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L'auteur remercie M. Lukacs et M. Lusinchi de lui avoir proposé le sujet de ce travail et de lui avoir fourni de très beaux cristaux.
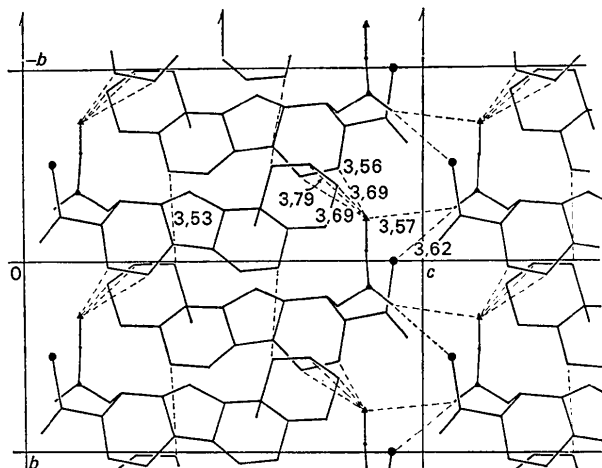

Fig. 5. Distances intermoléculaires courtes et empilement des molécules.

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The Crystal and Molecular Structure of Symmetrical Cedrone, a Dimeric Oxidation Product of Trimethylphloroglucinol

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Symmetrical cedrone, $C_{18}H_{20}O_6$, obtained by dimerization of trimethylphloroglucinol has been shown to be a centrosymmetric pentacyclic structure in the crystal of its dimethylformamide solvate and has a considerable number of very long carbon–carbon bonds. Three independent bonds have lengths of 1·597 (3), 1·597 (3) and 1·577 (3) Å. The molecule forms two, strong hydrogen bonds (2·668 Å) to related molecules of the dimethylformamide solvate and is possibly stabilized by these bonds. There are two molecules of symmetrical cedrone and four molecules of dimethylformamide in the unit cell. Crystal data: monoclinic $P2_1/c$, $a = 9·322$ (3), $b = 8·250$ (2), $c = 15·804$ (4) Å, $\beta = 101·86$ (3)°, $Z = 2$, $D_x = 1·335$ g.cm^{-3}, $D_m = 1·34$ (1) g.cm^{-3}, Mo $K\alpha$ X-radiation ($\lambda = 0·7107$ Å). The structure was solved by direct methods using counter measured X-ray intensity data (maximum sin $\theta/\lambda = 0·595$ Å^{-1}, 2096 reflections, 366 unobserved). Refinement by full-matrix least-squares was terminated at $R = 0·058$.

Introduction

Weidel & Wenzel (1898), and Bohm (1898) working independently in the same year, studied the phenolic coupling reaction of trimethylphloroglucinol with ferric chloride. In the following year Cecelsky (1899), during the course of a reinvestigation of the reaction, named the product 'cedrone' because its hydrogen iodide reduction product had the odor of cedar wood. Many

years later Erdtman (1934) proposed a dimeric structure (I) for cedrone

(I)
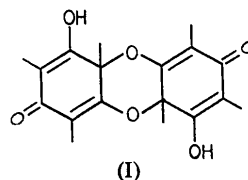
which he revised in 1969 (Erdtman, Moussa & Niels-son, 1969) on the basis of results from analogous work and with the benefit of spectroscopic analysis of both cedrone and its derived acetates and methyl ethers. He concluded that the structure of cedrone could be re-presented by a pair of bis-enol dimeric structures: a 'symmetric' form (IIa) and an 'unsymmetric' form (IIb).

(IIa)   (IIb)
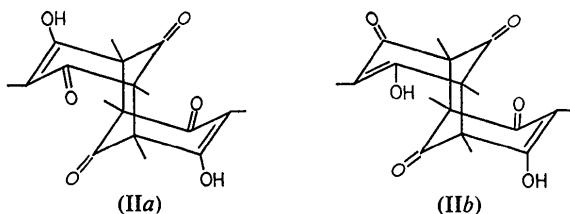
However, it was felt that the spectra of cedrone and its derivatives could not be adequately interpreted on the basis of these structures, and therefore, the X-ray analysis of a crystalline, dimethylformamide (DMF) solvate of cedrone was undertaken. The chemical and spectroscopic details of cedrone and its derivatives has been discussed in full elsewhere (Beisler, Silverton, Pent-tila, Horn & Fales, 1971).

