The Crystal and Molecular Structure of Averufin

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The crystal structure of averufin has been determined by means of the X-ray diffraction method. The space group is $P2_1/a$, with $a=23.70$ Å, $b=7.24$ Å, $c=9.48$ Å, and $\beta=105.5°$. The structure was solved by the interpretation of the three-dimensional Patterson function and was refined by the least-squares method. The molecular structure is in agreement with that proposed by Roffey and Grandjean. In the crystal, the molecules are linked to form a molecular pair by a OH----O hydrogen bond across the center of symmetry.

Aspergillus versicolor (Vuillemin) Tiraboschi produces a number of xanthones and anthraquinones. The fact that all these metabolites are produced by the same mold leads to the postulate that some of them may be biogenetic precursors of the carsinogenic sterigmatocystin. In a previous paper, the crystal structure of *p*-bromobenzoate of sterigmatocystin was reported by Tanaka *et al.*[1]

Averufin was isolated as the metabolite of this mold by Pusey *et al.*,[2] and its chemical structure was proposed by Holker *et al.*[3] and Roffey and Sargent.[4]

The present paper will describe the crystal and molecular structure of averufin, as analyzed by means of the X-ray diffraction method, as one of a series of studies of the crystal structures of some metabolites from this mold. After this study was completed, it was discovered that the structure of averufin had been elucidated by Grandjean by means of NMR spectroscopy.[5] The molecular structure determined by us is in agreement with that proposed by Roffey and Sargent[4] and Grandjean.[5]

Experimental

The crystal grown from an acetone solution was in the form of a reddish, flat, rectangular plate elongated in the *a*-axis direction. The unit cell dimensions are shown in Table 1.

TABLE 1. CRYSTAL DATA OF AVERUFIN

Molecular formula; $C_{20}H_{16}O_7$
$M=368.328$
Monoclinic; space group $P2_1/a$
$a=23.704$Å
$b=7.239$Å
$c=9.483$Å
$\beta=105.46°$
$V=1568.3$Å^3
d(obs) $=1.562$ g/cm^3
d(cal) $=1.558$ g/cm^3
$Z=4$

Mo-K_α radiation filtered by means of a zirconium foil was used to collect all the reflections in the $0<\sin\theta/\lambda<0.651$ range, within the (hkl) and ($hk\bar{l}$) octants. All the intensities were measured on a Rigaku Denki computer-controlled four-circle diffractometer (AFC-II). A scintillation counter with a pulse-height discriminator was used. Altogether, 2909 independent reflections were collected. A crystal of the approximate dimensions of $0.23\times0.22\times0.13$ mm^3 ($0.964<e^{-\mu r}<0.968$) was mounted with the *b*-axis parallel to the ϕ-axis of the diffractometer. The ω–2θ scan technique was employed, with a scan speed of 1°/min by ω, backgrounds were measured for 10 seconds at each start and end points of the scan range. The scan range for each reflection was calculated by means of the formula indicated by Alexander *et al.*[6]: ω scan range$=0.70°+0.40°\tan\theta$. Attenuators were automatically inserted when the maximum counting rate exceeded 5000 cps. The intensities were corrected only for Lorentz and polarization factors. Measurements of three reference reflections, (14 0 0), (0 0 8), and (0 4 0), were repeated every fifty reflections; for 62 repetitions of the measurements, $|F_0(14\ 0\ 0)|=144.26\pm0.33$, $|F_0(0\ 0\ 8)|=42.78\pm0.11$, and $|F_0(0\ 4\ 0)|=56.37\pm0.10$.

Determination of the Structure

The angular coordinates defining the orientation of the planar anthraquinone group in the molecule were readily established by means of the vector-set-seeking method;[7] the vector set of the anthraquinone skeleton was superposed on the three-dimensional Patterson function and rotated until the best fit was obtained. The location of this planar group in the unit cell was determined from the Patterson function, in which a large non-Harker peak is expected corresponding to the anthraquinone-anthraquinone vector from molecules related by a center of symmetry. Of several possible peaks, the one which satisfied a reasonable packing condition in the crystal and which gave the best match with the Patterson function was selected. This interpretation was proved to be correct. The 780 largest structure factors were calculated by the use of the atomic positions of the anthraquinone group only, and the R value defined by $R=\sum||F_o|-|F_c||/\sum|F_o|$ was 0.69. The Fourier synthesis phased by the anthraquinone group was computed. The peaks corresponding to some additional atoms were clearly visible, their peak-heights were approximately

