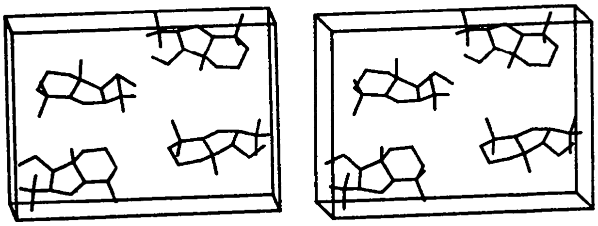

Fig. 3. Stereoscopic view of the crystal packing (*ESTER*; Gaete, 1985).

C10···C12 = 3·29 (1) Å, shorter than a normal van der Waals separation. The five-membered ring exhibits a half-chair conformation $[\Delta C_2^8 = 5\cdot2(6)]$. Both C12 and the two substituents at C8 and C9 point to the same side of the molecule. The ring junction is *trans*.* The molecules are linked by intermolecular hydrogen bonds forming infinite double chains along the *x* axis, O16—H···O17 ($x+1, y, z$) and O17—H···O16 ($-\frac{1}{2}+x, 1\frac{1}{2}-y, -z$) with O···O distances of 2·827 (6) and 2·744 (6) Å.† The crystal packing is depicted in Fig. 3.

We are greatly indebted to Drs J. J. Bonet and A. Planas (Instituto Químico de Sarriá, Barcelona, Spain) and Dr M. Cortés (Pontificia Universidad Católica de Chile) for suggesting the problem and providing the sample.

References

Appel, H. H., Brooks, C. J. W. & Overton, K. H. (1959). *J. Chem. Soc.* pp. 3322–3332.

Brunke, E. J. (1980). *Dragoco Rep.* **9**(1).

Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure*, Vol. I, pp. 18–19. New York: Plenum.

Escobar, C. & Wittke, O. (1984). *Acta Cryst.* C**40**, 1469–1471.

Gaete, W. (1985). *ESTER*. Program for crystal structure representation. Univ. Autónoma de Barcelona (Spain).

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Ley, S. V. & Mahon, M. (1981). *Tetrahedron Lett.* pp. 3909–3912.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Planas, A., Cortés, M. & Bonet, J. J. (1985). *Afinidad*, **42**, 375–376.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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* Torsion angles C2—C1—C6—C5 and C9—C1—C6—C7 −54 and 49°, respectively.

† Details of the hydrogen bonding have been deposited. See deposition footnote.

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Structure of 1-Acetyl-2,4,5,7-tetrahydroxy-9,10-anthracenedione

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Abstract. $C_{16}H_{10}O_7$, $M_r = 314\cdot2$, orthorhombic, *Pbca*, $a = 15\cdot400$ (7), $b = 6\cdot930$ (2), $c = 23\cdot92$ (1) Å, $V = 2552\cdot8$ Å^3, $Z = 8$, $D_x = 1\cdot63$, $D_m = 1\cdot62$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 1\cdot15$ mm^{-1}, $F(000) = 1296$, $T = 293$ K, final $R = 0\cdot052$ for 812 unique observed reflections. The crystal structure consists of stacks of 'dimerized' planar molecules related by the *b* glide plane and interlinked by a hydrogen-bond network to form a densely packed arrangement. The molecular structure is analysed in detail and results are compared with those of five other analogues reported (with comparable accuracy) earlier. There is crystallographic evidence for the existence of a significant attractive charge-transfer interaction which is probably of the n–π^* type and involves an sp^3-like lone pair of a carbonyl oxygen as *n* donor and the π system of the

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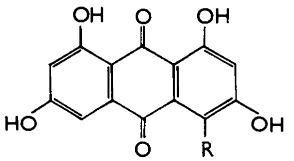
neighbouring molecule. The unique behaviour of the title compound seems to be related to a significant contribution from a zwitterionic resonance structure which, in turn, is enhanced by the polarizing and electron donating of the hydroxy groups.

