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The Crystal Structures of Some Anthracene Derivatives. IV. 9:10-Dinitroanthracene

By James Trotter*

Division of Pure Physics, National Research Council, Ottawa, Canada

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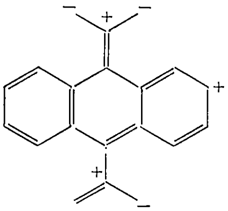
Crystals of 9:10-dinitroanthracene are triclinic with one molecule in the unit cell. The structure has been determined from projections along the three crystallographic axes, and details of the molecular geometry and dimensions have been obtained. The molecule is centrosymmetrical, and the anthracene skeleton is planar but not coplanar with the nitro groups, the angle between the planes being 64°.

Introduction

The crystal structure of 9:10-dinitroanthracene has been examined to establish approximate atomic positions to assist in the interpretation of photoconduction effects in substituted anthracenes (Trotter, 1958*a*). In addition, however, since it is of interest to compare the bond lengths in the molecule with those in anthracene, the approximate structure has been further refined and more accurate atomic parameters and molecular dimensions obtained.

In the 9:10-dibromo and 9:10-dichloro derivatives the halogen atoms are attached to the 9 and 10 carbon atoms by single bonds and the C–C bond lengths do not differ significantly from those in anthracene (Trotter, 1958*b*, 1959). In 9:10-dinitroanthracene, however, contributions to the ground state of the molecule are possible from structures of the type



and the bond lengths in the nucleus may differ from those in anthracene, and in addition the bonded C–N distances may not correspond to pure single bonds. Resonance of this type however is most likely if the nitro groups and the anthracene nucleus are coplanar, and this involves distances which are much less than the normal van der Waals separations between the oxygen atoms and the hydrogen atoms attached to positions 1, 4, 5 and 8.

There are three possible molecular configurations:

(i) the molecule is completely planar (symmetry *mmm* if resonance within the nitro group requires that the two N–O bonds be equivalent),

(ii) the nitro groups are not coplanar with the anthracene nucleus, and are tilted out of the plane of the carbon atoms so that the molecule has a centre of symmetry,

(iii) the nitro groups are again tilted out of the plane of the rings, but in such a way that the molecule has a two-fold symmetry axis perpendicular to the aromatic plane.

The first configuration seems unlikely since it involves short intramolecular non-bonded O–H distances. In either of the other configurations resonance between the nitro groups and the anthracene nucleus may be inhibited, and if the tilt is sufficiently large, the nitro group may have little effect on the bond lengths in the nucleus, with the C–N distances differing little from the normal single-bond distance.

Experimental

Crystals of 9:10-dinitroanthracene, which were obtained by crystallization from petroleum ether, are yellow in colour, and consist of prisms elongated along the *a*-axis with (010) and (001) faces developed. The density was determined using a Berman balance (Berman, 1939) with chloroform as displacement liquid. The unit-cell dimensions were determined from rotation and oscillation photographs of a crystal rotating about the *a*-axis, an 0*kl* Weissenberg film, and *h*0*l* and *hk*0 precession films.

Crystal data

9:10-Dinitroanthracene, $C_{14}H_8O_4N_2$; $M = 268{\cdot}2$; m.p. 294°.

Triclinic, $a = 3{\cdot}95 \pm 0{\cdot}01$, $b = 8{\cdot}68 \pm 0{\cdot}02$, $c = 8{\cdot}76 \pm 0{\cdot}02$ Å, $\alpha = 106°\,46' \pm 10'$, $\beta = 98°\,59' \pm 10'$, $\gamma = 98°\,01' \pm 10'$.

Volume of the unit cell = 278·6 Å^3.

Density, calculated (with $Z = 1$) = 1·589, measured = 1·591 g.cm^{-3}.

Absorption coefficient for X-rays, $\lambda = 1{\cdot}542$ Å, $\mu = 11{\cdot}72$ cm.$^{-1}$; $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}45$ cm.$^{-1}$.

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Total number of electrons per unit cell
$= F(000) = 138$.

No systematic absences; space group is either $P1-C_1^1$ or $P\bar{1}-C_i^1$.

