

angle not too close to 45° is ideal for obtaining information about perfection by the polarization method. This is so because for a strong reflection, α_{PA} is not reduced much below the value of α_{PN} by absorption and the full range from $|\cos 2\theta|$ to $\cos^2 2\theta$ is available.

The author wishes to thank Prof. G. N. Ramachandran for valuable guidance during the course of this study.

References

- CHANDRASEKARAN, K. S. (1955a). *Acta Cryst.* **8**, 361.
 CHANDRASEKARAN, K. S. (1955b). *Proc. Indian Acad. Sci. A*, **41**, 185.
 CHANDRASEKARAN, K. S. (1956). *Proc. Indian Acad. Sci. A*, **44**, 387.
 COMPTON, A. H. & ALLISON, S. K. (1935). *X-rays in Theory and Practice*. New York: Van Nostrand.
 EVANS, R. C., HIRSCH, P. B. & KELLAR, J. N. (1948). *Acta Cryst.* **1**, 124.
 HIRSCH, P. B. & RAMACHANDRAN, G. N. (1950). *Acta Cryst.* **3**, 187.
 RAMASESHAN, S. & RAMACHANDRAN, G. N. (1954). *Proc. Indian Acad. Sci. A*, **39**, 20.
 RENNINGER, M. (1952). *Acta Cryst.* **5**, 711.
 RAMACHANDRAN, G. N. (1944). *Proc. Indian Acad. Sci. A*, **20**, 245.
 WYCKOFF, R. W. G. (1948). *Crystal Structures*. New York: Interscience.
 ZACHARIASEN, W. H. (1945). *The Theory of X-ray Diffraction in crystals*. New York: Wiley.

Acta Cryst. (1959). **12**, 922

The Crystal Structures of some Anthracene Derivatives VI. 9-Anthraldehyde

BY JAMES TROTTER*

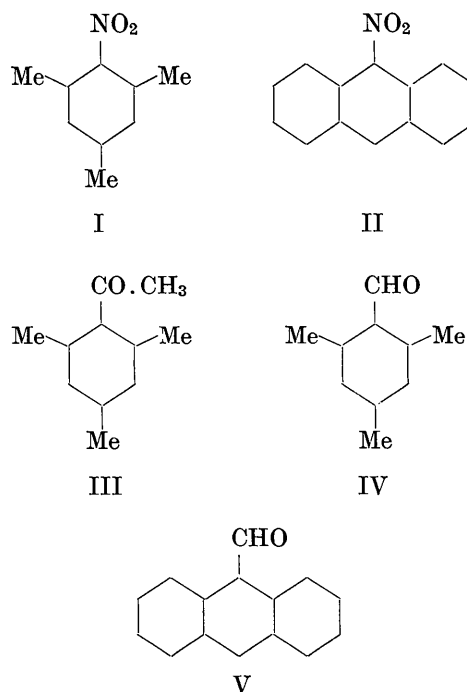
Division of Pure Physics, National Research Council, Ottawa, Canada

(Received 12 May 1959)

Crystals of 9-anthraldehyde are orthorhombic, space group $P2_12_12_1$, with four molecules in the unit cell. The structure has been determined from the projection along the short a -axis, and refined by three-dimensional differential syntheses. The anthracene skeleton is completely planar, but not coplanar with the plane of the aldehyde group, the angle between the planes being 27° .

Introduction

The physical properties of nitromesitylene (I), such as Raman and infrared frequencies, dipole moment and ultraviolet absorption spectrum, indicate that resonance interaction between the nitro group and the aromatic ring is markedly reduced in comparison with nitrobenzene, suggesting that the steric effect of the ortho methyl groups prevents the attainment of a completely coplanar configuration (see, for example, Wheland, 1955). Recently this deviation from planarity has been confirmed and in addition accurately measured by a detailed X-ray analysis of crystals of nitromesitylene (Trotter, 1959a, b); the nitro group is rotated about the C-N bond 66° out of the plane of the aromatic ring, and this measured angle can be correlated with the characteristic NO_2 vibration frequencies (Trotter, 1959f). The X-ray investigations have also been extended to 9-nitroanthracene (II) and 9:10-dinitroanthracene (Trotter, 1958, 1959c, d), where the environments of the nitro groups are very similar to those in nitromesitylene, and the measured deviations from coplanarity have been correlated with the



* National Research Council Postdoctorate Fellow.

infrared frequencies and ultraviolet spectra (Trotter, 1959*e, f*).

