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The Crystal and Molecular Structure of 1:2,5:6-Dibenzanthraquinone

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The crystal structure of 1:2,5:6-dibenzanthraquinone has been determined by the use of the weighted reciprocal lattice to determine the molecular orientation, and by a trial-and-error computer program, to determine the molecular position in the unit cell. The crystals are orthorhombic with $a=28{\cdot}54$, $b=3{\cdot}85$, $c=12{\cdot}90$ Å and the space group is $Pca2_1$ with four molecules per unit cell. The atomic coordinates and anisotropic temperature parameters have been refined by the least-squares method, to a final R value of 0·0965 for 1354 observed reflexions. The standard deviations of the coordinates are approximately 0·008 Å. The molecular structure consists of two planar naphthalene portions with an angle of 14·1° between the normals to the planes.

Introduction

The interest in 1:2,5:6-dibenzanthraquinone (DBAQ, Fig. 1) arose because of its relationship to the carcinogenic compound 1:2,5:6-dibenzanthracene, although DBAQ shows no biological activity itself. It was also of interest to determine how much the DBAQ molecule departs from planarity, and to compare the results with the molecules of 5-methyl- and 2′-methyl-1:2-benzanthraquinones, which have a similar close approach of a quinone oxygen atom to the 1′ carbon and hydrogen atoms. These latter compounds show little deviation from planarity (Ferrier & Iball, 1963*a*, *b*) though there is some evidence of steric repulsion within the molecules.

Experimental

Early attempts to determine the structure with two-dimensional methods had given reasonable atomic coordinates in the (010) plane but no satisfactory three-dimensional coordinates were obtained. It was decided therefore to collect full three-dimensional data and the compound was recrystallized from dimethylformamide, which, of the many solvents tried, gave the largest crystals in the form of orange needles. The unit cell was measured by calibration of zero-layer Weissenberg photographs with NaCl powder lines, and the crystal density was measured by flotation in a density gradient column. The cell is orthorhombic with

$a=28{\cdot}54\pm0{\cdot}02$, $b=3{\cdot}85\pm0{\cdot}005$, $c=12{\cdot}90\pm0{\cdot}01$ Å
Cell volume $=1417$ Å^3;
Observed density $=1{\cdot}443\pm0{\cdot}003$ g.cm^{-3};
Calculated density $=1{\cdot}441$ with 4 molecules per unit cell.

The systematic absences were $h0l$ absent when h is odd, and $0kl$ absent when l is odd. The space group

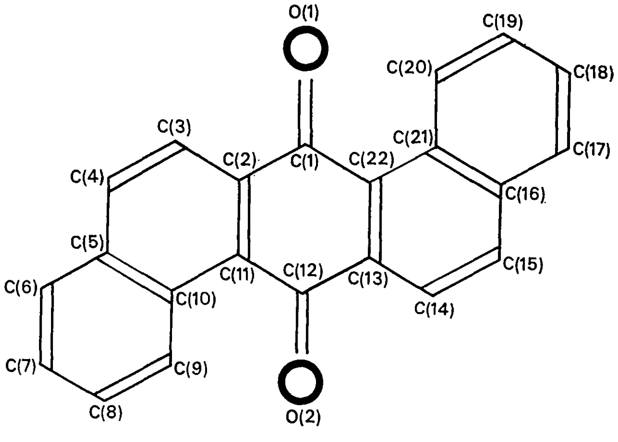

Fig. 1. 1:2,5:6-Dibenzanthraquinone (DBAQ).

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is therefore $Pca2_1$ or *Pcam*. The latter space group is, however, ruled out by packing considerations.

Crystals were mounted on the *a*, *b*, and *c* axes and the following layers were photographed using the equi-inclination Weissenberg technique with Cu *Kα* radiation; *a*-axis layers 0 . . . 6; *b*-axis layers 0 . . . 3; *c*-axis layers 0 . . . 8. A Leeds–Cox Weissenberg camera was used and the intensities of the spots were measured with a Joyce–Loebl recording micro-densitometer, except for very weak reflexions which were estimated visually. On each film the intensities of the spots corresponding to the symmetrically related reflexions were measured and averaged. The crystals used were small and the values of $|F_{\text{obs}}|$ obtained from different crystals and mountings were in good agreement with each other, so no absorption corrections were applied. A total of 1354 reflexions were observed, representing 65% of the possible number obtainable with Cu *Kα* radiation.

