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The Crystal Structures of Some Anthracene Derivatives. V. 9-Nitroanthracene

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The structure of 9-nitroanthracene has been determined from projections along the three principal crystallographic axes, and details of the molecular geometry and dimensions have been obtained. The nitrogen atom and all the carbon atoms lie on one plane, but the plane of the nitro group is tilted 85° out of the aromatic plane about the C–N bond.

Introduction

An analysis of the crystal structure of 9:10-dinitroanthracene has shown that the nitro groups are tilted 64° out of the plane of the aromatic rings about the C–N bonds, and that resonance interaction between the aromatic π-electrons and the nitro group is very slight (Trotter, 1959*b*). The crystal structure of 9-nitroanthracene has now been investigated to establish the molecular dimensions and geometry of the molecule, for comparison with the dinitro derivative and with other meso-substituted anthracenes (Trotter, 1958*a*, *b*; 1959*a*).

Experimental

Crystals of 9-nitroanthracene, 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 by flotation in aqueous potassium iodide solution. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of a crystal rotating about the *a*-axis, *hkl* Weissenberg films with $h = 0, 1, 2, 3$, and *h0l*, *h1l*, *hk0* and *hk1* precession films.

Crystal data

9-Nitroanthracene, $C_{14}H_9NO_2$; $M = 223{\cdot}2$; m.p. 146 °C.
Monoclinic, $a = 7{\cdot}49 \pm 0{\cdot}02$, $b = 13{\cdot}77 \pm 0{\cdot}03$, $c = 11{\cdot}44 \pm 0{\cdot}03$ Å, $\beta = 115° \, 11' \pm 10'$.
Volume of the unit cell = 1068·5 Å^3.
Density, calculated (with four molecules per unit cell) = 1·379, measured = 1·375 g.cm^{-3}.
Absorption coefficient for X-rays $\lambda = 1{\cdot}542$ Å, $\mu = 8{\cdot}96$ cm.$^{-1}$; $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}12$ cm.$^{-1}$.
Total number of electrons per unit cell $= F(000) = 464$.

Absent spectra: *h0l* when *h* is odd, *0k0* when *k* is odd. Space group is uniquely determined as $P2_1/a$–C_{2h}^5.

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, and multiple-film technique to correlate strong and weak reflexions. The *h0l* and *hk0* reflexions were recorded on precession films with Mo $K\alpha$, using multiple exposures for intensity correlation. All the intensities were estimated visually, the range being about 8000 to 1. The same crystal was used for all the photographs; the cross-section normal to the *a*-axis was 0·40 × 0·30 mm., and no absorption corrections were applied. 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. 130 independent *0kl* reflexions, 65 *h0l* and 68 *hk0* were observed, representing 67%, 77% and 67% respectively of the possible observable with the radiations and experimental conditions used.

Structure analysis

[100] *projection*

Since the projection down the *a*-axis was expected to give best resolution of the atoms, the *0kl* zone was considered initially. The orientation of the molecule in this projection was found by comparing the *0kl* weighted reciprocal lattice with the optical transform of a completely planar model with all bond lengths taken as 1·40 Å. The position of the molecular centre was then deduced from a consideration of the structure factors of the axial reflexions. When the optical transform of this postulated structure was compared with the weighted reciprocal lattice however, some poor agreements were apparent for some of the low order reflexions, and this trial structure was abandoned.

The three axial Patterson projections were then computed; on the *0kl* zone map, the peaks corresponding to intramolecular vectors indicated that the previously determined orientation was correct, and in addition the multiple intermolecular peaks suggested the same position for the molecular centre. Structure factors were calculated for all the *0kl* reflexions, using McWeeny's scattering curves for carbon, nitrogen and oxygen, corrected for thermal vibration as usual,

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taking $B = 4{\cdot}6$ Å^2. The value of the discrepancy factor, R, was 48%, and there were some very poor agreements, as observed previously in the comparison between optical transform and weighted reciprocal lattice.