Spectroscopic and dipole moment evidence indicates similar deviations from coplanarity in acetyl derivatives, and although the deviations in this type of molecule have not been measured by X-ray methods, there is no doubt that in a molecule such as 2:4:6-trimethylacetophenone (III) (acetylmesitylene) the $-\text{CO}\cdot\text{CH}_3$ group is rotated at least 66° out of the aromatic plane. In the case of aldehydes, however, the evidence is much more confused. Raman spectra and dipole moment data have been interpreted as indicating no deviation from coplanarity (Saunders, Murray & Cleveland, 1941; Kadesch & Weller, 1941), but consideration of van der Waals separations would suggest that the $-\text{CHO}$ group must be twisted markedly out of the aromatic plane in such molecules as mesitylene aldehyde (IV) and 9-anthraldehyde (V) (Jones, 1945). It might be noted though that in these molecules the strain in a planar model could be relieved somewhat by a small in-plane displacement of the C(aromatic)–C(aldehyde) bond, as well as by an out-of-plane displacement of the oxygen atom. More recent investigations of the ultraviolet spectra of molecules of this type have suggested angles of about 20° between the planes of the aldehyde groups and the aromatic rings (Braude & Sondheimer, 1955), and these authors also show that a 20° twist is not incompatible with the dipole moment data.

A direct investigation of the structure and configuration of a molecule of this type would be useful; a suitable molecule for X-ray examination is 9-anthraldehyde, and its crystal structure has now been determined by X-ray diffraction methods.

Experimental

Crystals of 9-anthraldehyde are yellow in colour, and consist of needles elongated along the a -axis. The density was determined by flotation in aqueous potassium iodide solution. The unit-cell dimensions and space group were determined from rotation and oscillation photographs, and zero and first layer Weissenberg films of crystals rotating about the a and b axes, and from $h0l$ and $hk0$ precession films.

Crystal data

9-Anthraldehyde, $\text{C}_{15}\text{H}_{10}\text{O}$

Molecular weight = 206.2; melting point = 104°C .

Orthorhombic, $a = 4.29 \pm 0.01$, $b = 14.11 \pm 0.04$,

$c = 17.18 \pm 0.04$ Å.

Volume of the unit cell = $U = 1039.9$ Å³.

D_m (measured density) = 1.304 g.cm.⁻³,

$Z = 4$, D_x (calculated density) = 1.309 g.cm.⁻³.

Absorption coefficients for X-rays, $\lambda = 1.542$ Å

$\mu = 7.54$ cm.⁻¹; $\lambda = 0.7107$ Å, $\mu = 0.95$ cm.⁻¹.

Total number of electrons in the unit cell = $F(000) = 432$. Absent spectra: $h00$ when h is odd, $0k0$ when

k is odd, $00l$ when l is odd. Space group is $P2_12_12_1-D_2^4$.

The intensities of the hkl reflexions were recorded on Weissenberg photographs for crystals rotating about the a and b axes, using Cu $K\alpha$ radiation, the multiple-film technique being used to correlate strong and weak reflexions. For the crystal rotating about the a -axis layers with $h = 0, 1, 2, 3$ were recorded, and for the crystal rotating about b layers with $k = 0, 1, 2, 3$, the equi-inclination method being used for all nonequatorial layers. In the $0kl$ and $1kl$ zones only about 45% of the reflexions within the Cu $K\alpha$ sphere were observed; the percentage of observed reflexions became smaller as h increased, and only a small number of reflexions with $h = 3$ and 4 were observed (only the region of the $4kl$ zone with $k < 4$ has been explored, but all the observed reflexions in this zone are very weak). All the intensities were estimated visually, the range being about 2500 to 1. The values of the structure amplitudes were derived by the usual formulae for a mosaic crystal, Lorentz and polarization factors being applied together with the rotation factors appropriate to equi-inclination Weissenberg photographs (Tunell, 1939). The absolute scale was established later by correlation with the calculated structure factors. Small crystals were used and no absorption corrections were applied.