The intensities of the $0kl$ reflexions were recorded on moving-film exposures for a crystal rotating about the a-axis, using Cu $K\alpha$ radiation, the multiple-film technique being used to correlate strong and weak reflexions. The $h0l$ and $hk0$ reflexions were recorded on precession films, using Mo $K\alpha$, with multiple exposures to correlate strong and weak intensities. All the intensities were estimated visually, the range being about 2000 to 1. The crystals showed a great tendency to bend and twist, and it was not possible to obtain a crystal giving perfectly sharp reflexions, so that the photographs were of rather poor quality. This was especially so for the $h0l$ and $hk0$ photographs, so that these intensities are probably less accurate than the $0kl$ data.

The same crystal was used for all the photographs; the cross-section normal to the a-axis was $0{\cdot}30 \times 0{\cdot}20$ mm., and no absorption corrections were applied. The values of the structure amplitudes were derived by the usual formulae for a mosaic crystal, the absolute scale being established later by correlation with the calculated structure factors. 121 independent $0kl$ reflexions, 36 $h0l$ and 36 $hk0$ were observed, representing 65%, 51% and 51% respectively of the possible number observable with the radiations and experimental conditions used.

Structure analysis

The space group is either $P1$ or $P\bar{1}$, and these cannot of course be distinguished by means of X-rays. $P\bar{1}$ corresponds to either a planar molecule or a non-planar centrosymmetrical molecule—(i) or (ii) above—and $P1$ to a non-planar, non-centrosymmetrical molecule (iii). Since in the non-centred space group only the oxygen atoms contribute to the B parts of the structure factors, it seemed unlikely that the $N(z)$ test (Howells, Phillips & Rogers, 1950) would distinguish between the space groups. Space group $P\bar{1}$ was assumed initially on the basis that except for the oxygen atoms the molecule is certainly centrosymmetrical, and any deviations from centrosymmetry would be revealed by poor resolution of the oxygen atoms. The projection along the short a-axis was considered initially.

[100] *projection*

Using as a model a planar molecule with all the carbon, nitrogen and oxygen atoms given equal weight and all bond lengths taken as 1·40 Å, an optical transform was prepared, and by tilting the transform an excellent fit was easily obtained with the $0kl$ weighted reciprocal lattice. Comparison of the transform with that for a similar model with an extra hole at the centre allowed signs to be allotted to each area of the transform, and hence to most of the reciprocal lattice points. A Fourier synthesis was computed using these signs together with the measured structure amplitudes. All the atoms were well resolved including the oxygen atoms, so that at this stage it seemed that the true space group was indeed $P\bar{1}$, and that configuration (iii) was incorrect. In addition the map indicated that the nitro groups are tilted out of the plane of the carbon atoms; the molecule is tilted in this projection along the long axis of the anthracene nucleus, and since the nitro groups might be tilted in either the same or the opposite sense, the NO_2 planes make angles of about 20° or about 60° with the anthracene plane. Atomic positions were obtained from the map and structure factors calculated for all the $0kl$ reflexions. McWeeny's scattering factors for carbon, nitrogen and oxygen were used, and corrected for thermal vibration as usual, taking $B = 4{\cdot}6$ Å^2. The value of R, the usual discrepancy factor, was 34·9%.

Refinement of positional and temperature parameters proceeded by computing successive $(F_o - F_c)$ syntheses, and after four cycles the R value had dropped to 16·6%. Observed and calculated structure factors are listed in Table 4, and the final F_o synthesis, computed with measured structure amplitudes and calculated signs, is shown in Fig. 1. As a final check that the molecule and the space group were centrosymmetrical, structure factors were calculated for a model with the nitro groups tilted so that the molecule had a two-fold symmetry axis (this involved shifting only two of the oxygen atoms). The discrepancy was 42% with some very poor agreements, and this non-centrosymmetrical model was discarded. In the final $(F_o - F_c)$ map there were regions of high density close to the expected hydrogen positions, and density

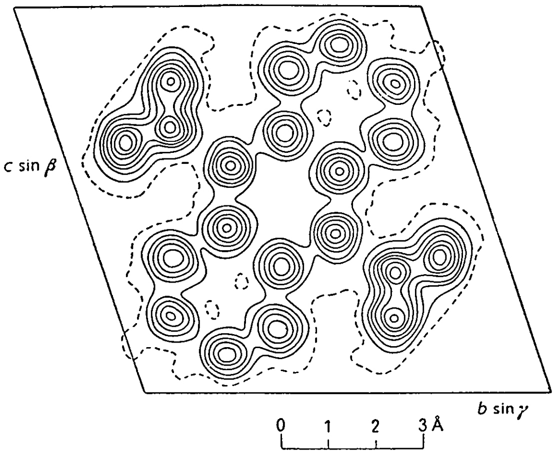

Fig. 1. Electron-density projection along the a-axis. Contours at intervals of 1 e.Å^{-2}, with the one-electron line dotted.