In spite of these poor agreements however, the fact that two different methods led to the same structure suggested that it might be close to the true one, and it seemed worth while to make an effort to refine it. A difference synthesis was computed, including as many of the large terms as possible; for some planes which had large observed values and small calculated ones, the sign of F_o was deduced from the transform. The difference map showed large fluctuations of positive and negative density, but these all appeared to be related to peaks and troughs near the postulated oxygen atom positions, which suggested that these oxygen coordinates were grossly in error, and that the nitro group was tilted very markedly out of the plane of the anthracene nucleus. The oxygen atoms were moved to minimize the electron-density slopes, and the structure factors were recalculated. The R value was 35%. Refinement proceeded by computing successive (F_o-F_c) syntheses, and after three more cycles R had dropped to 12·4%, indicating that the structure was certainly correct, the initial poor agreement being due chiefly to incorrect positioning of the oxygen atoms. 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.

[010] *and* [001] *projections*

The Patterson projections indicated that the anthracene nucleus was approximately parallel to the b-axis, so that relative x-coordinates of the carbon and nitrogen atoms were easily obtained from the $h0l$ zone Patterson map. The position of the molecule was deduced from the multiple intermolecular vectors, which were clearly resolved on this map. There were two possible positions for the molecular centre, separated by $\frac{1}{4}a$. In addition, by assuming N–O bond lengths of about 1·2 Å, there were two possible positions for the oxygen atoms—these two positions being almost indistinguishable in the c-axis projection because of the small difference in the oxygen y-coordinates.

The correct position for the molecular centre was then found by consideration of the $hk0$ planes with $h = 2n+1$, and the correct oxygen positions deduced from the $h0l$ zone data. Structure factors were calculated for each zone, and the discrepancy factors were: $R_{h0l} = 29\%$, $R_{hk0} = 24\%$. Refinement proceeded by $h0l$ and $hk0(F_o-F_c)$ syntheses, relying on the $hk0$ zone maps for the carbon shifts, and both maps for

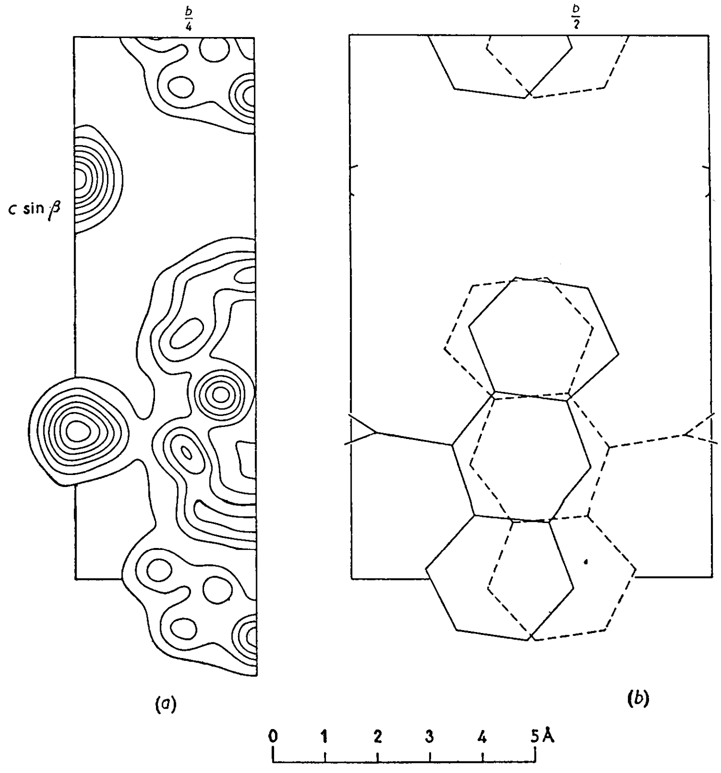

Fig. 1. (a) Electron-density projection along the a-axis, with contours at intervals of 2 e.Å^{-2}.
(b) Projection of the structure along [100].

the oxygen shifts; only the x-coordinates were refined. After 2 cycles on each zone the R values had dropped to 19·9% and 13·7% for the $h0l$ and $hk0$ zones respectively. The agreement for the $h0l$ reflexions is a little poorer than for the other two zones, and structure factors were calculated for the other possible oxygen positions as a check that the derived oxygen coordinates were correct. The R value was 34% with some very poor agreements, so that the present structure appears to be the correct one. The final $h0l$ difference map indicated that the oxygen atoms are vibrating anisotropically, but no allowance was made for this effect in the structure factor calculations. Measured and calculated structure factors are listed in Table 4, and F_o syntheses are shown in Figs. 2 and 3. The resolution of the individual atoms on these maps is of course poor, but the large deviation from coplanarity is clearly illustrated.