Structure analysis

[100] projection

In deriving an approximate trial structure it was assumed initially that the molecule was completely planar with C–C bond lengths 1.40 Å, C–O bond length 1.20 Å, and all valency angles 120° . The molecular orientation in the a -axis projection was determined from an examination of the $0kl$ weighted reciprocal lattice, and the position of the molecular centre was then found by the usual methods (Taylor, 1954; Trotter, 1959*g*). The trial structure deduced was checked by interpreting the peaks corresponding to multiple intramolecular and intermolecular vectors on the $0kl$ Patterson map. Taking the origin of the projection on a two-fold screw axis (so that the B parts of the structure factors are zero) structure factors were calculated for about 40 of the stronger reflexions, and a Fourier series then computed using measured structure amplitudes and calculated signs. On the resulting electron-density map all the carbon atoms and the oxygen atom were well resolved; the map indicated clearly that the oxygen atom deviates from its idealized position in the trial structure, but from this projection alone it could not of course be deduced whether this involves an in-plane or out-of-plane displacement.

New atomic centres were chosen and structure factors calculated for all the $0kl$ reflexions, using McWeeny's curves for carbon and oxygen, corrected for thermal vibration as usual, taking $B_C = 5.4$ Å² and

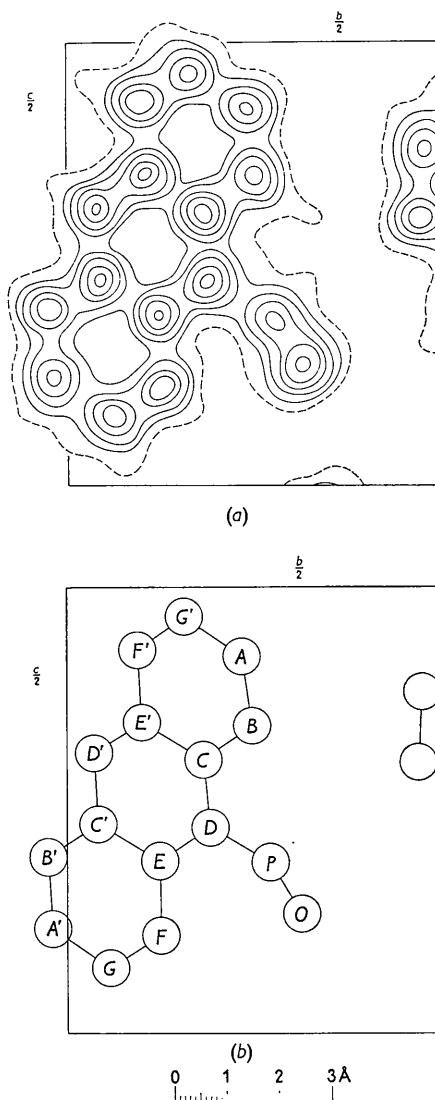


Fig. 1. (a) Electron-density projection along the a -axis; contours at intervals of $1 \text{ e.}\text{\AA}^{-2}$, with the one-electron line broken. (b) Projection of the structure on (100).

$B_0 = 6.0 \text{ \AA}^2$. The value of R , the usual discrepancy factor, was 33.6% over the observed reflexions.

Refinement proceeded by computing successive $(F_o - F_c)$ syntheses and shifting the atoms to minimize the slopes at the atomic centres, no changes being made in the temperature parameters. After three cycles R had dropped to 15.9%; an electron-density projection along the a -axis, computed using all the observed $0kl$ reflexions, is shown in Fig. 1.

x -Coordinates

The approximate orientation of the molecule in three-dimensions was then deduced from an examination of the three-dimensional weighted reciprocal lattice, and the x -coordinate of the molecular centre

obtained by computing the variation of the calculated structure factors of the $1k0$ and $10l$ reflexions as the molecule was moved along the a -axis. The positional parameters giving best agreement between F_o and F_c for these reflexions were used in computing structure factors for all the $1kl$ reflexions, the origin now being taken midway between the three sets of non-intersecting two-fold screw axes, as given in the *International Tables for X-ray Crystallography* (1952). The discrepancy factor over the observed reflexions was 45.8%, a discouragingly poor value. Generalized projections were computed using the measured structure amplitudes and calculated phase angles, and new x -coordinates obtained from the relation

$$\tan 2\pi x_j = S_1(y_j, z_j)/C_1(y_j, z_j),$$

where $S_1(y, z)$, $C_1(y, z)$ are the sine and cosine generalized projections. Comparison with the previous x -

