1375 (4)	0·2728 (4)	0·7018 (3)	0·043 (2)
C(7)	0·0798 (5)	0·3417 (4)	0·6483 (3)	0·050 (2)
C(8)	0·0200 (5)	0·3053 (4)	0·5751 (4)	0·053 (2)
C(9)	0·0145 (4)	0·2016 (4)	0·5578 (3)	0·046 (2)
C(10)	0·0558 (4)	0·1262 (4)	0·6196 (3)	0·042 (2)
C(11)	0·1253 (4)	0·1642 (4)	0·6872 (3)	0·040 (2)
C(12)	0·1888 (4)	0·0959 (4)	0·7398 (3)	0·039 (2)
C(13)	0·1885 (4)	−0·0094 (4)	0·7195 (3)	0·042 (2)
C(14)	0·1103 (4)	−0·0488 (4)	0·6604 (3)	0·041 (2)
C(15)	0·0380 (4)	0·0178 (4)	0·6145 (3)	0·040 (2)
C(16)	−0·0530 (4)	−0·0310 (4)	0·5704 (3)	0·045 (2)
C(17)	−0·0555 (4)	−0·1360 (5)	0·5563 (4)	0·050 (2)
C(18)	0·0247 (5)	−0·1995 (4)	0·5928 (4)	0·051 (2)
C(19)	0·1059 (4)	−0·1580 (4)	0·6477 (3)	0·044 (2)
C(20)	0·1832 (5)	−0·2241 (4)	0·6882 (4)	0·051 (2)
C(21)	0·2639 (4)	−0·1793 (4)	0·7442 (3)	0·048 (2)
C(22)	0·2679 (4)	−0·0762 (4)	0·7586 (3)	0·042 (2)
C(23)	0·4485 (4)	0·0131 (4)	0·7613 (3)	0·046 (2)
C(24)	0·5493	0·0356	0·8124	0·061 (2)
C(25)	0·2369 (5)	0·0131 (5)	0·9467 (3)	0·056 (2)
C(26)	0·1788	0·0881	1·0015	0·067 (2)
C(27)	0·4254	0·3223	0·8655	0·068 (2)
C(28)	−0·0862	0·2308	0·4237	0·066 (2)
C(29)	−0·2284	−0·0120	0·5076	0·059 (2)
C(30)	0·3015	−0·3096	0·8484	0·070 (2)

alternating bond lengths in the series C(3)—C(4), C(4)—C(5), C(5)—O(4), and C(22)—C(21), C(21)—C(20), C(20)—O(9), which are indeed observed.

As seen in the **b** direction, the packing of the molecules is in a tiled-roof fashion with the plane of the molecule roughly perpendicular to the *ac* plane (tilt 9°) directed along the *ac* diagonal, with the C(6)—C(19) molecular axis almost in the **b** direction (angle 9·5°). The average distance between the molecular plane and the 2_1 axis is 2·0 Å. The shortest intermolecular distance [3·12 (1) Å] is observed between O(8) and C(26′) [molecules interrelated by $(-x, \frac{1}{2}+y, 1\frac{1}{2}-z)$].

The origin of the non-planar configuration of the molecule (X-shape), with the two acetyl groups pointing perpendicular to the average molecular plane (diaxial *trans* configuration) and the two H atoms at C(1) and C(2) in diequatorial positions, must lie in the strong steric hindrance between O(6) and O(7) [distance 2·51 (1) Å].

As a measure of the degree of non-planarity in the molecule we have taken the dihedral angles between rings 1 and 2, rings 1 and 3, and rings 2 and 3, which are 14·5 (2), 16·6 (2), and 13·0 (2)° respectively in elsinochrome A (Table 3). A similar situation in which the molecule is distorted by steric hindrance occurs in compounds (9) and (10) (Fig. 3), that have essential parts in common with elsinochrome A. In compound (9) the dihedral angles (Table 3) are much larger than in compound (7) [the latter has no substituents that cause steric hindrance (Glusker, Carrell & Zacharias, 1974)], while the dihedral angles in compound (10) are extremely large (Table 3), thus indicating a large degree of distortion. The fact that in elsinochrome A the distortion is less than in compound (10) must be attributed to the fact that in

Table 2. *Selected bond distances* (Å) *and bond angles* (°) *for the non-*H *atoms with e.s.d.'s in parentheses*