fluctuations corresponding to anisotropic vibration of the oxygen atoms, but no allowance for these effects was made in the structure-factor calculations.

x-coordinates

Since the $h0l$ and $hk0$ intensities are very similar, the projections along the b and c crystal axes must be nearly identical. Utilizing this information and using the y- and z-coordinates already determined, trial x-coordinates were easily obtained. A 60° tilt of the nitro groups gave better agreement than a 20° tilt. The y- and z-coordinates were retained at the values determined from the $0kl$ data, since the $h0l$ and $hk0$ intensities have not been measured so accurately, and only the x-coordinates were further refined.

The initial $h0l$ discrepancy was 29·9% and this was reduced by three (F_o-F_c) syntheses to 16·9%. At this stage the $hk0$ structure factors were calculated and the value of R was 21·6%. Difference syntheses were computed for both zones and although the maps suggested some shifts in x-coordinates these were generally not consistent, and refinement was terminated at this point. Measured and calculated structure factors are listed in Table 4, and the final $h0l$ F_o synthesis is shown in Fig. 2. The $hk0$ map is very similar and is not shown.

Table 1. *Coordinates of the atoms*

Atom	x/a	y/b	z/c
A	0·6210	0·3702	0·2983
B	0·4213	0·3188	0·1455
C	0·2158	0·1603	0·0654
D	0·0086	0·1006	−0·0906
E	−0·1931	−0·0579	−0·1700
F	−0·4006	−0·1166	−0·3291
G	−0·6058	−0·2662	−0·3941
N	0·0281	0·2101	−0·1878
O_1	−0·0746	0·3416	−0·1443
O_2	0·1571	0·1741	−0·3108

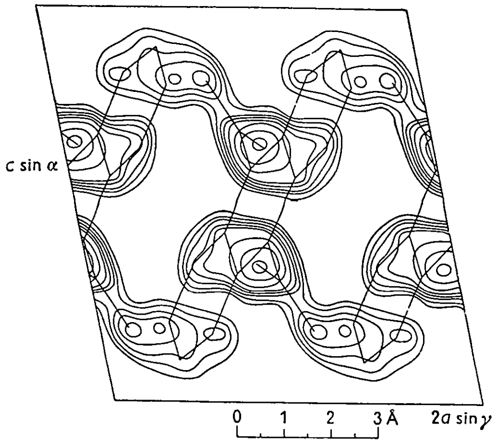

Fig. 2. Electron-density projection along [010]. Contours at intervals of 1 e.Å^{-2}, except above 10 e.Å^{-2} where the interval is 2 e.Å^{-2}. The lowest contour is at 4 e.Å^{-2}.

Coordinates and molecular dimensions

The final coordinates of the atoms, expressed as fractions of the unit-cell edges, are listed in Table 1, the labelling of the atoms being shown in Fig. 3. The coordinates of the carbon atoms can be fitted to an equation of the form

$$lX+mY+nZ+p=0\,,$$

where X, Y, and Z are coordinates expressed in Ångström units and referred to the triclinic crystal axes. l, m, n and p were determined by the method of least squares. The atoms of the nitro group can of course be fitted to a similar equation. The equations of the two planes are

Aromatic rings:

$$0{\cdot}9058X-0{\cdot}3886Y-0{\cdot}3642Z=0$$

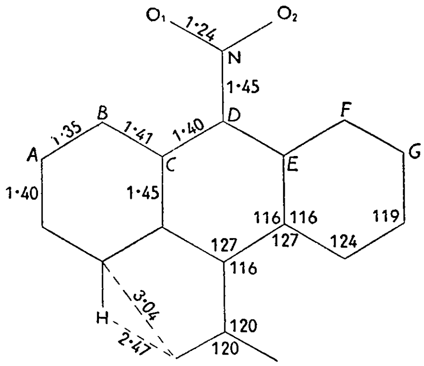

Fig. 3. Bond lengths, valency angles and intramolecular 'overcrowded' distances.