Experimental

Cedrone, made according to the directions of Erdtman (1934), separated from DMF solution as a solvate in the form of colorless monoclinic prisms. Precession photographs determined the space group uniquely as $P2_1/c$; systematic absences: $0k0$ absent with k odd and $h0l$ absent with l odd. No evidence of disorder scat-tering was noticed. Cell parameters taken from zero-level photographs were refined by a least-squares meth-od (Stewart, 1967) from 2θ measurements determined at room temperature (ca. 25 °C) with the diffractometer (Table 1). The crystal density was measured by the

Fig. 1. Thermal ellipsoid plot (Johnson, 1965) of symmetrical cedrone.

flotation method using a carbon tetrachloride–dimethyl formamide mixture. The calculated density requires two cedrone molecules and four DMF molecules in the unit cell, and thus, cedrone has a molecular center of symmetry.

Table 1. Crystal data for symmetrical cedrone dime-thylformamide solvate

Empirical formula	$C_{18}H_{20}O_6 \cdot 2C_3H_7NO$
Formula weight	478·55
Melting point	270–290 °C (decomp.)
Space group	$P2_1/c$ (C_{2h}^5)
a	9·322 (3) Å
b	8·250 (2)
c	15·804 (4)
β	101·86 (3)°
V	1189·5 (6) Å^3
Z	2
D_x	1·335 g.cm^{-3}
D_m	1·34 (1) g.cm^{-3}
$\mu_{Mo\ K\alpha}$	1·09 cm^{-1}
Radiation	Mo $K\alpha$, $\lambda=0.7107$ Å

A crystal, approximately 0·3 mm in length and equi-dimensional in cross section with a side of 0·2 mm, was sealed in a thin-walled Pyrex capillary and mount-ed along the b axis on a Picker four-circle diffrac-tometer. For data collection Mo $K\alpha$ X-radiation (Zr-filtered) was produced by a Picker constant potential generator operated at 44 kV and 14 mA. A tube take-off angle of 5° was used. A NaI(Tl) crystal scintillation counter was employed to measure reflection intensities with a pulse height analyser set symmetrically to accept 75% of the signal due to the Mo $K\alpha$ X-radiation. Ten-second stationary counts were collected for each reflexion at the calculated 2θ angle and at one degree on each side of this value to established the background. Intensities from 2096 planes were measured with a max-imum $\sin\theta/\lambda$ of 0·595 Å^{-1}. A reflection was considered observed if the difference between the peak height and the average background was greater than twice its standard deviation based on counting statistics. Ac-cordingly, 1730 reflections were regarded as observed and 366 unobserved. If a reflection was rated unob-served the measured intensity was replaced by a value equal to twice the statistical standard deviation. The data were corrected for Lorentz and polarization fac-tors but not for absorption since, given the linear ab-sorption coefficient for Mo $K\alpha$ X-radiation is 1·09 cm^{-1}, the maximum and minimum transmission fac-tors for the crystal used were 0·979 and 0·955.

Determination and refinement of the structure

Quasi-normalized structure factor magnitudes, $|E|$, were calculated with the $DATFIX$ segment of the X-RAY 67 System of Stewart (1967). Except where otherwise noted, all calculations were done with this system. The statistical averages of $|E|$ and $|E^2-1|$ were 0·798 and 1·006 respectively, as compared to the theoretical
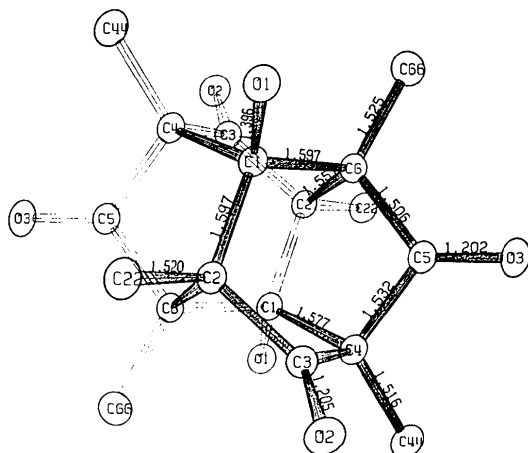
Table 2. *Observed and calculated structure factors* (× 10)