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Table 2. Final parameters of carbon and oxygen atoms
The anisotropic temperature factors are of the form
$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$

	x	y	z	$\beta_{ij}\times10^4$					
				β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C (1)	−0.1346	0.0387	−0.0667	13	120	65	0	10	−1
C (2)	−0.1123	−0.1356	−0.0806	13	123	62	−7	17	−17
C (3)	−0.0610	−0.1911	0.0203	14	118	70	9	19	−5
C (4)	−0.0320	−0.0741	0.1348	12	121	59	6	13	−9
C (5)	0.0199	−0.1364	0.2438	12	122	80	−2	17	−23
C (6)	0.0468	−0.0149	0.3653	11	133	75	−3	17	1
C (7)	0.0953	−0.0737	0.4775	11	160	86	2	14	−12
C (8)	0.1202	0.0404	0.5952	12	180	71	0	4	−6
C (9)	0.0978	0.2156	0.6008	14	153	72	−21	15	−26
C (10)	0.0507	0.2794	0.4908	13	127	85	−9	10	−19
C (11)	0.0248	0.1635	0.3747	11	129	68	−2	11	8
C (12)	−0.0280	0.2293	0.2655	14	116	77	−1	18	2
C (13)	−0.0559	0.1022	0.1443	13	109	67	0	11	−14
C (14)	−0.1061	0.1587	0.0441	15	101	86	13	9	−4
C (15)	−0.2183	−0.0273	−0.2706	14	138	73	−7	7	−13
C (16)	−0.1461	−0.2590	−0.2015	17	129	77	5	8	−49
C (17)	−0.1867	−0.3891	−0.1489	20	120	120	−16	−8	21
C (18)	−0.2312	−0.2773	−0.0949	19	212	110	−24	18	87
C (19)	−0.2606	−0.1351	−0.2086	14	174	85	−12	4	−4
C (20)	−0.2480	0.0933	−0.3976	18	206	87	0	−13	53
O (1)	−0.1850	0.1001	−0.1588	15	123	91	12	−11	−11
O (2)	−0.1789	−0.1426	−0.3168	16	171	59	1	7	−7
O (3)	−0.0410	−0.3615	0.0034	18	132	108	25	2	−84
O (4)	0.0404	−0.2946	0.2355	16	138	111	27	−3	−41
O (5)	0.1184	−0.2443	0.4770	16	184	114	35	−10	−31
O (6)	0.1228	0.3207	0.7189	15	210	90	−9	−5	−83
O (7)	−0.0491	0.3800	0.2774	21	131	105	16	−3	−55

Table 3. Atomic parameters of hydrogen atoms

Atom	x	y	z	B	Atom	x	y	z	B
H (1)	−0.124	0.279	0.050	1.3Å^2	H (9)	−0.208	−0.464	−0.228	3.5Å^2
H (2)	0.032	0.411	0.488	1.9	H (10)	−0.212	−0.208	−0.002	2.2
H (3)	0.099	0.421	0.717	5.1	H (11)	−0.260	−0.350	−0.068	2.8
H (4)	0.155	−0.002	0.674	2.9	H (12)	−0.284	−0.046	−0.170	3.5
H (5)	0.096	−0.300	0.400	5.3	H (13)	−0.285	−0.194	−0.288	2.2
H (6)	−0.008	−0.390	0.085	5.2	H (14)	−0.273	0.181	−0.355	3.4
H (7)	−0.115	−0.330	−0.242	3.0	H (15)	−0.275	0.025	−0.461	3.9
H (8)	−0.162	−0.458	−0.067	3.1	H (16)	−0.216	0.154	−0.444	4.9

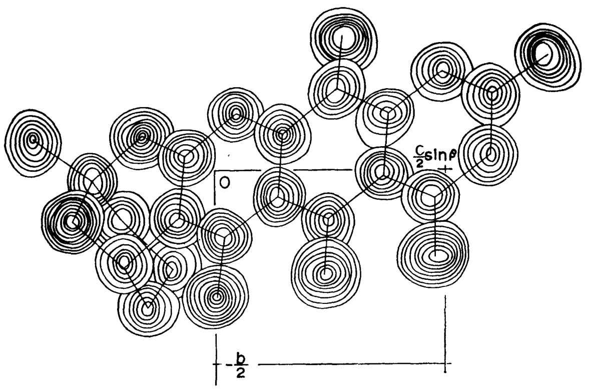

Fig. 1. The electron density map.
The contours are at equally spaced intervals on an arbitrary scale.