Introduction. Hydroxyanthraquinones are secondary metabolites of various fungi, plants and lower animals (*viz.* crinoids). Several fungal hydroxyanthraquinones are known as mycotoxins, carcinogens, mutagens and uncouplers of respiration and oxidative phosphorylation (Ueno, 1984).

From a colour mutant of the fungus *Trichoderma viride* two hydroxyanthraquinones were recently isolated and spectroscopically identified as 1,3,6,8-tetrahydroxyanthraquinone (*A*) and 1-acetyl-2,4,5,7-tetrahydroxy-9,10-anthracenedione (*B*) (Betina, Sedmera, Vokoun & Podojil, 1986). The former was a known metabolite of the fungus *Aspergillus versicolor* (Berger, 1980) whereas the latter was found in the crinoids *Heterometra savingii* and *Lamprometra kluzingeri* and was named rhodolamprometrin (Erdman & Thomson, 1972). Both compounds were found to possess uncoupling activity in rat liver mitochondria (Betina & Kuželа, in preparation).



(*A*) R = H
(*B*) R = $COCH_3$

In the present paper, the results of our X-ray investigations of rhodolamprometrin are reported. We have confirmed the structural formula of the compound and elucidated its crystal structure and stereochemistry.

Experimental. The sample used in our studies was isolated by one of us (VB) from *T. viride* mutant CCM F-742; orange crystals obtained from ethyl acetate solution, crystal used: 0·1 × 0·05 × 0·04 mm; D_m by flotation; systematically absent reflections: $0kl$ for k odd, $h0l$ for l odd, $hk0$ for h odd, from precession and Weissenberg photographs; Syntex $P2_1$ diffractometer; accurate unit-cell parameters by least-squares refinement of 12 reflections, $15 < \theta < 45°$; intensity data ($h = 0$ to 15, $k = 0$ to 6, $l = 0$ to 23) by $\theta/2\theta$ scans, variable rate 4·9 to 29·3° min^{-1} in 2θ, background-to-scan-time ratio = 1·0, scan width 2° plus α_1—α_2 dispersion, Cu $K\alpha$ radiation filtered by graphite monochromator; two standards every 98 reflections; no appreciable trends; 1311 unique reflections, $2 < \theta \leq 50°$, 812 with $I \geq 1{\cdot}96\sigma(I)$ considered observed and included in the refinement; Lp correction but none for absorption or extinction; structure solved by direct methods, automatic use of *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) only gave orientation of the anthraquinone moiety (16-atom fragment) with many erroneous peaks; in a subsequent *MULTAN* run the known orientation of the fragment with random position was used as input, the *E* map computed from the best phase set revealed all 23 non-hydrogen atoms; refinement by block-diagonal least-squares method, $\Delta\rho$ map showed positions of all H atoms, refinement continued on all positional and anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms; in final cycle $R = 0{\cdot}052$, $wR = 0{\cdot}057$ for observed reflections only, max. shift/e.s.d. = 0·13, function minimized $\sum w(\Delta F)^2$, where $w = 1$ if $|F_o| < 70$ and $w = 70/|F_o|$ if $|F_o| \geq 70$, max. and min. height in final $\Delta\rho$ synthesis 0·20 and 0·24 e Å^{-3}, scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974); all calculations except *MULTAN* performed with local version of the NRC system (Ahmed, Hall, Pippy & Huber, 1973).