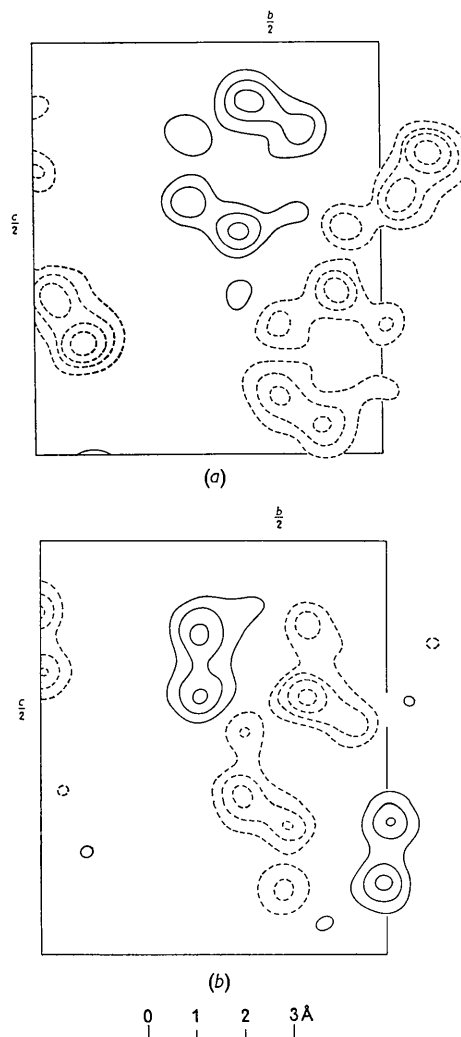


Fig. 2. (a) Cosine and (b) sine generalized projections along the a -axis; using the $1kl$ data. Contours at intervals of $1 \text{ e.}\text{\AA}^{-2}$, negative contours broken, zero contour omitted.

Table 1. *Peak heights and curvatures in final cycle*

Atom	ρ (e.Å ⁻³)		$\partial^2\rho/\partial x^2$ (e.Å ⁻⁵)		$\partial^2\rho/\partial y^2$ (e.Å ⁻⁵)		$\partial^2\rho/\partial z^2$ (e.Å ⁻⁵)	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
A	4.28	4.27	-13.92	-13.83	-23.68	-23.50	-22.99	-21.54
B	4.49	4.52	-14.84	-14.84	-26.64	-26.18	-25.51	-25.15
C	4.84	4.80	-14.70	-14.78	-30.33	-29.28	-29.88	-28.53
D	4.78	4.74	-15.35	-15.16	-27.10	-27.69	-27.39	-26.38
E	4.91	4.71	-15.86	-15.09	-28.27	-27.86	-31.08	-28.12
F	4.35	4.25	-13.71	-13.17	-22.39	-22.44	-26.01	-23.21
G	4.13	4.19	-12.68	-13.13	-21.96	-22.12	-24.28	-23.28
A'	3.88	3.98	-11.47	-11.88	-21.65	-21.96	-19.08	-19.33
B'	4.29	4.36	-13.77	-13.88	-24.05	-24.85	-24.26	-24.83
C'	4.56	4.66	-13.90	-14.32	-28.66	-29.25	-25.42	-25.03
D'	4.76	4.75	-15.60	-14.99	-28.47	-28.25	-29.04	-27.43
E'	4.74	4.78	-16.24	-16.26	-27.30	-27.78	-29.96	-28.53
F'	4.19	4.18	-12.86	-12.53	-21.58	-23.03	-24.44	-22.69
G'	4.09	4.22	-13.28	-13.34	-21.43	-22.37	-22.33	-22.75
P	4.15	4.29	-12.50	-13.02	-22.21	-23.43	-19.60	-19.11
O	4.72	5.05	-13.89	-15.56	-19.64	-20.97	-19.96	-19.86

coordinates showed that there were some quite large changes in fractional coordinate, although these changes did not appear to be quite so drastic when expressed in Å units, and the molecular orientation and position were changed only slightly. New coordinates were obtained by applying double shifts, and recalculation of the *lkl* structure factors revealed that *R* had dropped to 29.6%, an encouraging improvement. A second cycle reduced *R* to 22.7%; the cosine and sine generalized projections at this stage are shown in Fig. 2.