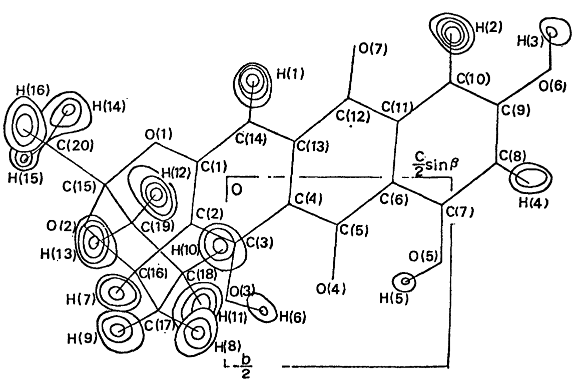

Fig. 2. The difference electron density map, for which the contributions of hydrogen atoms were excluded from the calculated structure factors.

Table 4. Interatomic distances and angles

Bond	Length (Å)	Bond	Length (Å)	Bond	Length (Å)
C (1)-C (2)	1.387(5)	C (1)-C (14)	1.392(5)	C (1)-O (1)	1.354(4)
C (2)-C (3)	1.393(5)	C (2)-C (16)	1.504(5)	C (3)-C (4)	1.406(5)
C (3)-O (3)	1.344(4)	C (4)-C (5)	1.456(5)	C (4)-C (13)	1.404(5)
C (5)-C (6)	1.455(5)	C (5)-O (4)	1.252(4)	C (6)-C (7)	1.410(5)
C (6)-C (11)	1.407(5)	C (7)-C (8)	1.385(5)	C (7)-O (5)	1.353(5)
C (8)-C (9)	1.382(5)	C (9)-O (6)	1.353(4)	C (9)-C (10)	1.388(5)
C (10)-C (11)	1.386(5)	C (11)-C (12)	1.474(5)	C (12)-C (13)	1.485(5)
C (12)-O (7)	1.219(4)	C (13)-C (14)	1.375(5)	C (15)-C (19)	1.510(5)
C (15)-C (20)	1.505(5)	C (15)-O (1)	1.467(4)	C (15)-O (2)	1.403(4)
C (16)-C (17)	1.521(5)	C (16)-O (2)	1.435(4)	C (17)-C (18)	1.523(6)
C (18)-C (19)	1.518(6)	C (14)-H (1)	1.00 (4)	C (10)-H (2)	1.11 (4)
O (6)-H (3)	0.96 (5)	C (8)-H (4)	1.04 (4)	O (5)-H (5)	0.92 (5)
O (3)-H (6)	0.96 (5)	C (16)-H (7)	1.08 (5)	C (17)-H (8)	0.97 (5)
C (17)-H (9)	0.96 (5)	C (18)-H (10)	1.00 (4)	C (18)-H (11)	0.98 (4)
C (19)-H (12)	1.02 (5)	C (19)-H (13)	0.97 (4)	C (20)-H (14)	1.01 (5)
C (20)-H (15)	0.85 (5)	C (20)-H (16)	1.03 (5)		