Structure determination

The early two-dimensional work had given reasonable *x* and *z* coordinates for the molecule by use of the *h*0*l* weighted reciprocal lattice. As a first step these coordinates were refined by the least-squares method, using the new *h*0*l* reflexion data. This gave an *R* value of 0·116 for 235 structure factors, using individual isotropic temperature parameters. The projected benzene rings were well formed with parallel sides and though some of the projected bond lengths were rather long, it was felt that a valid solution had been reached for the *x* and *z* coordinates.

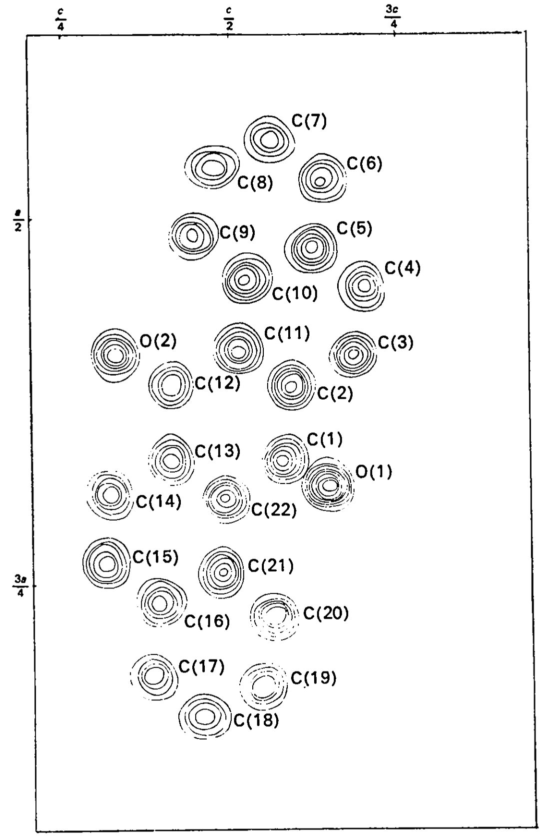

Fig. 2. Superimposed sections of the final three-dimensional Fourier map, with contours at an interval of 1 e.Å^{-3}, starting at 3 e.Å^{-3}.

These *x* and *z* coordinates were now used to calculate the orientation of the two naphthalene portions independently as it seemed clear that the molecule was not planar. Dreiding models showed that the probable configuration was produced by bending the molecule about a line joining the carbon atoms of the central ring. The angle between the planes of the two naphthalene nuclei lay in the range 5 to 15°, assuming an average C–C bond length of 1·41 Å.

The position of the molecule in the *y* direction was determined by means of a computer program written in FORTRAN II for an IBM 1620 machine. The *x* and *z* coordinates were kept fixed and their contributions to a set of 35 reflexions with low θ values were calculated and stored. The molecule was then moved in the *y* direction and the structure factors were efficiently calculated at chosen points using the stored information. This procedure quickly showed a minimum in the *R* value for this set of reflexions, for a molecular model having a bend of 10°, at one position in the *y* direction. When the three-dimensional coordinates were used to calculate the structure factors for all the observed reflexions the resultant *R* value was 0·31. (Some time was wasted in the early stages because the *x* coordinates were in error by *a*/4, owing to the symmetry of the space group in projection on the (010) plane resulting in two equivalent sets of *x* and *z* coordinates giving the same *R* value for the *h*0*l* structure factors.)

Refinement

The structure was refined by a least-squares program written by Dr G. A. Mair for the IBM 1620 machine, using the block-diagonal approximation. *R* was reduced to 0·149 after five cycles using isotropic temperature parameters (*B*). The hydrogen atom positions were calculated, assuming a C–H bond length of 1·05 Å, and temperature parameters, *B*, of 4·5 Å^2 were given to all the hydrogen atoms. Their parameters were not refined. Five cycles of refinement using anisotropic temperature parameters reduced *R* to 0·0965, with very small parameter shifts in the last cycle. The weighting scheme used was of the form

$$W = P^2/[P^2 + (F_o - Q)^2]\,,$$

with $P = 16$ and $Q = 10$, these values being chosen to represent the estimated accuracy of the photographic measurements.