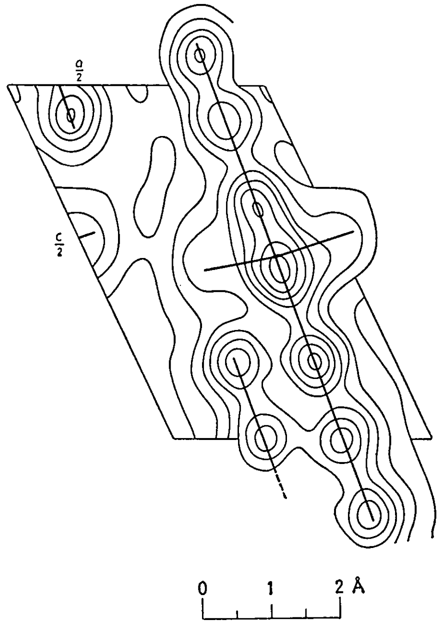

Fig. 2. Electron-density projection along [010]. Contours at intervals of 2 e.Å^{-2}.

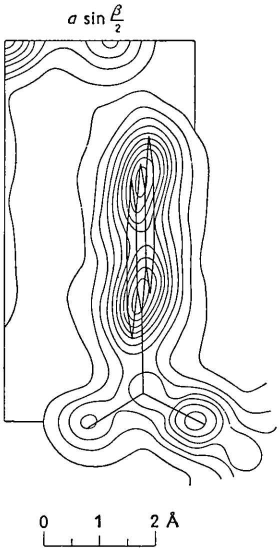

Fig. 3. Electron-density projection along [001]. Contours at intervals of 2 e.Å^{-2}.

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. 4. The coordinates of the carbon atoms can be fitted to an equation of the form

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

where X', Y', Z' are coordinates expressed in Ångström units and referred to orthogonal axes a', b and c where a' is perpendicular to b and c. 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

Table 1. *Coordinates of the atoms*

Atom	x/a	y/b	z/c
A	0·3165	0·1432	−0·0977
B	0·3331	0·1037	0·0176
C	0·3454	0·1715	0·1153
D	0·3599	0·1396	0·2370
E	0·3727	0·1994	0·3373
F	0·3860	0·1634	0·4586
G	0·3980	0·2283	0·5563
A'	0·3942	0·3314	0·5358
B'	0·3802	0·3710	0·4168
C'	0·3703	0·3018	0·3245
D'	0·3556	0·3358	0·2017
E'	0·3425	0·2769	0·1031
F'	0·3265	0·3114	−0·0222
G'	0·3143	0·2432	−0·1136
N	0·3631	0·0335	0·2592
O_1	0·2129	−0·0103	0·2417
O_2	0·5242	−0·0046	0·2958

Aromatic rings:

$$0·9971X'+0·0031Y'-0·0758Z'-2·3189 = 0$$

Nitro group:

$$0·1653X'+0·1686Y'+0·9717Z'-2·2415 = 0\,.$$

The deviations of the atoms from these planes are listed in Table 2. The angle between the planes is 84·7°.

The bond lengths and valency angles in the molecule were calculated from the coordinates of Table 1, and these values were averaged over chemically equivalent bonds and angles. In addition, however, these mean values showed that the anthracene nucleus does not deviate significantly from symmetry *mmm*; for example the lengths of those bonds which are related in

Table 2. *Deviations from the mean planes*

Atom	Deviation from anthracene plane	Deviation from NO_2 plane
A	−0·011	—
B	0·003	—
C	0·007	—
D	0·003	0·006
E	0·008	—
F	−0·007	—
G	−0·004	—
A′	−0·009	—
B′	−0·002	—
C′	0·006	—
D′	0·012	—
E′	0·002	—
F′	0·000	—
G′	−0·009	—
N	0·000	0·000
O_1	−1·039	0·000
O_2	1·096	0·000

anthracene, but theoretically non-equivalent in 9-nitroanthracene are

A–B	1·393 Å	*A′–B′*	1·404 Å
B–C	1·433	*B′–C′*	1·434
C–D	1·401	*C′–D′*	1·400

The values were therefore averaged, and the final mean values are shown in Fig. 4. Fig. 4 also shows the distances between those atoms which would be closer than the normal van der Waals separations if the molecule were completely planar (the hydrogen atoms were assumed to lie on the plane of the carbon atoms, with C–H = 1·08 Å).