	Angle(°)		Angle(°)
C (2)-C (1)-C (14)	121.4(3)	C (2)-C (1)-O (1)	122.0(3)
C (14)-C (1)-O (1)	116.6(3)	C (1)-C (2)-C (3)	118.9(3)
C (1)-C (2)-C (16)	118.3(3)	C (3)-C (2)-C (16)	122.8(3)
C (2)-C (3)-C (4)	120.8(3)	C (2)-C (3)-O (3)	117.1(3)
C (4)-C (3)-O (3)	122.2(3)	C (3)-C (4)-C (5)	120.4(3)
C (3)-C (4)-C (13)	118.5(3)	C (5)-C (4)-C (13)	121.0(3)
C (4)-C (5)-C (6)	118.9(3)	C (4)-C (5)-O (4)	120.7(3)
C (6)-C (5)-O (4)	120.4(3)	C (5)-C (6)-C (7)	120.9(3)
C (5)-C (6)-C (11)	121.1(3)	C (7)-C (6)-C (11)	118.0(3)
C (6)-C (7)-C (8)	121.1(3)	C (6)-C (7)-O (5)	121.4(3)
C (8)-C (7)-O (5)	117.5(3)	C (7)-C (8)-C (9)	119.4(3)
C (8)-C (9)-C (10)	121.1(3)	C (8)-C (9)-O (6)	117.3(3)
C (10)-C (9)-O (6)	121.6(3)	C (9)-C (10)-C (11)	119.7(3)
C (6)-C (11)-C (10)	120.7(3)	C (6)-C (11)-C (12)	120.6(3)
C (10)-C (11)-C (12)	118.6(3)	C (11)-C (12)-C (13)	117.7(3)
C (11)-C (12)-O (7)	121.0(3)	C (13)-C (12)-O (7)	121.3(3)
C (4)-C (13)-C (12)	120.6(3)	C (4)-C (13)-C (14)	121.1(3)
C (12)-C (13)-C (14)	118.3(3)	C (1)-C (14)-C (13)	119.4(3)
C (19)-C (15)-C (20)	113.4(3)	C (19)-C (15)-O (1)	109.0(3)
C (19)-C (15)-O (2)	112.5(3)	C (20)-C (15)-O (1)	104.9(3)
C (20)-C (15)-O (2)	107.7(3)	O (1)-C (15)-O (2)	109.0(3)
C (2)-C (16)-C (17)	112.0(3)	C (2)-C (16)-O (2)	107.6(3)
C (17)-C (16)-O (2)	110.6(3)	C (16)-C (17)-C (18)	109.7(3)
C (17)-C (18)-C (19)	110.6(3)	C (15)-C (19)-C (18)	113.6(3)
C (1)-O (1)-C (15)	118.1(3)	C (15)-O (2)-C (16)	112.4(3)
C (1)-C (14)-H (1)	118 (2)	C (13)-C (14)-H (1)	122 (2)
C (9)-C (10)-H (2)	123 (2)	C (11)-C (10)-H (2)	116 (2)
C (9)-O (6)-H (3)	106 (3)	C (7)-C (8)-H (4)	118 (3)
C (9)-C (8)-H (4)	122 (3)	C (7)-O (5)-H (5)	104 (3)
C (3)-O (3)-H (6)	109 (3)	C (2)-C (16)-H (7)	108 (3)
C (17)-C (16)-H (7)	109 (3)	O (2)-C (16)-H (7)	108 (3)
C (16)-C (17)-H (8)	106 (3)	C (18)-C (17)-H (8)	108 (3)
H (9)-C (17)-H (8)	116 (4)	C (16)-C (17)-H (9)	110 (3)
C (18)-C (17)-H (9)	104 (3)	C (17)-C (18)-H (10)	109 (3)
C (19)-C (18)-H (10)	105 (3)	H (11)-C (18)-H (10)	105 (4)
C (17)-C (18)-H (11)	112 (3)	C (19)-C (18)-H (11)	112 (3)
C (15)-C (19)-H (12)	111 (3)	C (18)-C (19)-H (12)	109 (3)
H (13)-C (19)-H (12)	108 (4)	C (15)-C (19)-H (13)	104 (3)
C (18)-C (19)-H (13)	110 (3)	C (15)-C (20)-H (14)	104 (3)
H (15)-C (20)-H (14)	102 (4)	H (16)-C (20)-H (14)	118 (4)
C (15)-C (20)-H (15)	108 (3)	H (16)-C (20)-H (15)	115 (4)
C (15)-C (20)-H (16)	109 (3)		

Intramolecular hydrogen bond:

O (3)············O (4) 2.561(4)Å O (4)············O (5) 2.554(4)Å O (4)············H (6) 1.72 (6)Å

O (4)············H (5) 1.70 (5)Å O (3)-H (6)···O (4) 151 (6)°Å O (5)-H (5)···O (4) 151 (5)°Å

Estimated standard deviations shown in parentheses refer to the last decimal positions.

half of those of the atoms of the anthraquinone group. The whole structure of the molecule except for the hydrogen atoms was revealed after three successive Fourier synthesis. At this stage, the R value was 0.46. The structure was refined by a diagonal-matrix least-squares procedure with the isotropic temperature factors, until the R value of 0.15 was reached. Further refinement was carried out by the least-squares of block-diagonal matrix approximations with anisotropic temperature factors, using all the reflections. The R value was thus reduced to 0.12. At this stage, the difference Fourier synthesis showed all the hydrogen atoms. The final refinement was made by including the positional parameters and the isotropic temperature factors of the hydrogen atoms, where upon the R value decreased to 0.083. The final atomic parameters are listed in Tables 2 and 3. The final electron density map is shown in Fig. 1. The difference electron density map, for which the contributions of the hydrogen atoms were excluded from the calculated structure factors, is shown in Fig. 2.