Table 1. *Final atomic coordinates* (× 10^4) *with e.s.d.'s in parentheses and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
C(1)	1913 (2)	3949 (5)	6333 (1)	2·53
C(2)	2686 (2)	4043 (5)	6674 (1)	2·33
C(3)	2649 (2)	4404 (5)	7245 (1)	2·70
C(4)	3399 (2)	4620 (5)	7564 (1)	2·94
C(5)	4196 (2)	4438 (5)	7308 (1)	2·67
C(6)	4279 (2)	4038 (5)	6743 (1)	2·38
C(7)	3524 (2)	3890 (5)	6423 (1)	2·51
C(8)	3602 (2)	3602 (5)	5809 (1)	2·52
C(9)	2795 (2)	3505 (4)	5470 (1)	1·98
C(10)	2846 (2)	3274 (5)	4905 (1)	2·70
C(11)	2088 (2)	3214 (5)	4583 (1)	2·56
C(12)	1283 (2)	3401 (5)	4826 (1)	3·12
C(13)	1224 (2)	3645 (5)	5399 (1)	2·61
C(14)	1968 (2)	3698 (5)	5741 (1)	2·42
C(15)	5178 (2)	3757 (5)	6510 (1)	2·32
C(16)	5665 (2)	5544 (6)	6339 (1)	3·71
O(1)	1177 (1)	4088 (4)	6569 (1)	3·23
O(2)	4312 (1)	3473 (4)	5590 (1)	3·62
O(3)	1889 (1)	4568 (3)	7534 (1)	3·32
O(4)	4955 (1)	4664 (4)	7601 (1)	3·44
O(5)	2193 (1)	2999 (4)	4021 (1)	3·68
O(6)	415 (1)	3835 (4)	5614 (1)	3·48
O(7)	5527 (1)	2169 (3)	6521 (1)	2·70

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters for the title compound [hereafter referred to as (6)] are given in Table 1.[*]

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[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters, best planes, selected torsion angles and hydrogen-bond parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43402 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2 is a list of bond lengths arranged in groups of similar type; corresponding bond angles are listed in Table 3. A view of the molecule with atom numbering is shown in Fig. 1. The structural results given here are directly comparable to those published previously with sufficient accuracy for three other anthraquinone derivatives – the parent, unsubstituted anthraquinone [compound (1)] (Prakash, 1967); 1-[2-(diethylamino)-ethylamino]anthraquinone (2) (Almond, Cutbush, Islam, Kuroda, Neidle, Gandecha & Brown, 1983); 1,8-dinitro-4,5-dihydroxyanthraquinone (3) (Brown & Colclough, 1983) as well as closely related anthralin dimer (4) (Ahmed & Neville, 1982) and anthralin (5) (Ahmed, 1980).

Disregarding the acetyl group bonded to C(6), the molecule of (6) has, as far as bond lengths and endocyclic angles are concerned, an approximate mirror plane, passing through C(1) and C(8) and perpendicular to the molecular plane. Equivalent distances and angles across the pseudo-mirror plane agree to within 4σ, with two significant exceptions; the C(9)—C(10)—C(11) and C(5)—C(6)—C(7) angles differ by 6σ, and Δ/σ for C(9)—C(10) and C(6)—C(7) is 7·2, which is highly significant. A probable reason for this lengthening of the C(6)—C(7) bond [compared with C(9)—C(10)] will be given later.

Table 2. *Intramolecular distances* (Å) *arranged in groups of similar bonds* (*e.s.d.'s in parentheses*)

C—C		C=O	
C(1)—C(2)	1·446 (4)	C(1)=O(1)	1·270 (4)
C(2)—C(3)	1·388 (4)	C(8)=O(2)	1·217 (4)
C(3)—C(4)	1·393 (5)	C(15)=O(7)	1·225 (4)
C(4)—C(5)	1·378 (5)		
C(5)—C(6)	1·386 (4)	C—OH	
C(6)—C(7)	1·396 (5)	C(3)—O(3)H	1·364 (4)
C(7)—C(8)	1·486 (5)	C(5)—O(4)H	1·371 (4)
C(8)—C(9)	1·485 (4)	C(11)—O(5)H	1·362 (4)
C(9)—C(10)	1·364 (4)	C(13)—O(6)H	1·354 (4)
C(10)—C(11)	1·399 (5)		
C(11)—C(12)	1·375 (5)		
C(12)—C(13)	1·383 (5)		
C(13)—C(14)	1·409 (5)		
C(14)—C(1)	1·429 (5)		
C(2)—C(7)	1·428 (4)		
C(14)—C(9)	1·435 (4)		
C(6)—C(15)	1·505 (4)		
C(15)—C(16)	1·504 (5)		

Table 3. *Valence angles* (°) *involving atoms in the molecule* (*e.s.d.'s in parentheses*)