A three-dimensional Fourier map of the electron density was calculated making use of phases from the final set of parameters (Fig. 2). The hydrogen coordinates were then omitted from the structure factor cal-

Table 1. *Fractional coordinates with estimated standard deviations* (Å)

	x/a	$\sigma(x)$	y/b	$\sigma(y)$	z/c	$\sigma(z)$
O(1)	0·6839	0·005	0·7642	0·006	0·6396	0·006
O(2)	0·5917	0·006	0·2440	0·009	0·3261	0·007
C(1)	0·6660	0·007	0·5764	0·009	0·5756	0·008
C(2)	0·6142	0·007	0·4881	0·008	0·5874	0·007
C(3)	0·5930	0·007	0·5737	0·008	0·6818	0·008
C(4)	0·5467	0·009	0·4984	0·009	0·6989	0·008
C(5)	0·5201	0·007	0·3425	0·008	0·6209	0·008
C(6)	0·4726	0·008	0·2514	0·010	0·6400	0·010
C(7)	0·4459	0·008	0·1029	0·010	0·5640	0·011
C(8)	0·4649	0·008	0·0231	0·010	0·4711	0·011
C(9)	0·5110	0·007	0·1058	0·009	0·4459	0·010
C(10)	0·5400	0·008	0·2603	0·008	0·5228	0·009
C(11)	0·5883	0·007	0·3445	0·007	0·5078	0·008
C(12)	0·6130	0·008	0·2969	0·010	0·4081	0·008
C(13)	0·6648	0·008	0·3019	0·008	0·4053	0·008
C(14)	0·6869	0·008	0·1802	0·009	0·3149	0·009
C(15)	0·7346	0·008	0·1730	0·009	0·3068	0·008
C(16)	0·7623	0·007	0·3020	0·008	0·3873	0·009
C(17)	0·8128	0·009	0·2977	0·011	0·3768	0·010
C(18)	0·8402	0·008	0·4141	0·010	0·4543	0·011
C(19)	0·8204	0·009	0·5395	0·010	0·5451	0·010
C(20)	0·7726	0·007	0·5504	0·009	0·5609	0·008
C(21)	0·7421	0·007	0·4339	0·008	0·4797	0·007
C(22)	0·6916	0·006	0·4315	0·008	0·4867	0·007
H(1)	0·612		0·691		0·741	
H(2)	0·532		0·564		0·771	
H(3)	0·459		0·326		0·711	
H(4)	0·410		0·037		0·575	
H(5)	0·443		−0·116		0·417	
H(6)	0·524		0·051		0·371	
H(7)	0·667		0·102		0·249	
H(8)	0·752		0·062		0·243	
H(9)	0·832		0·208		0·311	
H(10)	0·877		0·403		0·442	
H(11)	0·843		0·611		0·608	
H(12)	0·759		0·646		0·631	

culation and a difference Fourier map was computed (Fig. 3) by the use of Dr Mair's program for the IBM 1620 machine.

The final parameters are given in Tables 1 and 2. A list of the observed and calculated structure factors is available on request from the authors.

Table 2. *Temperature parameters* ($b_{ij} \times 10^5$)

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

	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
O(1)	88	9665	487	−1623	55	−100
O(2)	131	18773	409	−1391	1	−820
C(1)	101	5822	445	40	−24	−52
C(2)	94	5081	428	310	−8	290
C(3)	90	6044	420	472	−8	141
C(4)	136	6979	383	−9	4	412
C(5)	84	5337	544	1012	0	432
C(6)	103	7582	711	1031	106	291
C(7)	99	8136	907	1723	67	227
C(8)	94	7474	966	−193	−110	−109
C(9)	79	6517	717	323	−18	−186
C(10)	98	4583	632	44	−92	419
C(11)	106	4443	432	215	−19	74
C(12)	134	9293	339	−340	−33	−95
C(13)	126	5167	384	−136	65	−97
C(14)	139	6765	477	485	102	172
C(15)	136	5579	449	169	112	171

Table 2 (*cont.*)

	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
C(16)	108	4525	656	−13	37	74
C(17)	126	8331	733	1180	229	367
C(18)	106	8468	866	530	35	−21
C(19)	121	8542	622	1421	−14	−97
C(20)	94	7564	484	72	−23	26
C(21)	121	4995	348	1486	−3	−127
C(22)	90	5050	341	912	6	229

Discussion

The bond lengths and bond angles are given in Tables 3 and 4, and also in Fig. 4. The results of an intermolecular contacts scan are summarized in Table 5.