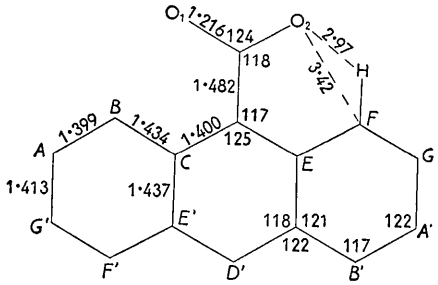

Fig. 4. Bond lengths, valency angles and intramolecular 'overcrowded' distances.

Table 3. *Bond lengths in anthracene and 9-nitroanthracene*

Bond	Anthracene	9-Nitro-anthracene
A–B	1·366±0·004 Å	1·399±0·008 Å
B–C	1·433±0·003	1·434±0·008
C–D	1·399±0·003	1·400±0·008
C–E′	1·419±0·006	1·413±0·011
A–G′	1·436±0·004	1·437±0·011
D–N	—	1·482±0·015
N–O_1	—	1·216±0·009
N–O_2	—	1·216±0·009

Standard deviations

The standard deviations of the atomic positions, calculated from Cruickshank's (1949) formulae, are $\sigma(x) = \sigma(y) = \sigma(z) = 0{\cdot}011$ Å for carbon, 0·010 Å for nitrogen and 0·009 Å for oxygen, but since there is appreciable overlap in all projections, these values are possibly rather optimistic. The standard deviations of the mean bond lengths are included in Table 3.

Discussion

The anthracene nucleus in 9-nitroanthracene is completely planar within the limits of experimental error, the maximum deviation of the carbon atoms from the mean plane being 0·012 Å and the root mean square deviation 0·007 Å. The nitrogen atom also lies on this plane, but the oxygen atoms lie one above and one below the plane at distances of 1·07 Å. The nitro group is thus tilted out of the plane of the carbon atoms about the C–N bond, and the angle of tilt is 85°. This deviation from planarity increases the distances between the oxygen atoms and neighbouring carbon and hydrogen atoms to values which are greater than the normal van der Waals separations (Fig. 4). In the structure analysis of 9:10-dinitroanthracene (Trotter, 1959*b*) it was observed that the tilt of 64° was just sufficient to make these intramolecular separations about equal to the normal van der Waals distances.

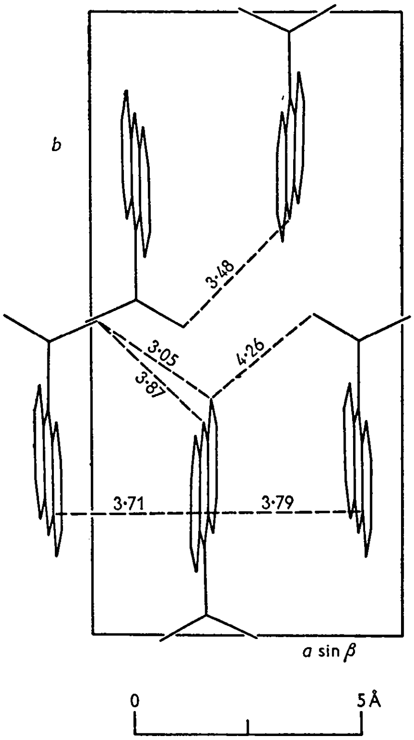

Fig. 5. Projection of the structure along [001] showing the shorter intermolecular distances.