C(14)—C(1)—C(2)	121·1 (3)	C(9)—C(10)—C(11)	120·1 (3)
C(1)—C(2)—C(3)	122·0 (3)	C(10)—C(11)—C(12)	121·1 (3)
C(1)—C(2)—C(7)	120·2 (3)	C(11)—C(12)—C(13)	119·4 (3)
C(3)—C(2)—C(7)	117·7 (3)	C(12)—C(13)—C(14)	121·6 (3)
C(2)—C(3)—C(4)	121·6 (3)	C(13)—C(14)—C(1)	122·0 (3)
C(3)—C(4)—C(5)	119·0 (3)	C(9)—C(14)—C(1)	120·8 (3)
C(4)—C(5)—C(6)	122·3 (3)	C(9)—C(14)—C(13)	117·3 (3)
C(5)—C(6)—C(7)	118·2 (3)	C(6)—C(15)—C(16)	116·9 (3)
C(5)—C(6)—C(15)	118·2 (3)		
C(7)—C(6)—C(15)	123·6 (3)	C(14)—C(1)—O(1)	120·2 (3)
C(6)—C(7)—C(8)	119·0 (3)	C(2)—C(1)—O(1)	118·7 (3)
C(6)—C(7)—C(2)	121·1 (3)	C(7)—C(8)—O(2)	120·6 (3)
C(8)—C(7)—C(2)	120·0 (3)	C(9)—C(8)—O(2)	120·9 (3)
C(7)—C(8)—C(9)	118·6 (3)	C(6)—C(15)—O(7)	120·7 (3)
C(8)—C(9)—C(14)	119·5 (3)	C(16)—C(15)—O(7)	121·9 (3)
C(10)—C(9)—C(14)	120·6 (3)	C(2)—C(3)—O(3)	123·4 (3)
C(8)—C(9)—C(10)	120·0 (3)	C(4)—C(3)—O(3)	115·0 (3)
		C(4)—C(5)—O(4)	121·4 (3)
		C(6)—C(5)—O(4)	116·3 (3)
		C(10)—C(11)—O(5)	116·5 (3)
		C(12)—C(11)—O(5)	122·4 (3)
		C(12)—C(13)—O(6)	116·8 (3)
		C(14)—C(13)—O(6)	121·7 (3)

To minimize steric interactions, the acetyl group at C(6) is approximately perpendicular to the least-squares plane of the respective phenyl ring, the dihedral angle being 88·7°. The lack of conjugation between these two groups is further confirmed by the bond length C(6)—C(15) [1·505 (4) Å] which is still longer than the normal value of 1·487 Å reported for the C(sp^2)—C(sp^2) single bond (Shmueli, Shanan-Atidi, Horwitz & Shvo, 1973); similarly, the C(15)—O(7) distance [1·225 (4) Å] is very close to the range of 1·21–1·22 Å normally accepted for a C=O double bond.

Regarding the dimensions of the anthraquinone nucleus, C(8)—O(2) [1·217 (4) Å] is within the typical C=O double-bond range; thus C(8)—O(2) has localized double-bond character. In contrast, the formal double bond C(1)—O(1) is about 0·05 Å longer than C(8)—O(2). A similar effect, but to a lesser extent, has been observed in (3)–(5) and attributed to a polarization of the π electron cloud from the C(1)=O(1) bond to O(1) due to formation of two strong intramolecular hydrogen bonds, O(8)—H···O(1)···H—O(3). Within the central ring of the anthraquinone moiety, bonds C(1)—C(2) and C(1)—C(14) [1·446 (4) and 1·429 (8) Å respectively] are considerably shorter than bonds C(7)—C(8) and C(8)—C(9) [1·486 (5) and 1·485 (4) Å], the latter showing pure C(sp^2)—C(sp^2) single-bond character. Furthermore, bonds C(2)—C(7) and C(9)—C(14) [1·428 (5) and 1·435 (4) Å] have apparently less double-bond character than other C—C aromatic bonds in the benzo rings.