Table 2. *Deviations from the mean planes* (Å)

Atom	Distance from plane of rings	Distance from NO_2 plane
A	0·02	—
B	−0·03	—
C	0·02	—
D	−0·02	0·04
E	−0·04	—
F	−0·01	—
G	0·01	—
N	−0·01	0
O_1	−0·96	0
O_2	0·97	0

Table 3. *Bond lengths in anthracene and 9:10-dinitroanthracene*

Bond	Anthracene	9 : 10-Dinitro-anthracene
A–B	1·37	1·35 Å
B–C	1·43	1·41
C–D	1·40	1·40
A–G′	1·42	1·40
C–E′	1·44	1·45
D–N	—	1·45
N–O_1	—	1·24
N–O_2	—	1·24

Table 4. *Observed and calculated structure factors*

hkl	F_o	F_c
001	21·8	+23·1
002	25·9	−27·7
003	3·5	−4·5
004	21·2	−20·7
005	5·3	−7·1
006	5·3	+7·8
007	1·9	+2·4
008	5·7	−4·8
009	2·2	−2·2
0,0,10	1·3	+0·5
$0,1,\overline{10}$	< 1·1	+0·2
$01\bar{9}$	1·3	+1·2
$01\bar{8}$	1·9	−1·8
$01\bar{7}$	5·5	−6·7
$01\bar{6}$	2·3	+2·9
$01\bar{5}$	< 1·1	+1·7
$01\bar{4}$	2·4	+3·2
$01\bar{3}$	16·5	+15·7
$01\bar{2}$	14·8	−16·4
$01\bar{1}$	3·7	+6·1
010	20·8	+22·1
011	4·4	+9·4
012	12·4	+13·8
013	5·5	−3·4
014	4·9	−4·8
015	1·6	−4·0
016	1·5	−1·4
017	< 1·5	−2·7
018	5·0	−4·9
019	< 1·2	−0·5
0,1,10	< 0·7	+0·4
$0,2,\overline{11}$	1·6	−0·7
$0,2,\overline{10}$	1·0	−0·2
$02\bar{9}$	5·3	+3·5
$02\bar{8}$	< 1·5	+0·7
$02\bar{7}$	< 1·4	−0·1
$02\bar{6}$	3·3	+1·8
$02\bar{5}$	4·5	−5·0
$02\bar{4}$	2·5	+0·8
$02\bar{3}$	8·5	+8·4
$02\bar{2}$	18·0	+18·1
$02\bar{1}$	6·4	−7·2
020	28·7	−31·7
021	4·8	+8·5
022	< 0·9	−2·3
023	2·5	−5·0
024	5·3	+8·8
025	< 1·3	+0·4
026	3·8	−3·7
027	2·2	−2·1
$0,3,\overline{11}$	1·9	−1·0
$0,3,\overline{10}$	1·3	−1·0
$03\bar{9}$	1·8	−2·7
$03\bar{8}$	6·5	+5·9
$03\bar{7}$	17·6	+16·7
$03\bar{6}$	3·0	+2·0
$03\bar{5}$	< 1·2	−0·8
$03\bar{4}$	8·3	−9·1
$03\bar{3}$	36·2	−36·4
$03\bar{2}$	2·9	−2·7
$03\bar{1}$	16·7	+17·0
030	1·3	−1·8
031	6·5	−6·4
032	1·3	+0·1
033	2·0	−2·4
034	3·9	−4·4
035	4·9	+4·7
036	3·8	+1·9
037	< 1·4	−0·3
038	2·2	+2·3
$04\bar{9}$	2·3	−2·1
$04\bar{8}$	6·3	+5·1
$04\bar{7}$	4·2	+4·7
$04\bar{6}$	2·2	−2·7
$04\bar{5}$	8·2	+5·7
$04\bar{4}$	3·2	−2·8
$04\bar{3}$	17·3	−17·0
$04\bar{2}$	3·2	−2·9
$04\bar{1}$	3·9	+8·0
040	17·4	−15·8
041	18·4	−18·3
042	4·9	+7·0
043	< 1·3	+1·5
044	5·1	+5·2
045	14·1	+11·5
046	< 1·4	−0·4
047	2·2	−2·5
$05\bar{6}$	1·6	+0·5
$05\bar{5}$	4·4	−5·0
$05\bar{4}$	2·8	+0·9
$05\bar{3}$	3·9	+4·6
$05\bar{2}$	4·7	−5·5
$05\bar{1}$	1·8	+1·1
050	3·4	−2·2
051	3·4	−5·4
052	2·7	−3·4
053	< 1·4	+0·9
054	10·0	+8·1
055	3·9	+3·3
$0,6,\overline{10}$	2·8	−3·0
$06\bar{9}$	< 1·3	−1·0