Three-dimensional refinement

At this stage structure factors were calculated for all the observed reflexions, using the *y*- and *z*-coordinates from the *OkI* zone refinement, the *x*-coordinates from the *lkl* refinement, and the original temperature parameters (*B*_C=5.4, *B*_O=6.0). The *R* value was 21.3%.

Refinement proceeded by computing observed and calculated differential syntheses, new positional parameters being obtained from the corrections of the *F*_o synthesis, combined with the back-shift (series-termination) corrections from the *F*_c synthesis, and new temperature parameters being chosen to minimize the differences between the observed and calculated peak electron-densities and curvatures. In making the coordinate changes, the shifts applied were 1½ times those obtained from the differential syntheses. Recalculation of the structure factors for all the observed *hkl* reflexions showed that *R* had been reduced to 14.9%.

A second set of observed and calculated differential syntheses was computed, and some further small changes in the positional parameters were indicated. The 1½ shift in the previous cycle had apparently been a reasonable value, since some of the atoms had been overshifted and others undershifted. In this second cycle the shifts applied were taken directly from the differential syntheses. The values of the observed and

calculated peak electron-densities and curvatures are listed in Table 1, and these indicate that some further small changes are required in the temperature parameters, especially for the oxygen atom. The final *B* values adopted are included in Table 2.

Table 2. *Final positional and temperature parameters of the carbon and oxygen atoms (and deviations, Δ, from the anthracene plane)*

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)	Δ (Å)
A	0.7427	-0.0117	0.4223	6.0	+0.06
B	0.6500	+0.0015	0.3437	5.4	+0.00
C	0.4783	-0.0650	0.3064	5.0	+0.04
D	0.3747	-0.0564	0.2295	4.5	-0.03
E	0.2011	-0.1247	0.1923	5.0	+0.01
F	0.0996	-0.1240	0.1098	5.4	+0.03
G	-0.0951	-0.1919	0.0733	6.0	-0.01
A'	-0.2012	-0.2699	0.1173	6.0	-0.03
B'	-0.1161	-0.2751	0.1967	5.4	-0.06
C'	0.0856	-0.2072	0.2329	5.0	+0.00
D'	0.1895	-0.2125	0.3137	4.5	+0.04
E'	0.3642	-0.1475	0.3473	5.0	+0.04
F'	0.4337	-0.1533	0.4294	5.4	-0.05
G'	0.6234	-0.0892	0.4667	6.0	-0.01
P	0.5244	+0.0236	0.1906	5.8	+0.10
O	0.4314	+0.0655	0.1334	9.0	-0.26

Further refinement would require that allowance be made for the contribution of the hydrogen atoms, and for the anisotropic thermal vibrations of the carbon and oxygen atoms. In view, however, of the rather small proportion of reflexions observed (this is reflected in the low peak heights and curvatures) it is doubtful whether such further refinement would be of much value. In any case the required information about the molecular configuration and dimensions can be obtained with fair accuracy at this stage, and so refinement was terminated at this point. The values of the measured structure amplitudes for the observed reflexions are listed in Table 4. To save space the calculated amplitudes and phase angles have not been listed (we actually did not trouble to compute the final

Table 3. Bond lengths in anthracene and 9-anthraldehyde

Bond	Anthracene	9-Anthraldehyde
<i>a</i>	1.37 Å	1.41 Å
<i>b</i>	1.43	1.43
<i>c</i>	1.40	1.39
<i>d</i>	1.42	1.42
<i>e</i>	1.44	1.45
C _{ar} -C _{al}	—	1.46
C=O	—	1.21

the strain due to this overcrowding is relieved by a 27° rotation of the aldehyde group, about the C(aromatic)-C(aldehyde) bond, out of the anthracene plane. In addition there is a displacement of the C_{al} atom out of the anthracene plane in the opposite direction from the oxygen displacement, and a repulsion of the C_{al} and oxygen atoms away from atom *F*, so that the angles *EDP* and *DPO* are increased from their normal values to 125° and 127° respectively, with the angle *CDP* consequently being reduced to only 111°. These deviations from the ideal planar structure increase the distances between the oxygen atom, and atom *F* and its hydrogen atom, to 3.06 Å and 2.34 Å respectively, these distances being almost exactly equal to the sums of the corresponding van der Waals radii (1.7 Å for carbon, 1.4 Å for oxygen and 1.0-1.2 Å for hydrogen). The distortions of the valency angles from 120° are such that the angle between the planes of the anthracene nucleus and the aldehyde group is reduced to as small a value as is possible without

introducing any undue strain due to close intramolecular distances.