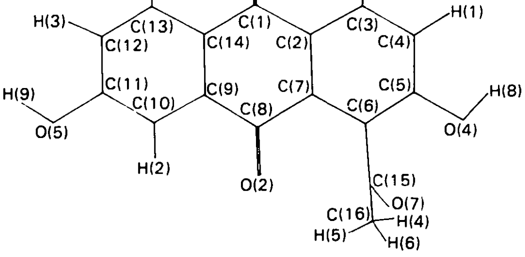
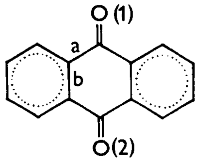
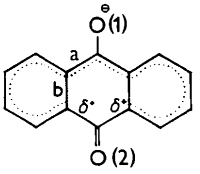


Fig. 1. A molecule of the title compound, showing the atom labelling (intramolecular hydrogen bonds dashed).

Thus the molecular structure of the anthraquinone nucleus cannot be expressed in a satisfactory way by a single canonical formula; consequently, two forms (I) and (II) should contribute to the electronic configuration of the molecule.



(I)



(II)

Form (I) corresponds to the quinonoid structure normally encountered in anthraquinone derivatives while form (II) represents an extension of π electron delocalization from the benzo rings to the C(2)—C(1)—C(14) bridge resulting in a shifting of one half of the central ring from a quinonoid to a benzenoid structure. The zwitterionic structure (II) implies an anionic character for O(1) whereas the positive charge is delocalized in the cyclic anthraquinone framework. Thus electron transfer from the C=O(1) bond to O(1) is accompanied by a change in hybridization of O(1) from sp^2 to sp^3.

We denote two relevant C—C bond-length averages (in the central ring) by *a* and *b* [see formulae (I) and (II)] and define $\Delta = a - b$. An estimation of bond order of the formal double bond C=O(1) and hence the significance of (I) and (II) cannot be made simply from consideration of the C—O(1) bond length as the C_{ar}—O^- distance tends to be highly sensitive to a partial charge on the aromatic carbon (see below). Nevertheless, from a comparison of bond lengths in compounds (1) – (6), a good correlation between Δ and the C—O(1) bond length can be found. This correlation is clearly reflected in the trend from (1) [$\Delta = 0{\cdot}07$ (1), C—O(1) = 1·21 (1) Å] through (5) [$\Delta = 0{\cdot}038$ (4), C—O(1) = 1·261 (3) Å] to (6) [$\Delta = 0{\cdot}006$ (5), C—O(1) = 1·270 (4) Å], indicating that the percentage of (II) gradually increases from 0 in (1) through *ca* 25% in (5) to as much as ~50% (Δ~0) in (6). Thus it may be concluded that in (6) both (I) and (II) are approximately equal contributors to the ground state of the anthraquinone nucleus.

In the title compound (6) the four C—OH distances are approximately 0·03 – 0·05 Å shorter than the normal value 1·403 Å accepted for the C(sp^2)—O bond; in addition, all hydroxy groups show a tendency to be coplanar with the anthraquinone moiety with concomitant distortion of the exocyclic angles from 120°. These features appear to be common characteristics of both alkoxy and hydroxy bonded to the aromatic systems; in the case of alkoxy groups they have been explained as being due to some degree of conjugation between the O non-bonding orbital and the adjacent aromatic system (Domiano, Nardelli, Balsamo, Macchia & Macchia, 1979). However, a survey of the literature shows that, at least in the case of aromatic–hydroxyl compounds (phenols, naphthoquinols, *etc.*), two general trends are clearly discernible. The first is seen in the sensitivity of the C—OH bond length to the ionization state of the O atom; the C—OH distance decreases upon deprotonation and (partially ionized) hydrogen-bonded hydroxyls have C—O length intermediate between C—O^- and C—OH of non-hydrogen-bonded OH groups. The second trend reflects a shortening of the C—OH distances owing to introduction of electron-withdrawing substituents, *e.g.* nitro groups, which result in charge deficiency on aromatic carbons. This implies that the expected values 1·40–1·41 Å for C(sp^2)—O bond lengths are actually observed only if the hydroxyl is not involved in hydrogen bonding and if it is bonded to essentially neutral or negatively charged aromatic carbon irrespective of the orientation of the O lone-pair orbital with respect to the aromatic system. From the above reasoning it is inferred that the C_{ar}—OH bond lengths are mainly determined by partial charges on C_{ar} and O atoms and hence by an electrostatic attractive effect through a σ bond rather than by π conjugation. Consequently, the shortening of the C—OH bonds observed in the present structure is mainly attributable to the involvement of the hydroxyl groups in strong intra- and intermolecular H-bond interactions (see below).