Table 4. *Measured and calculated structure factors*

hkl	F_o	F_c
200	50·3	−50·2
400	64·0	−61·4
600	18·0	+17·0
800	5·4	+4·7
020	78·2	−77·8
040	14·1	+19·9
060	75·7	+77·0
080	16·2	+16·5
0,10,0	4·8	+2·7
0,12,0	4·7	+5·9
0,14,0	< 2·6	−0·7
0,16,0	< 2·1	−0·6
001	7·4	+8·8
002	8·0	−16·2
003	2·7	+2·9
004	32·6	+34·9
005	26·9	−28·6
006	20·8	−23·5
007	12·7	+12·3
008	9·2	+6·4
009	27·7	+26·8
0,0,10	< 2·7	+1·5
0,0,11	7·2	+3·4
0,0,12	< 2·1	+0·1
0,0,13	2·8	−1·9
011	75·6	−76·3
021	7·0	−8·5
031	11·1	−9·4
041	3·4	−5·2
051	29·3	+29·8
061	15·4	−18·3
071	22·9	−23·6
081	5·9	+2·8
091	5·6	+7·4
0,10,1	< 2·5	+0·7
0,11,1	< 2·6	−3·7
0,12,1	< 2·7	+1·7
0,13,1	4·6	+4·7
0,14,1	4·1	−3·1
0,15,1	2·0	+0·5
0,17,1	2·5	+1·7
012	20·9	+20·9
022	90·6	−90·1
032	3·1	+3·6
042	56·3	−56·1
052	3·5	−5·8
062	34·1	−33·5
072	2·4	−3·8
082	11·6	−12·9
092	2·3	+3·5
0,10,2	5·1	−5·0
0,11,2	6·5	+5·1
0,12,2	< 2·7	+2·7
0,13,2	7·0	−5·4
0,14,2	4·8	−5·1
0,15,2	2·3	−2·3
0,17,2	5·2	+5·5
013	27·2	+27·6
023	27·7	+29·7
033	8·0	−9·2
043	15·0	+17·6
053	2·2	+4·2
063	3·9	−3·7
073	2·6	+2·9
083	5·1	−5·9
093	7·0	+9·6
0,10,3	21·6	+25·5
0,11,3	5·1	−6·9
0,12,3	11·7	−10·6
0,13,3	2·9	−1·3
0,14,3	< 2·5	+0·3
0,16,3	4·8	+3·6
014	8·3	−8·4
024	60·6	+58·9
034	24·7	+26·5
044	3·4	+3·6
054	26·3	−28·3
064	24·3	+25·7
074	2·2	+0·5
084	8·5	+3·2
094	14·3	+13·4
0,10,4	3·5	+5·8
0,11,4	10·8	−8·5
015	13·5	+14·9
025	14·4	+10·7
035	27·4	−29·2
045	26·8	−30·0
055	6·4	+4·0
065	7·4	−7·2
075	9·7	+10·7
085	< 2·5	−1·0
095	16·1	−14·7
0,10,5	1·9	+1·8
0,11,5	6·0	+3·7
0,12,5	3·0	−2·9
016	5·2	−8·9
026	14·7	−14·2
036	3·0	−0·8
046	8·0	−5·5
056	4·4	0·0
066	1·7	−3·0
076	9·7	+11·6
086	20·4	−19·3
096	8·8	−7·5
0,10,6	12·8	+13·2
0,11,6	3·0	+3·8
0,14,6	3·3	−3·1
017	< 2·4	+0·9
027	4·7	+5·0
037	< 2·4	+0·8
047	5·2	+5·5
057	2·5	+1·0
067	< 2·5	−3·4
077	< 2·7	+4·7
087	3·9	+5·1
097	4·1	+2·4
0,10,7	2·9	+2·4
0,14,7	2·7	−2·2
018	8·8	+6·5
028	7·4	+6·9
038	10·3	−10·4
058	< 2·7	−2·6
078	9·0	+9·2
088	4·2	+3·5
098	7·0	−8·0
0,10,8	3·1	−2·0
0,11,8	2·0	+0·8
019	2·3	+4·0
029	20·3	−19·2
039	8·4	−6·6
049	< 2·7	−1·0
069	4·2	+3·1
099	3·6	−3·3
0,1,10	6·8	−5·8
0,2,10	3·3	−2·6
0,3,10	5·9	−3·4
0,4,10	3·5	−2·5
0,5,10	9·5	+7·3
0,1,11	1·7	+2·1
0,2,11	2·1	−1·9
0,9,11	2·1	+0·9
0,1,12	2·9	+1·4
0,2,12	3·5	+2·4
0,6,12	1·4	−1·4
0,1,13	3·0	−2·0
0,2,13	2·0	+1·9
0,3,13	1·8	+0·6
2,0,$\overline{13}$	1·7	−1·7
2,0,$\overline{12}$	< 2·0	−3·2
2,0,$\overline{11}$	2·1	+3·4