The bond lengths in 9-anthraldehyde are compared in Table 3 with those in anthracene (Sinclair, Robertson & Mathieson, 1950; Cruickshank, 1956). Except for bond *a*, the differences are not significant; for bond *a* the difference is of the same order of magnitude as that found in 9-nitroanthracene (Trotter, 1959*d*), but, considering the standard deviations of the present results, the difference is of doubtful significance.

The C(aromatic)-C(aldehyde) bond length (1.46 Å) would appear to be a little shorter than the normal single bond distance in this type of molecule (1.50 Å), due no doubt to resonance interaction between the aldehyde group and the aromatic rings. It may be noted that the deviations from coplanarity reduce this resonance, but only to 0.79 (cos² 27°) of that in a planar model. The C=O bond distance (1.21 Å) is equal to the normal length of this bond in aldehydes.

The fact that the deviations from coplanarity reduce the resonance between the substituent aldehyde group and the anthracene nucleus by only about 20% compared with a planar model explains all the apparent inconsistencies in infrared and ultraviolet spectra and dipole moment data in this type of molecule. The aldehyde group is conjugated to a large extent with the aromatic π-electrons.

It is instructive to compare the deviations from coplanarity with those in the corresponding nitro

Table 4. Observed structure amplitudes

hkl	F _o	hkl	F _o	hkl	F _o	hkl	F _o	hkl	F _o	hkl	F _o	hkl	F _o	hkl	F _o
002	76.1	043	24.0	0,8,11	3.9	117	11.7	149	9.9	187	6.5	208	5.1	252	22.5
004	41.1	045	14.5	0,8,12	3.5	118	13.5	1,4,10	8.0	188	5.3	2,0,11	6.2	253	20.3
006	7.7	048	5.5	0,8,13	6.8	119	10.3	1,4,12	18.6	189	5.8	211	3.8	254	12.4
008	29.8	0,4,10	3.8	0,8,15	4.6	1,1,10	6.4	1,4,13	5.6	1,8,10	15.0	212	12.7	255	10.1
0,0,10	5.8	0,4,11	13.2	092	10.0	1,1,11	6.9	1,4,14	11.8	1,8,11	12.2	213	4.2	256	7.5
0,0,12	4.6	051	7.7	093	3.6	1,1,12	7.3	150	8.4	1,8,12	6.5	214	7.6	257	7.9
0,0,14	4.3	052	36.0	094	2.4	1,1,13	5.4	151	13.7	192	7.4	216	8.8	2,5,10	11.7
0,0,16	7.2	053	13.3	095	3.9	120	2.6	152	2.6	193	5.6	217	9.2	260	5.5
0,0,18	6.5	054	17.2	097	6.4	121	84.4	153	24.7	194	5.0	218	5.1	261	9.7
011	3.5	055	9.0	0,9,11	3.1	122	73.4	154	26.6	195	6.6	2,1,13	5.5	262	10.2
012	7.3	056	18.2	0,9,12	4.9	123	18.2	155	23.9	196	6.0	2,1,14	7.7	263	8.3
013	13.9	0,5,10	4.2	0,9,13	11.1	124	19.4	156	5.2	197	6.9	2,1,15	5.4	270	9.6
014	27.8	0,5,11	11.4	0,10,5	5.2	125	16.2	158	5.2	199	7.2	221	2.8	280	11.0