$06\bar{8}$	< 1·4	−0·3
$06\bar{7}$	1·9	+1·3
$06\bar{6}$	1·5	+1·3
$06\bar{5}$	1·9	−1·0
$06\bar{4}$	1·3	+1·1
$06\bar{3}$	< 1·3	−1·7
$06\bar{2}$	< 1·3	−1·5
$06\bar{1}$	< 1·3	−0·7
060	4·8	+4·8
061	5·4	+6·3
062	2·3	−2·3
063	< 1·5	+0·3
064	1·3	−0·9
065	3·9	−3·0
066	2·7	+1·7
$0,7,\overline{10}$	2·3	−2·3
$07\bar{9}$	< 1·2	+1·2
$07\bar{8}$	< 1·4	0
$07\bar{7}$	4·9	−3·8
$07\bar{6}$	2·2	−2·2
$07\bar{5}$	< 1·5	+1·8
$07\bar{4}$	< 1·5	−1·5
$07\bar{3}$	10·4	+9·6
$07\bar{2}$	13·5	+13·0
$07\bar{1}$	5·1	−5·8
070	4·6	−3·5
071	< 1·5	0
072	2·7	−3·2
073	1·3	+0·8
$08\bar{6}$	2·6	−0·3
$08\bar{5}$	< 1·5	−0·7
$08\bar{4}$	1·5	−0·8
$08\bar{3}$	9·8	+8·9
$08\bar{2}$	7·3	+6·1
$08\bar{1}$	< 1·5	−0·2
080	< 1·5	−1·2
081	6·1	−4·5
082	4·1	−2·6
083	< 1·2	+0·6
084	1·2	+0·8
$09\bar{6}$	1·2	+1·6
$09\bar{5}$	1·3	+0·4
$09\bar{4}$	1·3	+1·0
$09\bar{3}$	3·1	−1·9
$09\bar{2}$	2·2	−2·0
$09\bar{1}$	3·3	+2·8
090	< 1·3	+0·2
$0,10,\bar{6}$	1·3	−1·3
$0,10,\bar{5}$	1·3	−1·8
$0,10,\bar{4}$	1·4	+1·2
$0,10,\bar{3}$	< 1·1	−0·2
$0,10,\bar{2}$	< 1·1	−0·9
$0,10,\bar{1}$	1·3	−0·3
0,10,0	< 0·9	−0·2
$10\bar{7}$	< 2	−1
$10\bar{6}$	2	+2
$10\bar{5}$	3	−4
$10\bar{4}$	6	−8
$10\bar{3}$	5	−7
$10\bar{2}$	26	+27
$10\bar{1}$	28	+27
100	11	+14
101	19	+20
102	28	−27
103	23	−22
104	< 2	+3
105	< 2	+2
106	< 2	−1
107	3	−3
$20\bar{7}$	< 2	−2
$20\bar{6}$	< 2	+2
$20\bar{5}$	3	+3
$20\bar{4}$	6	−11
$20\bar{3}$	7	−3
$20\bar{2}$	< 2	+2
$20\bar{1}$	2	+4
200	5	+8
201	8	+3
202	6	−6
203	7	−9
204	< 2	0
205	2	−1
206	< 2	0
207	< 2	+2
$30\bar{5}$	3	−4
$30\bar{4}$	3	−2
$30\bar{3}$	< 2	−2
$30\bar{2}$	2	+3
$30\bar{1}$	2	0
300	2	+1
301	< 2	+1
302	2	−2
303	< 2	0
304	< 2	0
305	< 2	+2
$40\bar{2}$	< 2	−1
$40\bar{1}$	< 2	+2
400	< 2	−2
401	< 2	+4
402	6	+4
$1\bar{7}0$	< 2	0
$1\bar{6}0$	3	+2
$1\bar{5}0$	3	+3
$1\bar{4}0$	6	−9
$1\bar{3}0$	5	−5
$1\bar{2}0$	31	+31
$1\bar{1}0$	29	+28
100	11	+14
110	10	+1
120	27	−30
130	17	−14
140	2	+3
150	3	+6
160	< 2	+2
170	4	−7
$2\bar{7}0$	< 2	−3
$2\bar{6}0$	< 2	+3
$2\bar{5}0$	4	+1
$2\bar{4}0$	6	−9
$2\bar{3}0$	7	+2
$2\bar{2}0$	< 2	+2
$2\bar{1}0$	2	+3
200	5	+8
210	9	−9
220	7	−11
230	6	+6
240	< 2	+4
250	3	−5
260	< 2	−4
270	< 2	−1
$3\bar{5}0$	3	−1
$3\bar{4}0$	4	−2
$3\bar{3}0$	< 2	+2
$3\bar{2}0$	3	+3
$3\bar{1}0$	3	−4
300	2	+1
310	< 2	0
320	4	−4
330	< 2	+1
340	< 2	0
350	< 2	−1
$4\bar{2}0$	3	+1
$4\bar{1}0$	< 2	−1
400	< 2	−2
410	< 2	+4
420	< 2	+2