Successive columns contain h, $K|F_o|$ and F_c. Unobserved reflections are indicated by an asterisk after $K|F_o|$.

values of 0·798 and 0·968 for a centrosymmetric crystal structure. A program written by Bright & Cannon (1970) was used to find and list $\sum_2$ relationships (Hauptman & Karle, 1953) among 265 reflections whose E values were greater than 1·5, and the probability of each relationship was calculated using the formula of Cochran & Woolfson (1955). The symbolic addition method (Karle & Karle, 1966) applied to the phase problem gave the same single solution in two independent calculations. A subsequent E map (Karle, Hauptman, Karle & Wing, 1958), calculated with 243 reflections to which phases could be assigned with confidence, showed all of the anticipated atoms in the asymmetric unit at reasonable bonding distances. However, three of the peaks, attributable to carbon atoms of the solvent, were somewhat weak and therefore were omitted from the initial refinement.

The coordinates of 14 atoms as read from the E map were subjected to full-matrix, least-squares (ORFLS) refinement using isotropic thermal parameters and minimizing the function $\sum w(F_o - F_c)^2$ where the weighting scheme used was that suggested by Peterson & Levy (1957) which in terms of the data taking method used here, gives:

$$w = 1/\mathrm{Lp}[F_o^2/(I_o + \tfrac{3}{4}(I_A + I_B) + 0·0016 I_o^2)]$$

where $\mathrm{Lp} = $ Lorentz–polarization factor, $F_o = $ scaled structure factor, $I_o = $ peak intensity corrected for background, and I_A & $I_B = $ background intensities.

Unobserved reflections were included in the refinement if F_c was greater than the threshold value assigned as described above. Scattering factors were those for neutral C, H, O and N atoms quoted in *International Tables for X-ray Crystallography* (1962) although initially all

heavier atoms were assumed to be carbon. The residual (R value $= \sum|F_o - F_c|/\sum|F_o|$) at this point was 0·326, and a difference map calculated with the refined parameters clearly showed the remaining non-hydrogen atoms. With all the non-hydrogen atoms loaded and after distinguishing atom types on the bases of bond lengths and thermal parameters, further refinement reduced the R value to 0·133. Two additional cycles of ORFLS, but with anisotropic thermal parameters, reduced the residual to 0·094 at which time a difference map unambiguously indicated all of the 17 hydrogen atoms in the asymmetric unit. Difference electron density peaks at potential hydrogen atom positions ranged from 0·33 e.Å^{-3} to 0·62 e.Å^{-3}. All other peaks were less than 0·15 e.Å^{-3}.

The hydrogen atoms were added to the structure and the positional parameters were refined by means of two cycles of ORFLS with isotropic thermal parameters held constant at values one unit higher than the isotropic parameters of the heavier atoms to which they were bonded. During the hydrogen-atom refinement, the other atoms were included in the structure factors as fixed-atom contributions. One final cycle of anisotropic refinement on all atoms, but with thermal parameters of the hydrogen atoms again held constant, reduced the R value to 0·058 at which point refinement appeared complete. The observed and calculated structure factors are given in Table 2, the positional and thermal parameters in Tables 3 and 4, and the final bond lengths and angles in Table 5. The low angle (100) and (002) planes gave F_o as 0·73 F_c and 0·51 F_c, respectively, and were excluded from the refinement and calculation of the R value. The deviations can probably be attributed to extinction effects.

Table 3. *Atomic coordinates as fractions of cell edges ($\times 10^4$) for symmetrical cedrone and dimethylformamide, and anisotropic thermal parameters ($\times 10^4$)*