Table 3. *Bond lengths* (Å) *with estimated standard deviations*

		e.s.d.
O(1)—C(1)	1·210	(0·010)
O(2)—C(12)	1·237	(0·011)
C(1)—C(2)	1·524	(0·010)
C(1)—C(22)	1·470	(0·011)
C(2)—C(3)	1·399	(0·011)
C(2)—C(11)	1·380	(0·011)
C(3)—C(4)	1·370	(0·011)
C(4)—C(5)	1·396	(0·011)

Table 3 (*cont.*)

		e.s.d.
C(5)—C(6)	1·421	(0·011)
C(5)—C(10)	1·422	(0·012)
C(6)—C(7)	1·366	(0·014)
C(7)—C(8)	1·351	(0·015)
C(8)—C(9)	1·393	(0·011)
C(9)—C(10)	1·421	(0·012)
C(10)-C(11)	1·430	(0·010)
C(11)-C(12)	1·478	(0·011)
C(12)-C(13)	1·479	(0·011)
C(13)-C(14)	1·406	(0·012)
C(13)-C(22)	1·391	(0·011)
C(14)-C(15)	1·367	(0·012)
C(15)-C(16)	1·397	(0·012)
C(16)-C(17)	1·448	(0·011)
C(16)-C(21)	1·417	(0·011)
C(17)-C(18)	1·347	(0·014)
C(18)-C(19)	1·387	(0·014)
C(19)-C(20)	1·381	(0·011)
C(20)-C(21)	1·433	(0·011)
(C21)-C(22)	1·446	(0·010)

All the interatomic contacts between molecules are of the normal van der Waals magnitudes. It was noted that there were more close contacts to O(1) than to O(2), a fact which agrees with the observation that the temperature parameters for O(2) show considerably greater amplitude of vibration than is the case for O(1). An illustration of the molecular packing is given in Fig. 5.

The best least-squares mean planes through the two naphthalene nuclei were calculated by the method of Schomaker, Waser, Marsh & Bergman (1959). Both halves of the molecule show little deviation from planarity, the maximum deviation being 0·04 Å with a mean of 0·013 Å (Table 6). The angle between the normals of the planes is 14·1°.

The anisotropic temperature parameters were analysed in terms of rigid body motion, using the program written by Dr J.T.McMullan (Burns, Ferrier & McMullan, 1967). The oxygen atoms were omitted from the calculation because in the structures of the 2′- and 5-methyl-1:2-benzanthraquinones a similar analysis

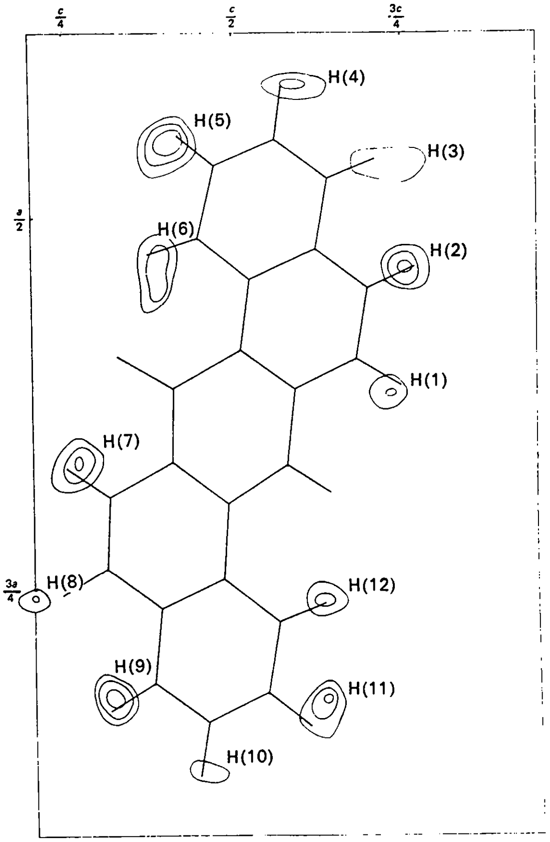

Fig. 3. Superimposed sections of the difference Fourier map, with contours at intervals of 0·1 e.Å^{-3}, starting at 0·2 e.Å^{-3}.