O(1)—C(23)	1·198 (6)	O(2)—C(25)	1·220 (8)	O(4)—C(5)	1·278 (7)
O(5)—C(7)	1·322 (7)	O(8)—C(18)	1·317 (7)	O(9)—C(20)	1·286 (7)
O(9)—C(20)	1·286 (7)	C(1)—C(2)	1·527 (7)	C(1)—C(22)	1·498 (7)
C(1)—C(23)	1·523 (7)	C(2)—C(3)	1·512 (7)	C(2)—C(25)	1·550 (7)
C(3)—C(4)	1·354 (7)	C(3)—C(12)	1·439 (7)	C(4)—C(5)	1·459 (7)
C(13)—C(22)	1·439 (7)	C(19)—C(20)	1·425 (8)	C(20)—C(21)	1·431 (8)
C(21)—C(22)	1·359 (7)	C(23)—C(24)	1·497 (5)	C(25)—C(26)	1·465 (6)

O(3)—C(4)—C(3)	120·0 (4)	O(3)—C(4)—C(5)	118·4 (4)
C(11)—C(12)—C(13)	119·2 (4)	C(12)—C(13)—C(14)	119·5 (5)
C(2)—C(1)—C(22)	110·0 (4)	C(2)—C(1)—C(23)	107·3 (4)
C(22)—C(1)—C(23)	113·7 (4)	C(1)—C(2)—C(3)	109·5 (4)
C(1)—C(2)—C(25)	110·1 (4)	C(3)—C(2)—C(25)	113·6 (4)
C(2)—C(3)—C(4)	121·5 (4)	C(2)—C(3)—C(12)	118·4 (4)
C(4)—C(3)—C(12)	120·1 (4)	C(3)—C(4)—C(5)	121·5 (4)
O(4)—C(5)—C(4)	120·4 (4)	O(4)—C(5)—C(6)	121·4 (5)
C(4)—C(5)—C(6)	118·2 (7)	O(5)—C(7)—C(6)	121·8 (5)
C(6)—C(7)—C(8)	120·1 (5)	C(6)—C(11)—C(12)	118·0 (4)
C(10)—C(11)—C(12)	120·9 (5)	C(3)—C(12)—C(11)	120·8 (5)
C(3)—C(12)—C(13)	120·0 (4)	C(12)—C(13)—C(22)	120·0 (4)
C(14)—C(13)—C(22)	120·6 (5)	O(8)—C(18)—C(17)	119·6 (5)
O(8)—C(18)—C(19)	119·6 (5)	C(17)—C(18)—C(19)	120·7 (5)
C(18)—C(19)—C(20)	120·0 (5)	O(9)—C(20)—C(19)	121·1 (5)
O(9)—C(20)—C(21)	120·4 (5)	O(10)—C(21)—C(20)	118·5 (5)
O(10)—C(21)—C(22)	120·0 (4)	C(20)—C(21)—C(22)	121·3 (5)
C(1)—C(22)—C(13)	119·1 (4)	C(1)—C(22)—C(21)	120·5 (4)
C(13)—C(22)—C(21)	120·4 (4)	C(1)—C(23)—C(24)	116·2 (3)
C(2)—C(25)—C(26)	116·6 (5)	O(1)—C(23)—C(1)	121·8 (4)
O(2)—C(25)—C(26)	123·3 (4)	O(1)—C(23)—C(24)	122·0 (4)
O(2)—C(25)—C(2)	119·5 (5)		

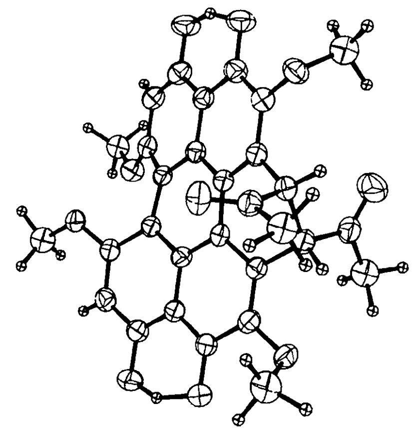


Fig. 2. Molecular conformation of elsinochrome A. Thermal ellipsoids are drawn at the 35% probability level; H atoms are represented by spheres of 0·1 Å radius.

elsinochrome A the presence of ring 4 tends to flatten the molecule [compare the dihedral angles in compounds (7) and (8) for a similar effect (Fig. 3, Table 3)]. In spite of the distortion of the elsinochrome A molecule there is evidence that there is no strain in ring 1. This evidence can be found from the fact that the dihedral angles in elsinochrome A are, in magnitude, comparable to those in the 9,10-dihydrophenanthrenes and a 4,5,9,10-tetrahydropyrene [compounds (2),(3),(4),(5) and (6) in Fig. 3, Table 3] which have no strain in ring 1 because of sufficient rotational freedom around the bond between rings 2 and 3.