The thermal parameters are used in the expression

$$T = \exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)\right].$$

Cedrone

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B[†]
C(1)	6275 (2)	722 (3)	4964 (1)	97 (3)	86 (3)	27 (1)	−4 (2)	16 (1)	0 (1)	2·50
C(2)	5674 (2)	924 (3)	5834 (1)	108 (3)	88 (3)	23 (1)	3 (2)	14 (1)	−3 (1)	2·64
C(3)	4339 (2)	624 (3)	3667 (1)	101 (3)	102 (3)	25 (1)	7 (2)	16 (1)	0 (1)	2·65
C(4)	5230 (2)	1836 (3)	4295 (1)	109 (3)	89 (3)	27 (1)	3 (2)	15 (1)	6 (1)	2·72
C(5)	4049 (2)	2359 (3)	4784 (1)	97 (3)	88 (3)	27 (1)	0 (3)	4 (1)	−5 (1)	2·55
C(6)	4004 (2)	1051 (2)	5443 (1)	100 (3)	89 (3)	25 (1)	9 (2)	16 (1)	−3 (1)	2·49
C(22)	6365 (3)	2356 (3)	6372 (2)	144 (4)	110 (4)	31 (1)	−13 (3)	10 (2)	−13 (2)	3·53
C(44)	5904 (3)	3207 (3)	3869 (3)	150 (4)	118 (4)	37 (1)	−14 (3)	23 (2)	16 (2)	3·75
C(66)	3022 (3)	1426 (4)	6080 (2)	134 (4)	148 (5)	36 (1)	25 (3)	34 (2)	−7 (2)	3·69
O(1)	7735 (2)	1209 (2)	5064 (1)	93 (2)	124 (3)	39 (1)	−15 (2)	14 (1)	6 (1)	3·15
O(2)	3841 (2)	857 (2)	2911 (1)	162 (3)	147 (3)	23 (1)	6 (2)	6 (1)	7 (1)	3·71
O(3)	3364 (2)	3604 (2)	4687 (1)	127 (2)	90 (2)	45 (1)	21 (2)	11 (1)	−1 (1)	3·45

DMF

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B[†]
O(S1)	917 (2)	1028 (2)	3834 (1)	155 (3)	148 (3)	54 (1)	10 (2)	−1 (1)	9 (1)	4·78
C(S2)	257 (3)	2267 (3)	3972 (2)	106 (3)	158 (5)	50 (1)	−3 (3)	5 (2)	8 (2)	4·05
N(S3)	214 (2)	3612 (3)	3519 (1)	119 (3)	149 (4)	47 (1)	13 (3)	11 (1)	12 (2)	3·89
C(S4)	542 (4)	4953 (4)	6268 (3)	165 (5)	167 (6)	82 (2)	38 (4)	25 (3)	2 (3)	5·72
C(S5)	1022 (5)	3759 (5)	2824 (2)	208 (6)	217 (7)	47 (2)	28 (5)	33 (3)	23 (3)	5·44

† Isotropic thermal parameters immediately prior to anisotropic refinement.

Table 4. *Approximate atomic coordinates as fractions of cell edges* ($\times 10^3$) *for the hydrogen atoms*

H($nn-m$) is an atom attached to C(nn), except for H(01–1) which is attached to O(1).

Cedrone

	x	y	z	$B†$
H(22–1)	741 (4)	207 (5)	665 (2)	4·6
H(22–2)	583 (4)	262 (4)	683 (2)	4·6
H(22–3)	641 (4)	338 (5)	603 (2)	4·6
H(44–1)	673 (4)	283 (5)	357 (2)	4·9
H(44–2)	503 (4)	371 (4)	344 (2)	4·9
H(44–3)	637 (4)	397 (4)	432 (3)	4·9
H(66–1)	310 (4)	057 (4)	656 (2)	4·8
H(66–2)	199 (4)	153 (4)	574 (2)	4·8
H(66–3)	331 (4)	255 (5)	636 (2)	4·8
H(01–1)	826 (4)	47 (4)	545 (2)	4·2

DMF

	x	y	z	$B†$
H(S4–1)	104 (5)	525 (5)	577 (3)	6·5
H(S4–2)	− 18 (5)	412 (6)	609 (3)	6·5
H(S4–3)	126 (5)	462 (5)	678 (3)	6·5
H(S5–1)	154 (4)	267 (6)	273 (3)	6·7
H(S5–2)	41 (5)	408 (5)	240 (3)	6·7
H(S5–3)	176 (5)	477 (6)	293 (3)	6·7
H(S2–1)	29 (4)	767 (5)	556 (2)	5·1

† Isotropic thermal parameters held constant during refinement.