Table 4. *Bond angles with estimated standard deviations*

		e.s.d.			e.s.d.
O(1)—C(1)—C(2)	118·3°	0·7°	*O(2)—C(12)-C(11)	122·0°	0·7°
*O(1)—C(1)—C(22)	123·3	0·6	O(2)—C(12)-C(13)	118·2	0·7
C(2)—C(1)—C(22)	118·4	0·7	C(11)-C(12)-C(13)	119·7	0·7
C(1)—C(2)—C(3)	116·9	0·7	C(12)-C(13)-C(14)	117·6	0·7
C(1)—C(2)—C(11)	122·3	0·7	C(12)-C(13)-C(22)	122·4	0·7
C(3)—C(2)—C(11)	120·7	0·6	C(14)-C(13)-C(22)	119·9	0·7
C(2)—C(3)—C(4)	120·4	0·7	C(13)-C(14)-C(15)	121·1	0·8
C(3)—C(4)—C(5)	120·0	0·7	C(14)-C(15)-C(16)	120·0	0·8
C(4)—C(5)—C(6)	120·0	0·8	C(15)-C(16)-C(17)	119·3	0·8
C(4)—C(5)—C(10)	121·3	0·7	C(15)-C(16)-C(21)	121·5	0·7
C(6)—C(5)—C(10)	118·6	0·7	C(17)-C(16)-C(21)	119·2	0·8
C(5)—C(6)—C(7)	120·7	0·9	C(16)-C(17)-C(18)	120·3	0·9
C(6)—C(7)—C(8)	120·5	0·8	C(17)-C(18)-C(19)	120·4	0·8
C(7)—C(8)—C(9)	122·3	0·9	C(18)-C(19)-C(20)	122·6	0·8
C(8)—C(9)—C(10)	118·8	0·8	C(19)-C(20)-C(21)	118·8	0·8
C(5)—C(10)-C(9)	118·8	0·7	C(16)-C(21)-C(20)	118·7	0·7
C(5)—C(10)-C(11)	117·0	0·7	C(16)-C(21)-C(22)	117·1	0·6
*C(9)—C(10)-C(11)	124·2	0·8	*C(20)-C(21)-C(22)	124·2	0·7
C(2)—C(11)-C(10)	120·5	0·7	C(1)—C(22)-C(13)	116·8	0·6
C(2)—C(11)-C(12)	116·2	0·7	*C(1)—C(22)-C(21)	122·8	0·6
*C(10)-C(11)-C(12)	123·3	0·7	C(13)-C(22)-C(21)	120·3	0·7

* See text

showed them to be vibrating independently of the main molecular skeleton. It was noted that the oxygen atoms of these latter compounds show a similar magnitude of vibration perpendicular to the plane of the molecule compared to that found for DBAQ in a similar direction. Each half of the molecule was analysed separately, and then the whole molecule was considered. The results are very similar in each case and the values of U_{ij} are given for the complete molecule calculation in Table 7. It appears that there is a definite measure of agreement between observed and calculated values. However, when the parameters were further analysed according to the criteria of Burns, Ferrier & McMullan, the molecule could not be considered to show strict