Packing of the molecules and the pattern of the out-of-plane deviations reveal some interesting features. The crystal packing is dominated by stacks of nearly parallel molecules of (6) related by the *b* glide plane with an average stacking separation of 3·465 Å (*b*/2); the overlap diagram is shown in Fig. 2 as a normal projection along the *b* axis. Molecules in adjacent stacks related by the *a* glide plane are linked in an alternating (zigzag) manner by two asymetrically bifurcated hydrogen bonds, O(4)···O(1) and O(3)···O(4), to form zigzag chains parallel to (010) and

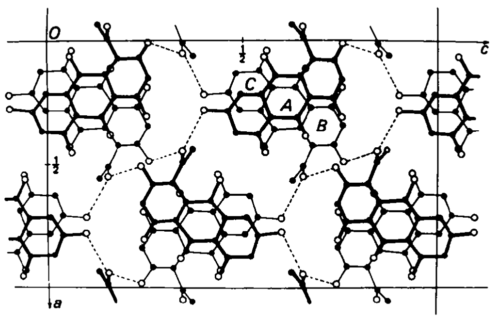


Fig. 2. Packing of the molecules in the unit cell. Broken lines show two major intermolecular hydrogen bonds (for details see the deposited material). The reference molecule has been distinguished by labelling its rings as *A*, *B*, and *C*.

running along the *a* axis. This situation is not shown in Fig. 2 for reasons of clarity. Thus O(1) is involved in three H-bond interactions, proving its sp^3-like character. The packing of adjacent chains, related to each other by the *c* glide symmetry (these chains are interpenetrating when viewed along the *c* axis), is through the O(5)···O(7) hydrogen bond (Fig. 2). Another hydrogen bond (shown in Fig. 2) links the chains in the **b** direction *via* the acetyl oxygen which lies between the chains.

Within the stacks the molecules are oriented so that rings *A* and *C* almost entirely overlap while the *B* ring is shifted sideways so that O(1) sits almost exactly above the mid-point of the C(6)—C(7) bond (Fig. 2); interestingly, this is the bond which was shown to be elongated by a significant amount [0·032(5) Å] relative to its pseudo-C_s counterpart. In addition, the reference molecule forms an intrastack contact O(1)···C(7) ($\frac{1}{2}-x$, $\frac{1}{2}+y$, z) which is a few tenths of an ångström shorter than the same contact with a translationally equivalent molecule at $\frac{1}{2}-x$, $-\frac{1}{2}+y$, z [3·377 (4) *vs* 3·649 (4) Å]. Molecular association along the stacking axis may thus be described as dimerization. These observations strongly suggest the existence of an attractive charge-transfer n–π^* interaction. In fact, keeping in mind that the hybridization state of O(1) is between sp^2 and sp^3 and that the orientation of two non-bonding sp^2 orbitals as well as that of two of three sp^3 orbitals (these two pairs roughly coincide) are fixed by two intramolecular hydrogen bonds, a third sp^3-like lone-pair lobe around O(1) is approximately normal to the molecular plane and hence points toward the π system localized mainly on the C(6)—C(7) bond of the second molecule in the dimer.