Table 5. *Bond distances and angles for symmetrical cedrone and dimethylformamide*

The estimated standard deviations, given in parentheses, refer to the last decimal position.
Superscripted atoms are related to the corresponding atoms without superscripts by means of the center of symmetry.
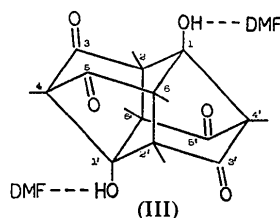
Cedrone

C(1)–C(2)	1·597 (3) Å	C(2) –C(1)–C(4')	103·8 (2)°
C(1)–C(6)	1·597 (3)	C(2) –C(1)–O(1)	112·2 (2)
C(1)–C(4')	1·577 (3)	C(2) –C(1)–C(6)	112·7 (2)
C(1)–O(1)	1·396 (3)	C(4')–C(1)–O(1)	111·2 (2)
		C(4')–C(1)–C(6)	103·7 (2)
		C(6) –C(1)–O(1)	112·6 (2)
C(2)–C(6')	1·557 (3)	C(6')–C(2)–C(1)	99·5 (1)
C(2)–C(22)	1·520 (3)	C(6')–C(2)–C(22)	116·4 (2)
C(2)–C(3)	1·502 (3)	C(6')–C(2)–C(3)	98·7 (2)
		C(1) –C(2)–C(22)	112·3 (2)
		C(1) –C(2)–C(3)	113·9 (2)
		C(3) –C(2)–C(22)	114·6 (2)
C(3)–C(4)	1·528 (3)	C(4) –C(3)–O(2)	125·9 (2)
C(3)–O(2)	1·205 (2)	C(4) –C(3)–C(2)	106·1 (2)
		C(2) –C(3)–O(2)	127·8 (2)
C(4)–C(5)	1·532 (3)	C(5) –C(4)–C(1)	103·6 (2)
C(4)–C(44)	1·516 (4)	C(5) –C(4)–C(3)	99·2 (2)
		C(5) –C(4)–C(44)	114·9 (2)
		C(1) –C(4)–C(3)	103·4 (2)
		C(1) –C(4)–C(44)	118·5 (2)
		C(3) –C(4)–C(44)	114·8 (2)
C(5)–C(6)	1·506 (3)	C(6) –C(5)–C(4)	105·8 (2)
C(5)–O(3)	1·202 (3)	C(6) –C(5)–O(3)	127·7 (2)
		C(4) –C(5)–O(3)	126·4 (2)
C(6)–C(2)	1·557 (3)	C(5) –C(6)–C(2)	98·9 (2)
C(6)–C(66)	1·525 (4)	C(5) –C(6)–C(66)	114·6 (2)
		C(5) –C(6)–C(1)	113·8 (2)
		C(2) –C(6)–C(66)	116·0 (2)
		C(2) –C(6)–C(1)	99·5 (2)
		C(1) –C(6)–C(66)	112·4 (2)

DMF

O(S1)–C(S2)	1·235 (4)	O(S1)–C(S2)–N(S3)	124·2 (3)
C(S2)–N(S3)	1·317 (4)	C(S2)–N(S3)–C(S5)	121·2 (3)
N(S3)–C(S5)	1·459 (5)	C(S2)–N(S3)–C(S4)	121·5 (3)
N(S3)–C(S4)	1·453 (5)	C(S4)–N(S3)–C(S5)	117·2 (3)

A final difference map did not show any areas of difference electron density numerically greater than 0·22 e.Å⁻³.

The refined structure of symmetrical cedrone (without the DMF solvate) is given as a thermal-ellipsoid plot (Johnson, 1965) in Fig. 1.

Discussion

A diagramatic representation of symmetrical cedrone as its DMF solvate is given in structure (III).

(III)

Perhaps the major departure of (III) from Erdtman's formulation of cedrone [structure (II)] lies in the heretofore unrecognized ability of cedrone to undergo a double self-condensation of the aldol type. The DMF probably plays an important role in stabilizing the double aldol isomer of cedrone in the crystal by contributing two strong hydrogen bonds (2·668 Å) between the tertiary alcohol groups and the carbonyl groups of DMF. Numerically, the atomic coordinates of the atoms involved in the hydrogen bond indicate a nearly linear bond (174°), but the estimated standard deviations do not allow too much reliance to be placed on this observation. Rather than extended in a chain fashion through the crystal, the hydrogen bonds are directed towards the cedrone molecule.