Nitro group:

$$0{\cdot}7770X+0{\cdot}1702Y+0{\cdot}3185Z+0{\cdot}1270 = 0\;.$$

The deviations of the atoms from these planes are listed in Table 2. The angle between the two planes is 63·7°.

The bond lengths and valency angles in the molecule were calculated from the coordinates of Table 1, and the values, after averaging over chemically equivalent bonds and angles, are shown in Fig. 3. Fig. 3 also shows the distances between those atoms which would be closer than the normal van der Waals separation if the molecule were planar. (The hydrogen atoms were assumed to lie on the plane of the carbon atoms with C–H = 1·08 Å.)

Standard deviations

The standard deviations of the atomic positions were calculated from Cruickshank's (1949) formulae. From the $0kl$ data the approximate values are $\sigma(y) = \sigma(z) = 0{\cdot}01$ Å and from the $h0l$ data $\sigma(x) = 0{\cdot}02$ Å. The standard deviations of the mean bond lengths are then about 0·015 Å.

Discussion

The anthracene nucleus is completely planar within the limits of experimental error, the maximum deviation from the mean plane being 0·04 Å and the root mean square deviation 0·024 Å. The nitrogen atoms also lie on this plane, but the oxygen atoms of a nitro group lie one above and one below the plane at distances of 0·96 Å. The nitro groups are thus tilted out of the plane of the carbon atoms about the C–N bonds and the angle between the planes of a nitro group and the aromatic rings is 64°. The nitro groups are tilted in such a way that the molecule is centrosymmetrical. The deviation from planarity is just sufficient to increase the distances between the oxygen atoms and the neighbouring carbon and hydrogen atoms to about the usual van der Waals separations (Fig. 3).

The bond lengths in the molecule are compared in Table 3 with those in anthracene (Sinclair, Robertson & Mathieson, 1950; Cruickshank, 1956). There are no significant differences between corresponding carbon–carbon bond lengths in the two molecules. The C–N bond length (1·45 Å) is slightly (but probably not significantly) shorter than the corresponding single bond in aliphatic nitro compounds – 1·47 Å (Allen & Sutton, 1950) and the N–O bonds (1·24 Å) are only slightly longer than those in the aliphatic compounds (1·22 Å). A small contraction in the C–N bond length would be expected due to the change from sp^3 to sp^2 hybridization. It appears then that the tilt of 64° is sufficient to inhibit completely, or at least almost completely, resonance between the nitro groups and the anthracene nucleus, and ionic structures involving C=N make little or no contribution to the ground state of the molecule.

Intermolecular distances

All the intermolecular distances correspond to normal van der Waals interactions. The perpendicular distance between molecules related by translation *a* is 3·58 Å, and the shortest contacts between these molecules are oxygen–carbon distances of 3·25 Å and 3·49 Å. The shortest oxygen–oxygen and oxygen–carbon intermolecular separations are 3·06 Å and 3·25 Å, all the carbon–carbon contacts being considerably greater than the sum of the van der Waals radii. The shorter lateral contacts are illustrated in Fig. 4.

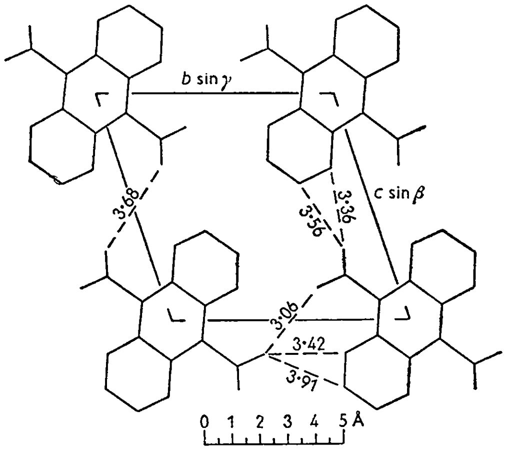

Fig. 4. Projection of the structure along [100], showing the shorter intermolecular contacts.

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