015	13.3	0,5,13	14.7	0,10,7	4.7	126	6.1	159	6.1	1,9,10	8.6	222	27.0	281	6.2
016	15.3	0,5,14	5.7	0,11,1	6.5	127	17.2	1,5,11	8.6	1,9,11	7.3	223	8.7	288	8.5
017	24.0	060	3.5	0,11,3	6.9	128	13.0	1,5,12	10.5	1,10,0	7.3	224	13.0	290	6.2
018	23.7	061	12.2	0,12,0	3.9	129	14.8	1,5,13	18.3	1,10,1	11.8	225	9.5	291	24.1
019	34.7	062	14.4	0,12,1	3.4	1,2,10	8.0	1,5,14	9.8	1,10,2	8.5	226	23.6	292	6.2
0,1,10	19.6	063	27.6	0,12,2	9.2	1,2,11	6.0	160	6.6	1,10,3	9.0	227	11.3	293	6.3
0,1,12	3.6	064	10.8	0,12,3	8.0	1,2,12	5.2	161	5.6	1,10,4	5.3	2,2,11	14.9	2,10,0	7.5
0,1,16	4.4	065	33.6	0,12,7	4.4	1,2,13	8.3	162	5.2	1,10,5	5.4	2,2,12	7.1	2,10,1	8.8
0,1,18	3.2	066	11.1	0,12,10	6.6	1,2,14	5.6	163	6.2	1,10,6	5.5	2,2,13	9.1	2,10,7	9.5
020	12.3	067	3.8	0,13,2	13.3	130	76.4	164	6.0	1,10,7	5.5	2,2,14	8.7	2,10,9	13.2
021	87.6	068	11.3	0,13,7	3.9	131	42.3	165	10.7	1,10,8	6.9	230	13.4	2,11,0	9.5
022	3.7	0,6,10	8.8	0,14,0	12.5	132	40.6	168	4.8	1,10,9	6.5	231	8.7	2,11,1	6.7
023	16.6	0,6,11	11.8	0,14,1	9.6	133	8.0	169	4.6	1,10,10	5.6	232	21.4	2,11,2	6.7
024	7.7	0,6,12	18.2	0,14,2	4.8	134	21.1	1,6,10	10.4	1,11,0	17.7	233	27.7	2,11,7	8.5
025	35.7	0,6,14	6.9	0,14,3	3.6	135	14.0	1,6,11	12.8	1,11,1	5.4	234	16.7	2,11,9	7.9
026	16.6	0,6,15	3.0			136	11.6	1,6,12	7.8	1,11,3	5.5	235	20.9	2,12,2	6.7
027	10.1	071	9.1	101	37.6	137	16.2	1,6,13	9.8	1,11,4	6.0	236	5.5		
028	4.1	072	9.6	102	6.5	138	18.7	170	20.9	1,11,8	6.1	237	11.7	301	7.7
029	11.7	073	25.5	103	7.6	139	14.4	171	11.4	1,12,0	10.3	2,3,11	15.6	309	12.2
0,2,10	5.2	074	21.2	104	11.0	1,3,10	6.7	172	12.0	1,12,1	8.0	2,3,12	7.6	3,0,10	11.0
031	61.9	076	19.0	105	15.2	1,3,11	7.3	173	16.7	1,12,2	6.5	2,3,13	6.7	3,0,14	8.2
033	19.4	0,7,10	2.6	107	25.3	1,3,12	12.5	174	5.0	1,12,8	7.7	2,3,15	8.4	3,0,15	6.9
034	24.8	0,7,11	7.2	109	11.8	1,3,13	6.7	175	6.3	1,13,1	6.9	240	5.4	310	13.7
036	2.4	0,7,12	31.7	1,0,10	10.4	1,3,14	8.0	177	8.8	1,16,0	4.4	241	17.6	311	8.6
037	9.0	0,7,13	8.9	1,0,11	6.8	140	9.3	179	7.4	1,16,2	5.8	242	12.5	312	7.8
038	10.5	0,7,14	13.8	1,0,12	5.9	141	12.7	1,7,10	8.8			243	32.5	316	7.9
0,3,10	4.0	0,7,15	4.6	110	17.3	142	12.4	1,7,11	5.6	200	3.6	244	13.5	317	8.0
0,3,11	7.7	082	8.1	111	36.4	143	8.5	180	4.4	201	10.2	245	6.0	319	7.7
0,3,14	4.8	083	13.8	112	76.4	144	38.7	181	10.2	202	4.5	246	16.8	321	5.3
0,3,15	4.0	084	18.0	113	28.3	145	14.4	182	7.3	203	5.4	247	6.8		
040	21.3	085	6.9	114	8.0	146	16.5	183	4.5	204	7.7	2,4,10	7.6	400	8.7
041	18.3	086	8.3	115	8.4	147	12.2	185	4.8	205	8.1	251	15.6	418	9.5
042	27.9	087	7.0	116	9.3	148	7.3	186	11.4	206	6.6				