The interesting cage structure revealed by our study has several bond lengths which are considerably longer than the normal carbon–carbon lengths, and moreover, a number of valence angles are more acute than the
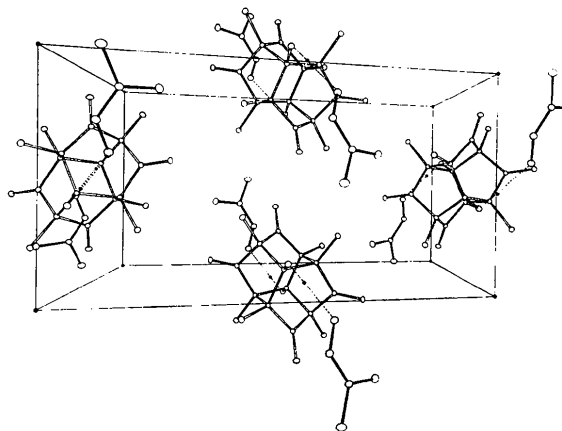

Fig. 2. The crystal structure of symmetrical cedrone DMF solvate. Projection onto the *bc* plane at *circa* 10° from the normal. The H-bonds are indicated by broken lines, and the associated hydrogen atoms, by blacked-in circles.

ideal, such that in solution molecular strain probably contributes to the establishment of an equilibrium among retro-aldolization products (Beisler, Silverton, Penttilla, Horn & Fales, 1971). Three exceptionally long carbon–carbon bonds incorporate the tertiary carbinol group into the ring system. These bonds, from C(1) to C(2), C(6) and C(4'), have lengths of 1·597, 1·597 and 1·577 Å respectively, an occurrence of long bonds about a single tetrahedral carbon atom which does not appear to have been observed previously. It is likely that the symmetrical cedrone molecule itself contains a greater fraction of long, formally sp^3 hybridized, carbon–carbon bonds than any other structure studied to date.

Symmetrical cedrone is composed of a pair of six-membered rings and two pairs of five-membered rings wherein an inversion center applied to a ring generates the other member of the pair in each case. Mean-plane calculations (Cannon, 1970) for the five-membered rings show a considerable deviation from the more commonly observed envelope conformation (Table 6, planes C and D). The pairs of five-membered rings are concatenated in such a way as to form a closed surface and the cross-section of the mean planes has the form of a parallelogram (acute angle of 54°). A similar calculation for one ring of the pair of symmetrically related six-membered rings gives a mean-plane (plane A) which also suggests distortion from the more commonly observed chair conformation. On inspection of the displacements of the atoms of plane A (which forms dihedral angles of 39° with plane C and 145° with plane D), it is apparent that distortion has resulted in a greater departure from planarity than would be the case in an unstrained chair-form. On the other hand, the internal six-membered ring (plane B), composed of three carbon atoms and their centrosymmetrically related equivalents, when similarly analyzed is more normal.

Table 6. *Equations of mean planes (X, Y and Z are orthogonal coordinates in Å) and displacement (Å) of atoms from the planes*

Plane A: C(1), C(2), C(3), C(4), C(5), C(6)
$0.2324X+0.9477Y-0.2188Z=$ 0·2456
Plane B: C(1), C(2), C(6), C(1'), C(2'), C(6')
$0.0790X+0.9899Y-0.1177Z=$ 0
Plane C: C(1'), C(2'), C(4), C(5), C(6)
$0.3221X+0.8405Y+0.4357Z=$ 5·3537
Plane D: C(1), C(2'), C(3'), C(4'), C(6)
$0.7049X+0.6136Y-0.3559Z=$ −0·6757

	A	B	C	D
C(1)	−0·115	−0·021		0·056
C(2)	0·218	0·039		
C(3)	−0·335			
C(4)	0·546		0·065	
C(5)	0·496		−0·221	
C(6)	−0·809	0·023	0·325	−0·403
C(1')		0·021	0·143	
C(2')		−0·039	−0·312	0·325
C(3')				0·366
C(4')				−0·343
C(6')		−0·023		

The molecular packing arrangement is illustrated in Fig. 2 which was plotted by *ORTEP* (Johnson, 1965) from the atomic parameters. No intermolecular distances are significantly shorter than the sums of the van der Waals radii except, as already mentioned, for the atoms involved in the hydrogen bond. However, the bond lengths of the three methyl groups [C(22), C(44), C(66)] in the asymmetric unit appear somewhat shortened, probably as a consequence of thermal motion.