Table 3. *Dihedral angles* (°) *between least-squares planes in elsinochrome A and in related compounds* (*structural formulae in Fig.* 3)

Compound No.*	Reference	Dihedral angle between planes† 1,2	1,3	2,3
(1)	Elsinochrome A	14·5	16·6	13·0
(2)	Cotrait & Marsau (1976)	12·2	14·2	16·5
(3)	Cotrait, Destrade & Gasparoux (1975)	11·5	11·2	14·1
(4)	Cotrait, Marsau & Pesquer (1979)	10·0	12·5	15·5
(5)	Lapouyade, Koussini, Nourmamode & Courseille (1980)	13·9	13·5	16·6
(6)	Bear, Hall, Waters & Waters (1973)	12·4 14·6‡	13·5 12·6‡	17·4
(7)	Glusker *et al.* (1974)	3·6	4·0	7·5
(8)	Glusker, Zacharias, Carrell, Fu & Harvey (1976)	2·8	2·5	5·1
(9)	Glusker *et al.* (1974)	14·2	15·1	28·7
(10)	Kuroda & Mason (1981)	23·4	23·9	39·4

* These compounds are: (2) 2-butyl-7-pentanoyl-9,10-dihydrophenanthrene, (3) 2-(2-methylbutyl)-7-pentanoyl-9,10-dihydrophenanthrene, (4) 7-hexanoyl-2-nonyl-9,10-dihydrophenanthrene, (5) *cis*-10-methyl-9-phenyl-9,10-dihydrophenanthrene, (6) 2-chloro-4,5,9,10-tetrahydropyrene, (7) 9,10-epoxyphenanthrene, (8) 4,5-epoxybenzo[*a*]pyrene, (9) 7,12-dimethyl-5,6-epoxybenz[*a*]anthracene, (10) (*S*)-(+)-9,10-dihydrodibenzo[*c,g*]phenanthrene.

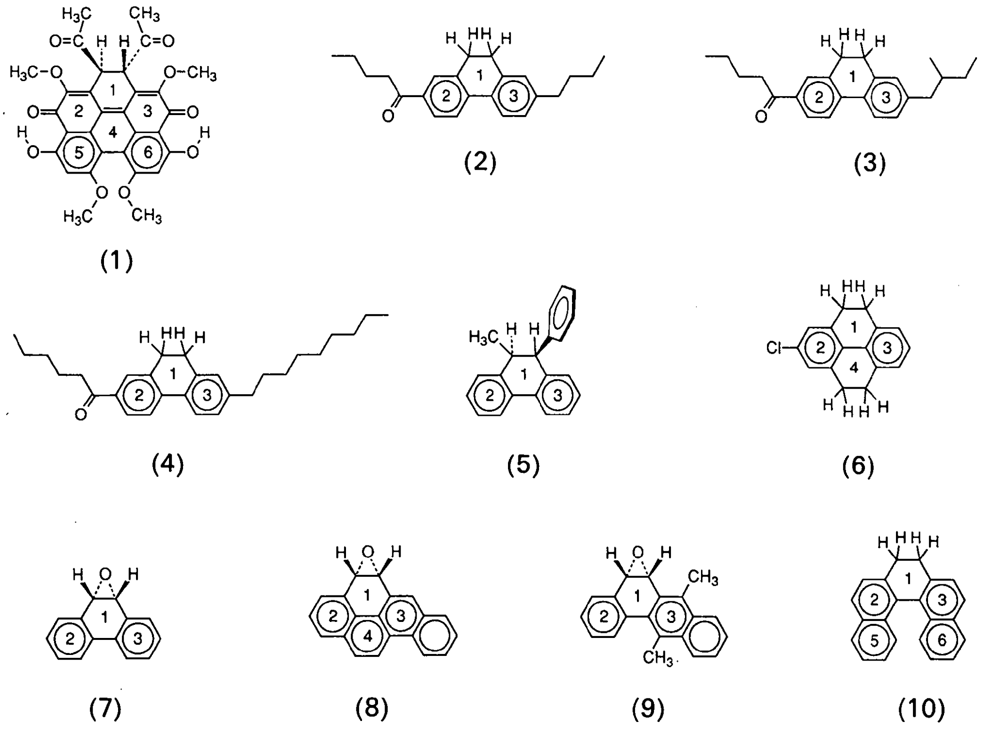
† The numbering scheme is similar to that adopted in Fig. 3; the standard deviations of the least-squares planes are between 0·1 and 0·5°.