compounds, 9:10-dinitroanthracene and 9-nitroanthracene. In both of these molecules the environments of the nitro groups are symmetrical, and the strain in planar models is relieved by a 64° rotation of the nitro groups out of the anthracene planes (in crystals of the 9-nitro derivative, crystal forces give an 85° rotation, but the most stable state of the isolated molecule has a 64° rotation (Trotter, 1959f)). The strain cannot be relieved by distortions of the valency angles or displacement of the nitrogen atoms from the mean planes, for any such distortion or displacement, while reducing the strain at one oxygen atom, would increase the overcrowding at the other oxygen. In 9-anthraldehyde, however, the substituent group is of course not symmetrical, and since the hydrogen atom is smaller than the oxygen the strain in a planar model can be partly relieved by a distortion of the valency angles and a displacement of the aldehydic carbon atom. These quite small variations in valency angles and aldehydic carbon atom position allow the plane of the aldehyde group to make a much smaller angle with the anthracene plane (27°) than the nitro groups in the nitro derivatives (64°)—the corresponding displace-

ments of the oxygen atoms from the aromatic plane are 0.26 \AA in the aldehyde and 0.96 \AA in the nitro derivatives. The deviations from coplanarity in both types of molecule are such as to make the resonance interaction between the substituent groups and the aromatic rings as large as possible while keeping the non-bonded intramolecular distances equal to the sums of the corresponding van der Waals radii.

Intermolecular distances

All the intermolecular distances correspond to normal van der Waals interactions. The perpendicular distance between the aromatic planes of molecules related by translation a is 3.52 \AA . The shorter lateral contacts are illustrated in Fig. 4.

The author is indebted to Dr W. H. Barnes for his interest in this problem, to Dr R. N. Jones for crystals of 9-anthraldehyde, and to Dr F. R. Ahmed for computational assistance.

References

- BRAUDE, E. A. & SONDEHEIMER, F. (1955). *J. Chem. Soc.* 3754.
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 915.
International Tables for X-ray Crystallography (1952). Birmingham: Kynoch Press.
 JONES, R. N. (1945). *J. Amer. Chem. Soc.* **67**, 2127.
 KADESCH, R. G. & WELLER, S. W. (1941). *J. Amer. Chem. Soc.* **63**, 1310.
 SAUNDERS, R. H., MURRAY, M. J. & CLEVELAND, F. F. (1941). *J. Amer. Chem. Soc.* **63**, 3121.
 SINCLAIR, V. C., ROBERTSON, J. M. & MATHIESON, A. MCL. (1950). *Acta Cryst.* **3**, 251.
 TAYLOR, C. A. (1954). *Acta Cryst.* **7**, 757.
 TROTTER, J. (1958). *Acta Cryst.* **11**, 564.
 TROTTER, J. (1959a). *Acta Cryst.* **12**, 173.
 TROTTER, J. (1959b). *Acta Cryst.* **12**, 605.
 TROTTER, J. (1959c). *Acta Cryst.* **12**, 232.
 TROTTER, J. (1959d). *Acta Cryst.* **12**, 237.
 TROTTER, J. (1959e). *Canad. J. Chem.* **37**, 351.
 TROTTER, J. (1959f). *Canad. J. Chem.* (In the press.)
 TROTTER, J. (1959g). *Acta Cryst.* **12**, 339.
 TUNELL, G. (1939). *Amer. Min.* **24**, 448.
 WHEELAND, G. W. (1955). *Resonance in Organic Chemistry*. New York: Wiley.

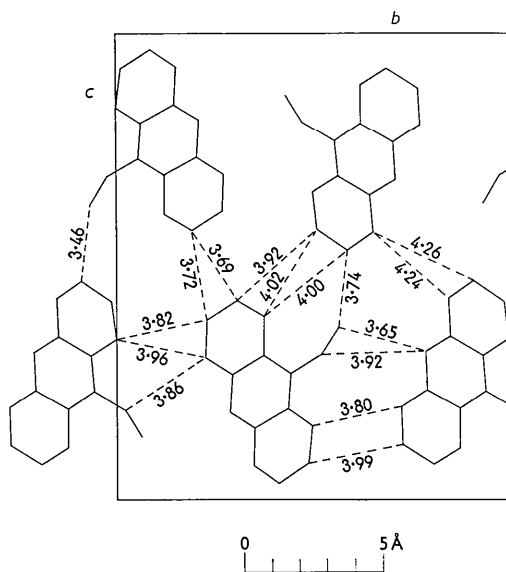


Fig. 4. Projection of the structure along [100], showing the shorter intermolecular distances.