A list of the observed and calculated structure factors is available from the authors on request.

Most of the calculations were done on the TOSBAC-3400 by the use of the programs written by the authors. The block-diagonal least-squares refinement was performed on the HITAC 5020E of the university of Tokyo using a program written by T. Ashida, the weighting scheme in the calculation was $w=1.0$ for reflections with $|F_o|\geq 1.5$ and $w=0.5$ for the others. The atomic scattering factors were taken from Ref. 8.

Description of the Structure and Discussion

The bond lengths and bond angles are given in Table 4. The mean bond length of the carbon-carbon bonds in the benzenoid rings is 1.393 Å, which is the same as the length, 1.397 Å, formed in the benzene ring[9] within the limits of error. However, the lengths of C–C bonds adjacent to the quinonoid carbonyl bonds, C(4)–C(5), C(5)–C(6), C(11)–C(12), and C(12)–C(13), are considerably longer than those in the benzenoid rings. The lenghts of the C(12)–O(7) and C(5)–O(4) of the quinonoid carbonyl bonds are 1.219 Å and 1.252 Å respectively. The former agrees well with the C–O bond length in acetaldehyde (1.215)[9] and may be a normal double bond. The latter is longer than the former, the elongation of the latter bond may be due to the influence of the adjacent hydroxyl groups. The lengths of the C–O bonds attached to the anthraquinone skeleton, C(1)–O(1), C(3)–O(3), C(7)–O(5), and C(9)–O(6), are almost constant and have a mean of 1.351 Å. All are in agreement with the length of a single bond between an oxygen and an sp^2-hybridized carbon atom.

The dimensions of the quinonoid group in the averufin show features similar to those in other related molecules whose structures have been studied: p-benzoquinone,[10] anthraquinone,[11] 1,5-dihydroxyanthraquinone,[12] 1:2,5:6-dibenzanthraquinone,[13] and some derivatives of anthraquinone.[14]

There are no significant differences among the five bond lenghts of $C(sp^3)$–$C(sp^3)$, and the mean value (1.515 Å) is shorter than that of a pure single C–C bond. The lengths of the C–O bonds involving $C(sp^3)$ have a mean of 1.435 Å and agree with the C–O single bond distance.

The least-squares plane for the aromatic condensed ring including O(3) to O(7) can be represented by the equation:

$$Z=1.3981X+0.6983Y+3.2390$$

where $X=ax+cz\cos\beta$, $Y=by$, and $Z=cz\sin\beta$. The perpendicular displacements of the atoms from the plane are given in Table 5. As may be seen in Table 5, these atoms are coplanar.

Table 5. Deviations from the least-squares plane

Atom	Deviation	Atom	Deviation
Atoms included in plane			
C(1)	−0.098Å	C(2)	−0.079Å
C(3)	−0.005	C(4)	0.051
C(5)	0.065	C(6)	0.045
C(7)	−0.014	C(8)	−0.062
C(9)	−0.023	C(10)	0.061
C(11)	0.076	C(12)	0.056
C(13)	0.039	C(14)	−0.020
O(3)	0.004	O(4)	0.058
O(5)	−0.063	O(6)	−0.098
O(7)	0.009		
Atoms not included in plane			
O(1)	−0.202	C(16)	−0.194
H(1)	−0.05	H(2)	−0.10
H(3)	−0.24	H(4)	−0.10
H(5)	−0.09	H(6)	−0.04

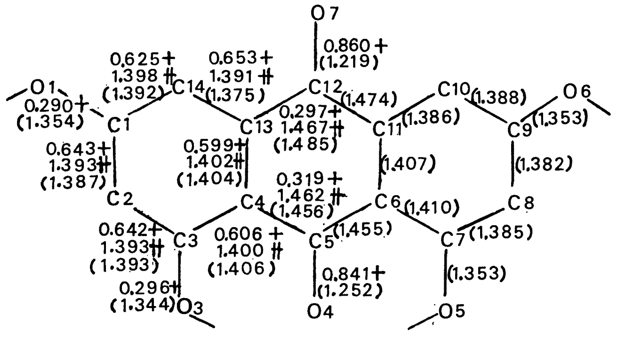

Fig. 3. The π-bond orders and the bond lenghts (Å).
+ the π-bond orders
ǂ the bond lenghts calculated from Coulson's equation
The values in the parentheses are the observed lengths (Å).