The ultraviolet absorption spectrum of symmetrical cedrone diacetate (Beisler, Silverton, Horn & Fales, 1971) disclosed an enhancement (ε_{312}^{max} 500) over the expected extinction coefficient at the maximum, as well as a second higher energy transition of a lesser intensity, which cannot be simply explained by independent contributions of the four ketonic chromophores present in the molecule. One possible model compound, 2,2,5,5-tetramethylcyclohexanedione-1,3, exhibits normal properties in the ultraviolet (ε_{292}^{max} 46). Neither fine structure nor additional transitions were recorded (Eistert & Reiss, 1954). The diacetate spectrum, at least in part, might be more fully interpreted by assuming a transannular interaction of the π-orbitals of the 1,3-diketone groups. Since it is not unreasonable to assume a close correspondence in molecular structure between symmetrical cedrone diacetate and symmetrical cedrone DMF solvate, it might be informative to discuss the structure of the latter in some detail in the region of the 1,3-diketone chromophore.

The structure of symmetrical cedrone requires that the carbonyl groups of the 1,3-diketones be forced toward the interiors of their respective six-membered rings to the extent that their longitudinal axes subtend an angle of 79°, thereby facilitating a non-parallel, π-orbital interaction. That the four atoms of the carbonyl groups are very nearly coplanar also geometrically favors this interaction. On the other hand, the distance between the carbon atoms of the carbonyls is rather long (2·332 Å) precluding a more pronounced effect than the observed two to threefold increase over the expected intensity at the maximum.

Although the spectra are not completely comparable, it is interesting to note that a transannular, electronic interaction has been suggested (Kosower, 1963) to rationalize the ultraviolet spectrum of tetramethyl-1,3-cyclobutanedione. In this case, the carbocyclic ring is probably planar but the carbonyl carbon atoms are distant by about 2·2 Å.

The bond lengths and angles of dimethylformamide in this structure determination are in good agreement with the relevant values given in *Tables of Interatomic Distances and Configuration in Molecules and Ions* (Sutton, Kennard, Powell & Whiffen, 1965).

Note added in proof: – It is interesting that a ring system similar to that reported here was observed in a heavy atom derivative of (+)-regulosin (Kobayashi, Iitaka & Shibate, 1970), but given that the derivative is a substituted anthraquinone dimer and that the

e.s.d.'s of bond lenghts are *ca.* 0·04Å, the results are not directly comparable.

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A Single-Crystal Structure Determination of DL-6-Thioctic Acid, C₈H₁₄O₂S₂

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Single crystals of DL-6-thioctic acid, (α-DL-lipoic acid), {5-[3(1,2-dithiolanyl)] pentanoic acid}, were obtained by recrystallization of a racemic mixture of DL-6-thioctic acid from cyclohexane. The crystals are predominantly twinned, and show a high degree of disordering. The space group is $P2_1/c$ with $a = 11\cdot744$, $b = 9\cdot895$, $c = 9\cdot246$ Å, and $\beta = 109°35'$. There are four molecules per unit cell, and the structure was solved by the heavy-atom technique. Hydrogen atoms were located using difference Fourier syntheses. The molecules are held together by hydrogen bonds between pairs of carboxyl groups, and by van der Waals contacts between sulphur atoms. Karle, Estlin & Britts (Acta Cryst. (1967) **22**, 567) previously solved the crystal structure of the twinned crystal of DL-6-thioctic acid, using a restricted data set. This single-crystal study reports more accurate bond distances and angles for the same molecule.

Introduction

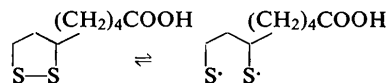Lipoic acid possesses fat soluble and acidic characteristics.
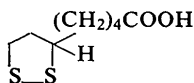
The current view suggests that is it concerned directly in photosynthesis, carrying energy from activated

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chlorophyll in illuminated chloroplasts (Calvin, Bartlop & Hayes, 1954), and then reducing pyridine nucleotides. Lipoic acid also acts to decarboxylate and, at the same time, dehydrogenate pyruvic acid in mammalian carbohydrate metabolism (Wagner & Folkers, 1964).

Many properties of α-lipoic acid accrue from the ease with which it can be reduced or oxidized according to:

and the present study was undertaken principally to find the conformation of the ring.

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