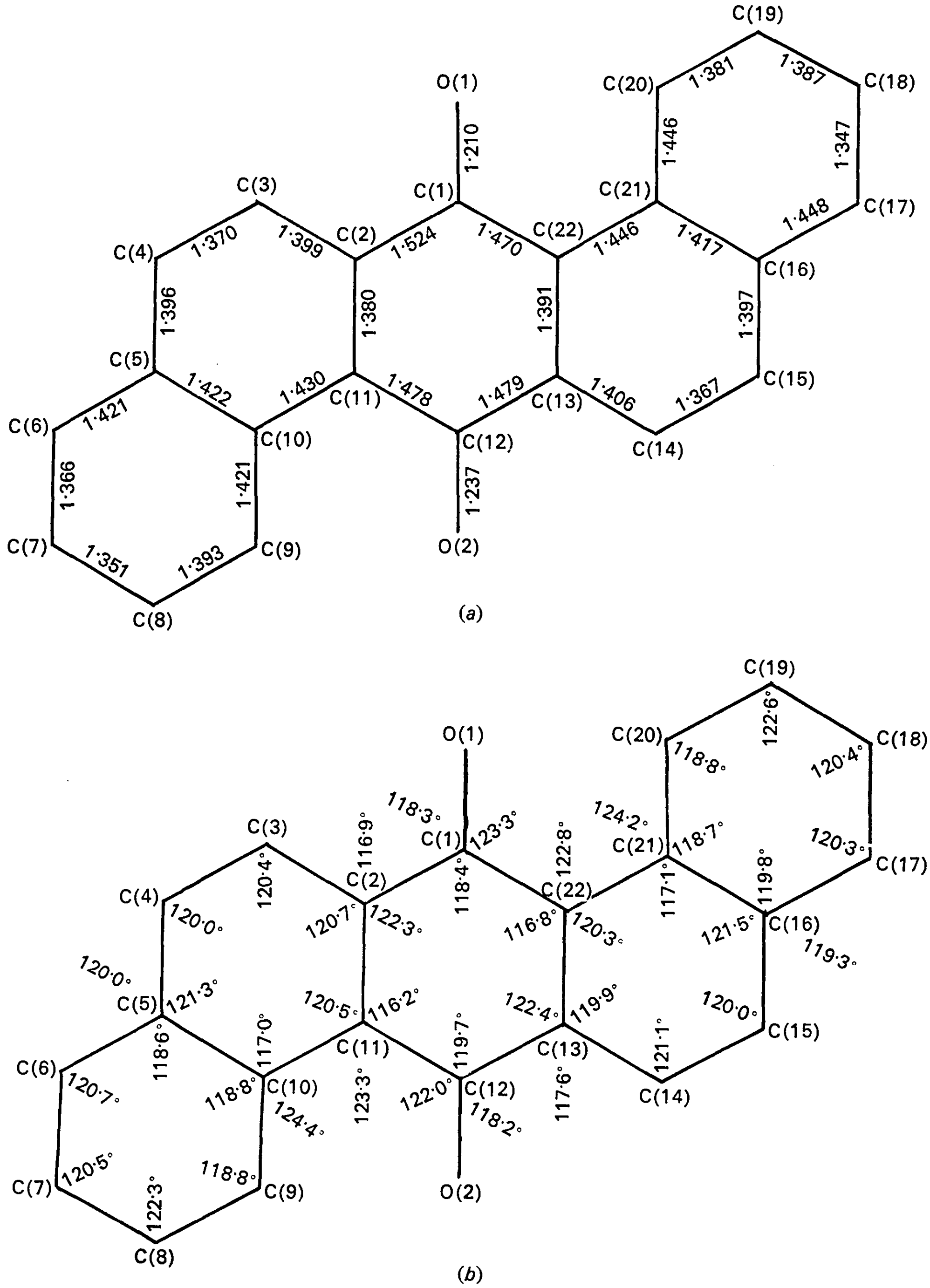

Fig. 4. (*a*) Bond lengths (Å) and (*b*) angles (°) for the final coordinates.

rigid body motion within the limits specified in their paper.