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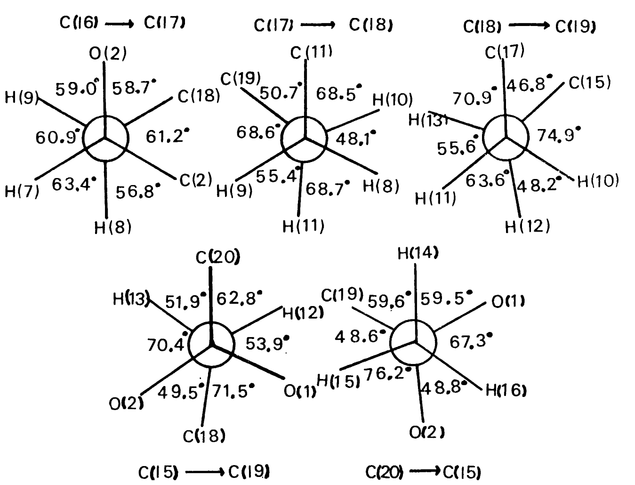

Fig. 4. Internal rotation angles.

The π-bond orders were obtained from a simple LCAO molecular orbital treatment (simple Hückel's method) for the π-electron system alone. The set of Coulomb and exchange integral values suggested by Pullman[15] were used. There are:

$$\alpha(\mathrm{C})=\alpha_0,\ \alpha(=\mathrm{O})=\alpha_0+1.2\beta_0,\ \alpha(-\mathrm{O}-)=\alpha_0+2.0\beta_0,$$
$$\beta(\mathrm{C{-}C})=\beta_0,\ \beta(\mathrm{C{=}O})=2.0\beta_0,\ \beta(\mathrm{C{-}O})=0.9\beta_0$$

where α_0 is the Coulomb integral of the carbon atom in the benzene and whose β_0 is the exchange integral of the C–C bond in the benzene. The lengths of the C–C bonds were estimated from the existing bond order-bond length curve.[16] In the C–C bonds, the agreement between the calculated and observed bond lengths is within 0.02 Å. The lengths of the C–O bonds were not predicated in the present work, because the C–O bond order–bond length data generally have a much wider range of values than the corresponding curve for the C–C bond. The results of the MO calculation are given in Fig. 3.

The conformation of the six-membered ring, C(16)–C(17)–C(18)–C(19)–C(15)–O(2), is a chair form. The internal rotation angles around the C(sp^3)–C(sp^3) bonds are illustrated in Fig. 4. They show a stable, staggered conformation. The average bond angle at the C(sp^3) is 109.8°, and that at the C(sp^2) is 119.9°. The C(15)–O(2)–C(16) angle in the six-membered ring of the chair form is 112.4°; this agrees well with the corresponding angles in sugars.[17] There are two intramolecular hydrogen bonds of the OH···O type: O(3)···O(4)=2.56 Å and O(4)···O(5)=2.55 Å. The molecule has, therefore, the conformation which might be expected to have the lowest energy. A stereoscopic drawing of the molecule is given in Fig. 5.

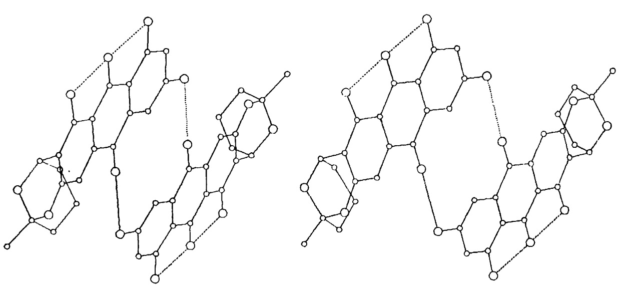

Fig. 5. Stereoscopic drawing of a pair of molecules.