2,0,$\overline{10}$	18·0	−10·2
20$\bar{9}$	10·8	−10·3
20$\bar{8}$	6·5	−15·2
20$\bar{7}$	6·3	+16·2
20$\bar{6}$	1·5	+6·9
20$\bar{5}$	4·4	−0·6
20$\bar{4}$	2·0	−6·6
20$\bar{3}$	35·1	+35·6
20$\bar{2}$	12·4	+12·2
20$\bar{1}$	138·4	−141·6
201	4·6	+5·1
202	9·2	−12·4
203	15·3	−4·8
204	10·2	+3·8
205	3·3	−8·8
206	5·9	+13·0
207	< 2·0	+1·3
208	12·3	−12·7
209	3·1	−6·5
4,0,$\overline{13}$	< 1·7	+0·4
4,0,$\overline{12}$	< 2·0	−1·7
4,0,$\overline{11}$	3·5	−1·6
4,0,$\overline{10}$	4·1	+3·9
40$\bar{9}$	20·7	−24·2
40$\bar{8}$	< 1·9	+3·7
40$\bar{7}$	7·4	+10·2
40$\bar{6}$	2·2	−3·4
40$\bar{5}$	< 1·7	−2·7
40$\bar{4}$	7·0	−3·4
40$\bar{3}$	7·0	+5·2
40$\bar{2}$	24·6	−26·4
40$\bar{1}$	17·7	+19·3
401	5·6	+6·1
402	2·4	−2·3
403	5·2	+7·5
404	3·0	+0·6
405	< 2·0	−1·0
406	< 2·0	+3·5
407	< 1·8	−3·4
408	1·5	+0·9
6,0,$\overline{12}$	6·1	+1·9
6,0,$\overline{11}$	< 2·0	−0·4
6,0,$\overline{10}$	19·8	+19·7
60$\bar{9}$	9·2	+6·3
60$\bar{8}$	9·2	+5·1
60$\bar{7}$	5·3	−7·4
60$\bar{6}$	9·8	−4·8
60$\bar{5}$	2·0	−1·6
60$\bar{4}$	4·0	+5·8
60$\bar{3}$	3·7	0·0
60$\bar{2}$	7·2	−4·6
60$\bar{1}$	41·3	+46·4
601	< 2·0	−3·6
602	3·1	−2·1
603	< 1·9	+5·3
604	4·3	−4·3
8,0,$\overline{10}$	8·7	−7·8
80$\bar{9}$	< 1·7	−1·7
80$\bar{8}$	1·7	+0·1
80$\bar{7}$	2·3	+3·1
80$\bar{6}$	6·6	+1·2
80$\bar{5}$	2·3	−3·0
80$\bar{4}$	2·3	+5·8
80$\bar{3}$	< 1·8	0·0
80$\bar{2}$	10·3	−7·3
80$\bar{1}$	13·4	−14·0
110	49·5	−45·9
120	27·5	−27·3
130	29·9	−27·9
140	15·3	−16·1
150	8·8	−11·8
160	10·0	+14·7
170	10·0	−12·0
180	11·0	−4·3
190	4·5	−7·7
1,10,0	3·4	−4·9
210	183·2	+182·7
220	13·7	+20·4
230	8·3	−9·4
240	3·4	+5·1
250	26·8	−27·0
260	< 2·0	0·0
270	23·4	+26·4
280	2·8	−1·6
290	5·2	+9·8
2,10,0	< 2·4	+2·5
310	< 2·0	−1·5
320	8·8	+0·7
330	15·5	−18·2
340	2·1	−6·0
350	24·8	−27·7
360	10·8	−14·2
370	3·4	−0·7
380	< 2·4	−2·1
390	12·3	−7·3
3,10,0	< 2·5	−4·9
3,11,0	7·4	−8·3
3,13,0	4·5	−1·0
410	23·0	−28·2
420	43·9	+39·7
430	< 2·3	−0·4
440	18·0	+19·1
450	< 2·4	+1·8
460	12·4	−10·0
470	< 2·5	−1·1
480	12·6	+9·9
490	3·0	−3·4
4,10,0	4·1	+5·3
4,11,0	< 2·5	−0·7
4,12,0	3·5	+3·2
510	5·0	−1·4
520	6·5	+6·4
530	3·6	+5·2
540	7·2	+6·9
550	7·5	+8·6
560	4·9	−3·6
570	7·3	−6·0
580	7·8	+5·3
5,10,0	2·4	+1·6
5,12,0	2·2	+0·7
610	17·1	−15·7
620	2·8	−3·2
630	< 2·5	+0·2
640	2·8	−0·9
650	7·2	+6·9
660	4·1	+2·5
670	8·1	−6·7
710	3·0	−5·2
720	2·8	−3·2
730	2·5	−4·1
740	< 2·2	−1·9
750	< 2·1	−0·7
760	5·9	+5·6
770	4·7	−3·3
810	5·0	+3·3
820	2·5	−0·7