As noted above, the mode of distortion of the molecule from planarity lends additional support to this suggestion. The molecule has no symmetry with respect to torsional parameters. Ring *C* is exactly planar ($\chi^2 = 2·85$) with no atom deviating from the six-atom plane by more than 0·003 (3) Å. The *A* 'quinone' ring is also virtually planar ($\chi^2 = 12·69$) with no atom disposed more than 0·006 (3) Å out of the plane. Ring *A*, however, shows slight but significant deviation from planarity ($\chi^2 = 57·30$), the ring being folded relative to the rest of the molecule (the dihedral angle between the mean planes of two benzo rings is 4·5 °). As a result, the 14-membered ring system is definitely non-planar ($\chi^2 = 2127·2$). A lack of planarity of the molecule originates from twisting around the C(6)—C(7) bond with an endocyclic C(5)—C(6)—C(7)—C(2) torsion angle of −3·3 (5)°. As a result, the acetyl C(15) atom is 0·085 (4) Å out of the mean plane of the 14-membered ring system. As regards other ring substituents, O(1) is displaced by 0·067 (3) Å on the same side as C(15) while the O(4) hydroxyl is displaced by 0·161 (3) Å in the opposite direction [O(2) lies approximately within the plane]. Such a pattern of out-of-plane deviations does not appear to be one which reduces steric crowding of the acetyl group [O(4)···O(7) and O(2)···O(7) distances are only 3·231 (3) and 3·046 (3) Å respectively] but reflects attractive effects of O(1) and C(6) to maximize the n–π^* overlap.

The above observations call for careful spectroscopic study, which should confirm the charge transfer predicted here, but the interaction is probably weak and restricted to the solid state. The crystal and molecular structure of the present compound (6) is quite radically different from those of (1)–(5). The only parameters which are varied in molecules (1)–(6) are the intramolecular hydrogen bond(s) and the nature of the substituent(s) on the aromatic skeleton. Weak hydrogen bonds [as in (2)] and/or electron-withdrawing substituents [as in (3)] favour a quinonoid resonance structure (I) while a zwitterionic structure (II) is enhanced by the introduction of extra hydroxyls as electron-donating substituents. This is readily apparent from a comparison of structure (4) [or (5)] with (6) [in the latter comparison the acetyl group is deconjugated and the electron-withdrawing effect of the C=O(2) function in (6) may be neglected]. We believe, therefore, that the unique crystallographic behaviour of the present compound derives from its electronic structure in the sense that a sufficient contribution of (II) is required to activate the exposed O(1) lone pair for charge transfer to occur.

References

AHMED, F. R. (1980). *Acta Cryst.* **B36**, 3184–3186.

AHMED, F. R., HALL, S. R., PIPPY, M. E. & HUBER, C. P. (1973). NRC crystallographic programs for the IBM/360 system. Accession Nos. 133–147 in *J. Appl. Cryst.* (1973). **6**, 309–346.

AHMED, F. R. & NEVILLE, G. A. (1982). *Acta Cryst.* **B38**, 2930–2933.

ALMOND, P., CUTBUSH, S. D., ISLAM, S. A., KURODA, R., NEIDLE, S., GANDECHA, B. M. & BROWN, J. R. (1983). *Acta Cryst.* **C39**, 627–630.

BERGER, Y. (1980). *Phytochemistry*, **19**, 2779–2780.

BETINA, V., SEDMERA, P., VOKOUN, J. & PODOJIL, M. (1986). *Experientia*, **42**, 196–197.

BROWN, C. J. & COLCLOUGH, M. L. (1983). *Acta Cryst.* **C39**, 300–302.

DOMIANO, P., NARDELLI, M. BALSAMO, A., MACCHIA, B. & MACCHIA, F. (1979). *Acta Cryst.* **B35**, 1363–1372.

ERDMAN, T. R. & THOMSON, R. R. (1972). *J. Chem. Soc. Perkin Trans.* 1, pp. 1291–1292.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

MAIN, P., HULL, S. E. LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

PRAKASH, A. (1967). *Acta Cryst.* **22**, 439–440.

SHMUELI, U., SHANAN-ATIDI, H., HORWITZ, H. & SHVO, Y. (1973). *J. Chem. Soc. Perkin Trans.* 2, pp. 657–662.

UENO, Y. (1984). *Mycotoxins – Production, Isolation, Separation and Purification*, edited by V. BETINA, ch. 15, p. 329. Amsterdam: Elsevier.