The bond lengths and angles are similar to those of 2′- and 5-methyl-1:2-benzanthraquinones. The distances between the oxygen atoms and the closest nonbonded carbon atoms are

DBAQ	O(1)–C(20)	2·851 Å
	O(2)–C(9)	2·824
2′-MBAQ		2·812
5-MBAQ		2·766

Table 5. *Intermolecular distances*

Position of molecule *J*

(*a*) $x, y+1, z$

(*b*) $-x+\frac{3}{2}, y, z-\frac{1}{2}$

Atom *I*	Atom *J*	Neighbour	d_{ij}
C(1)	C(1)	*a*	3·27 Å
O(1)	C(2)	*a*	3·49
O(1)	C(22)	*a*	3·25
C(4)	C(5)	*a*	3·48
C(6)	C(7)	*a*	3·50
C(9)	C(10)	*a*	3·50
C(15)	C(20)	*b*	3·49

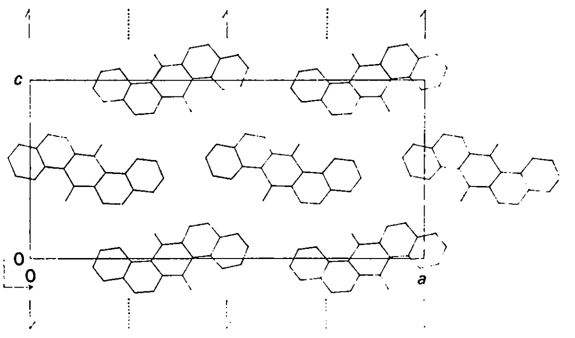

Fig. 5. Packing arrangement of molecules projected on (010).

Table 6. *Least-squares planes with deviations from the planes*

I $-0·2649x+0·9031y-0·3381z+5·468=0$

II $-0·0268x+0·9175y-0·3967z+1·506=0$

Plane I	Δ	Plane II	Δ
C(2)	−0·040 Å	C(13)	−0·011 Å
C(3)	0·006	C(14)	0·005
C(4)	0·020	C(15)	−0·015
C(5)	0·019	C(16)	0·007
C(6)	−0·021	C(17)	0·007
C(7)	−0·005	C(18)	0·001
C(8)	−0·021	C(19)	−0·006
C(9)	0·028	C(20)	−0·012
C(10)	0·011	C(21)	0·016
C(11)	0·004	C(22)	0·010

The repulsive interaction between the appropriate atoms is shown by the bond angles marked by an asterisk in Table 4. It can be seen from Fig. 4(*b*) that these angles are significantly greater than 120°, as would be expected from the interaction of the oxygen and carbon atoms concerned.

We wish to thank the British Empire Cancer Campaign for Research and the Science Research Council for financial support. We are also indebted to the computing laboratory staff at St. Andrews, to Dr G. A. Mair for his programs, and to Miss H. Ross for technical assistance.

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Table 7. *Observed and calculated U_{ij}* (Å × 10^4) *referred to principal axes of inertia*

	U_{11}		U_{22}		U_{33}		U_{23}		U_{13}		U_{12}	
	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
C(1)	421	435	381	346	426	364	27	58	−8	18	−16	14
C(2)	399	426	400	362	330	336	41	61	63	33	29	31
C(3)	377	464	414	397	386	419	81	82	28	56	13	68
C(4)	566	455	374	500	467	412	75	90	80	67	90	99
C(5)	364	417	552	561	289	364	79	61	91	54	26	46
C(6)	401	412	720	751	471	413	70	58	33	61	87	47
C(7)	401	424	912	846	470	507	94	13	29	47	16	−50
C(8)	442	473	714	726	606	601	−81	−18	55	32	−171	−120
C(9)	336	475	597	545	486	523	−8	0	−17	28	−81	−81
C(10)	458	426	494	481	328	373	−35	33	136	35	−52	−9
C(11)	442	426	378	383	314	335	10	41	6	25	2	8
C(12)	552	467	313	349	670	398	116	35	−14	8	16	3
C(13)	484	454	340	355	406	371	−6	32	−63	−5	73	38
C(14)	534	520	499	384	450	492	62	15	−19	−20	128	81
C(15)	518	509	439	475	400	489	9	12	−20	−30	136	129
C(16)	438	439	528	531	371	405	−80	38	8	−26	15	90
C(17)	451	433	795	708	516	457	75	46	1	−33	205	112
C(18)	434	411	764	799	604	512	11	81	4	−24	−22	30
C(19)	497	430	662	686	505	570	165	101	−45	−8	−24	−48
C(20)	398	433	433	522	531	491	68	86	24	−1	−14	−28
C(21)	481	417	439	460	247	375	150	57	−92	−10	14	28
C(22)	371	421	394	373	271	336	114	50	24	0	43	27