‡ Between planes 4,2 and 4,3.

The distortion of the molecule as found in the crystal structure may well persist in solution, because:

(1) The extremely short non-bonded distance between O(6) and O(7) indicates the presence of a large energy barrier for a transition from the observed conformation, with the two acetyl groups in a diaxial position, to that with the acetyl groups diequatorial. Elsinochrome A, in this respect, bears some comparison with compound (10) (Fig. 3); the latter is heavily distorted because of steric hindrance between rings 5 and 6, and it has a fixed non-planar configuration in solution (Kuroda & Mason, 1981) (this molecule has no stereocentres but has, nevertheless, high optical activity in solution).

(2) There is no preference for one conformation on the basis of the strain in ring 1, which for both possibilities would be minimal. On the other hand, with the acetyl groups in diequatorial positions, there would be an unfavourable overcrowding by the acetyl groups on ring 1.



(1) (2) (3) (4) (5) (6) (7) (8) (9) (10)

Fig. 3. Structural formulae of elsinochrome A and related compounds.

Lousberg, however, proposed a rapidly interchanging conformation for the two H atoms at C(1) and C(2) based on a coupling constant $J_{\mathrm{H-H}}$ of 5 Hz measured by ^{13}C NMR experiments, by comparing this coupling constant with those of disubstituted ethanes (Lousberg *et al.*, 1970). In this aspect [2.2]metacyclophane (Emsley, Feeney & Sutcliffe, 1967) would resemble elsinochrome A more than substituted ethanes (in substituted ethanes the rotational freedom around the C—C bond is larger than in [2.2]metacyclophane); here the equatorial coupling constant of 4·0 Hz is much closer to the measured value in elsinochrome A than the 12·3 Hz for the diaxial hydrogen position.

We conclude that a fixed non-planar configuration of the elsinochrome A molecule in solution, with a diequatorial position of the H atoms at C(1) and C(2), is most likely. Comparison with compound (10) (Fig. 3) indicates that part of the high optical activity of the elsinochrome A molecule in solution may then well be due to a fixed conformational asymmetry (in addition to a contribution from the two stereocentres).

Note: Following the acceptance of this paper, the results of an X-ray structure determination were published by Meille, Malpezzi, Allegra & Nasini (1989).

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Zwitterions in Crystalline Aminophosphonic Acids. I.* Structure of (2-Pyridylmethyl)phosphonic Acid

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Abstract. $C_6H_8NO_3P$, $M_r = 173{\cdot}11$, monoclinic, $P2_1/c$, $a = 7{\cdot}855\,(3)$, $b = 10{\cdot}857\,(4)$, $c = 8{\cdot}714\,(3)$ Å, $\beta = 106{\cdot}18\,(3)°$, $U = 713{\cdot}7\,(5)$ Å^3, $Z = 4$, $D_m = 1{\cdot}60$ (by flotation in aqueous KI solution), $D_x = 1{\cdot}61$ Mg m^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}54178$ Å, $\mu = 29{\cdot}28$ cm^{-1}, $F(000) = 360$, room temperature, $R = 0{\cdot}048$ for 935 observed reflections $[F > 3\sigma(F)]$. Hydrogen bonds link the molecules in a three-dimensional network. The negative charge is delocalized on the $\mathrm{O}\underline{\cdots}\overset{\ominus}{\mathrm{P}}\underline{\cdots}\mathrm{O}$ system, while the positive charge is spread over the pyridyl moiety.

Introduction. Organophosphorus derivatives of pyridine and quinoline with the phosphonic group *ortho*

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