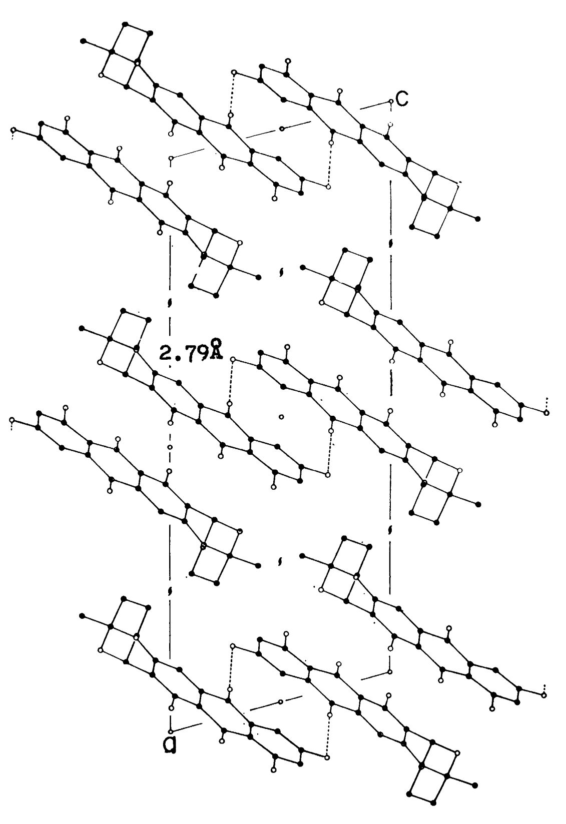

Fig. 6. The crystal structure projected along the *b*-axis.

The crystal structure projected along the *b*-axis is shown in Fig. 6. The closest intermolecular distances are listed in Table 6. The reference molecule at (x, y, z) is connected by the intermolecular hydrogen bond of OH···O of 2.79 Å with the molecule at ($-x$, $1-y$, $1-z$), thus forming a pair of molecules across the center of symmetry. Although the molecule itself has two asymmetric centers, the crystal of averufin is racemized by the molecules related by the centers of symmetry. The intermolecular approach distance between O(3) and O(3) in the "*b*-molecule" is 2.81 Å. Although this distance corresponds to the sum of the van der Waals radii, it is less than the intermolecular O···O distances found in common compounds and compares with the rather long intermolecular hydrogen bonds. Such a close distance has been found in 1,5-dihydroxyanthraquinone: according to Hall *et al.*,[12] this intermolecular interaction is due to the proton of the hydrogen atom in the hydroxyl group, which may participate in the interactions among the closest oxygen atoms. However, in averufin, it appears that the approach of these oxygen atoms may correspond to the van der Waals interaction, because the hydrogen atom attached to the O(3) atom may participate only in the formation of the intramolecular hydrogen bond.

The other intermolecular distances require no special comment; all correspond to the normal van der Waals interaction.

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TABLE 6. INTERMOLECULAR CONTACTS

Atom	Neighbour atom	Distance	Atom	Neighbour atom	Distance
C(1)	C(5) a	3.63 Å	C(7)	C(12) c	3.44Å
C(2)	C(5) a	3.59	C(8)	C(12) c	3.45
C(2)	C(6) a	3.62	C(8)	C(13) c	3.39
C(3)	C(4) a	3.53	C(9)	C(13) c	3.66
C(3)	C(13) a	3.59	C(11)	C(16) a	3.74
C(4)	C(4) a	3.47	C(11)	C(11) c	3.76
C(4)	C(9) c	3.44	O(6)	C(3) c	3.33
C(4)	C(13) a	3.79	O(6)	C(4) c	3.37
C(5)	C(9) c	3.53	O(7)	C(10) d	3.31
C(5)	C(10) c	3.53	O(2)	C(7) a	3.21
C(6)	C(16) a	3.72	O(2)	C(8) a	3.38
C(6)	C(10) c	3.54	O(2)	C(20) e	3.39
C(6)	C(11) c	3.51	O(3)	O(3) b	2.81
C(7)	C(11) c	3.56	O(7)	O(6) d	2.79

Key for position of molecules
a $(-x \quad -y \quad -z)$
b $(-x \quad -1.0-y \quad -z)$
c $(-x \quad -y \quad 1.0-z)$
d $(-x \quad 1.0-y \quad 1.0-z)$
e $(-0.5-x \quad -0.5+y \quad -1.0-z)$

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