It seems likely then that the plane of the nitro group in 9-nitroanthracene in solution or in the vapour phase might be free to oscillate between angles of 64° and 116° with the anthracene plane, but that in the crystal the most stable configuration is at 85°. The small amount of resonance interaction between the nitro group and the aromatic π-electrons, at 64° tilt, is not sufficient to hold the nitro group in this position in opposition to crystal forces, which apparently give minimum energy and best packing when the angle is 85°.

The measured bond lengths indicate that the symmetry of the anthracene nucleus is *mmm*, and the mean bond lengths are compared in Table 3 with those in anthracene (Sinclair, Robertson & Mathieson, 1950; Cruickshank, 1956). On the basis of the estimated standard deviations, the lengths of the bonds *A–B* differ significantly, but since there are no other significant differences between corresponding carbon–carbon bond lengths in the two molecules, and the values of the standard deviations are probably rather low, it is doubtful whether there is any real difference between the *A–B* bonds. The carbon–nitrogen bond distance corresponds to a single bond, and the N–O bond lengths are identical with those in aliphatic nitro compounds.

Intermolecular distances

The shortest intermolecular distance is 3·05 Å between atom B' of the standard molecule and atom O_2 of the molecule with coordinates $(-\frac{1}{2}+x, \frac{1}{2}-y, z)$. While this distance appears to be a little shorter than those usually found in structures of this type, it is almost exactly equal to the sum of the van der Waals radii (1·7 Å for the half-thickness of the aromatic rings plus 1·4 Å for the van der Waals radius of oxygen). The aromatic planes of those molecules related by the glide plane are almost exactly parallel, the distance between them being 3·50 Å, and the shortest carbon–carbon distances between these molecules are 3·71 Å and 3·79 Å. The shorter intermolecular contacts are illustrated in Fig. 5.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

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X-ray scattering factors of Al^{2+}, Al^{3+}, Mn^{2+}, Fe, Zr^{4+}, Au^{+} and U^{6+}.

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Some years ago we published a set of X-ray scattering factors (Berghuis *et al.*, 1955), computed from electron density data which had become available since the publication of the *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935). The present paper gives some more data, being the transforms of electron densities either published since 1935 or kindly submitted by the authors. The list is by no means complete: a growing interest in more accurate X-ray scattering factors has led several authors to compute transforms of recent self-consistent field (SCF) data (Piper, 1957; Freeman, 1959; Freeman & Wood, 1959; Ibers, 1957, 1958*a*, *b*; Hurst, Miller & Matsen, 1958). Also, *f*-factors of a large number of both atoms and ions have recently been computed from the Thomas–Fermi–Dirac field (TFD) by Thomas & Umeda (1957), while Tomiie & Stam (1958) calculated a number of scattering factors from Slater functions. We computed form factors for Al^{2+} and Al^{3+} from wave functions given by Katterbach (1953) who states that he gives a more accurate solution of the Hartree–Fock equation than Krichagina & Petrashen (1938) whose results were used by Freeman (1958); Katterbach also took into account polarization of the 2*p* shell in Al^{2+}. Our new data for Al^{3+} agree completely with those of Freeman (1959) derived from another source (Froese, 1957); those for Al^{2+} are occasionally slightly lower than Freeman's. See Table 1, in which our results (lefthand column for each atom or ion) are compared with those of other investigators. For Mn^{2+} we used the same input data as Freeman; between $\sin\theta/\lambda = 0{\cdot}10$ and 0·40 our values are consistently about one percent lower than Freeman's,

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