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The Crystal Structures of Some Mesitylene and Durene Derivatives. II. Nitromesitylene

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Crystals of nitromesitylene are orthorhombic, space group $Pna2_1$, with four molecules in the unit cell. The structure has been determined from projections along the three principal crystallographic axes and values of the molecular dimensions and intermolecular distances have been obtained. The nitro group is tilted about the C–N bond 66° out of the plane of the aromatic ring.

Introduction

The crystal structure of nitromesitylene has been examined to obtain accurate measurements of the deviations from coplanarity in this type of molecule (Trotter, 1959*a*).

Experimental

Crystals of nitromesitylene are colourless prisms elongated along *c*. The density was measured 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 *c*-axis, *hk*0 and *hk*1 Weissenberg films, and 0*kl* and *h*0*l* precession films.

Crystal data

Nitromesitylene, $C_9H_{11}O_2N$; $M = 165{\cdot}2$; m.p. 44 °C.

Orthorhombic, $a = 15{\cdot}14 \pm 0{\cdot}04$, $b = 8{\cdot}41 \pm 0{\cdot}02$, $c = 7{\cdot}26 \pm 0{\cdot}02$ Å.

Volume of the unit cell = 923·8 Å³.

Density, calculated (with four molecules per unit cell) = 1·180 g.cm.$^{-3}$, measured = 1·176 g.cm.$^{-3}$.

Absorption coefficients for X-rays, $\lambda = 1{\cdot}542$ Å, $\mu = 8{\cdot}01$ cm.$^{-1}$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}99$ cm.$^{-1}$.

Absent spectra: 0*kl* when $(k+l)$ is odd, *h*0*l* when *h* is odd. Space group is $Pna2_1$–C_{2v}^9 or $Pnam$–D_{2h}^{16}.

The intensities of the *hk*0 reflexions were recorded on moving-film exposures for a crystal rotating about the *c*-axis, using Cu $K\alpha$ radiation, the multiple-film technique being used to correlate strong and weak reflexions. The 0*kl* and *h*0*l* reflexions were recorded on precession films with Mo $K\alpha$ radiation, using multiple exposures for intensity correlation. All the intensities were estimated visually, the range being about 10,000 to 1. 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. A small crystal was used and no absorption corrections were applied.

Structure analysis

The space group is either $Pna2_1$ or *Pnam*, and since there are only four molecules in the unit cell, the centrosymmetric space group would require that the molecule has a mirror plane, so that the nitro group would lie either in the plane of the aromatic ring or perpendicular to it. The *c*-axis projection has plane group *pgg* for either space group and examination of this projection gave the symmetry of the molecule and the true space group.

[001] *projection*

The orientations of the benzene rings were readily deduced from the *hk*0 weighted reciprocal lattice, the planes of the rings being exactly perpendicular to the *c*-axis, so that the carbon and nitrogen atoms fit, at least approximately, space group *Pnam*. Steric considerations suggested that the nitro group is tilted at least 60° out of the aromatic plane, and taking the tilt as 60°, there were three possible non-equivalent orientations for the molecule. The correct orientation and the position of the molecule in the unit cell were determined by a modification of Taylor's method (Trotter, 1959*b*). Structure factors were calculated for all the *hk*0 reflexions, using McWeeny's scattering curves for carbon, nitrogen and oxygen, corrected for thermal vibration as usual, taking $B = 4{\cdot}8$ Å². The value of the discrepancy factor R was 27·5%.

Refinement proceeded by computing $(F_o - F_c)$ syntheses and after two cycles R had dropped to 17·4%. Observed and calculated structure factors are listed in Table 2. The final F_o synthesis, computed with measured structure amplitudes and calculated signs, is shown in Fig. 1(*a*), and a projection of the structure on (001) in Fig. 1(*b*). The molecule does not possess a mirror plane, so that the true space group is $Pna2_1$.

z-coordinates

Since the plane of the aromatic ring is at least approximately perpendicular to the *c*-axis, the *z*-coordinates of all the carbon and nitrogen atoms were

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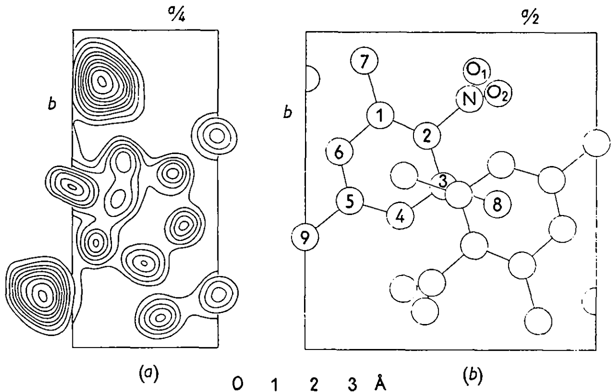

Fig. 1. (a) Electron-density projection along the c-axis, with contours at intervals of 1 e.Å^{-2}, starting at 2 e.Å^{-2}. (b) Projection of the structure onto (001).

taken as zero initially, and oxygen coordinates were obtained by assuming N–O bond distances of about 1·2 Å. Since the number of reflexions observed in the $0kl$ and $h0l$ zones is small, not much refinement is possible. Fourier projections along the a and b axes were computed (the final $h0l$ map is shown in Fig. 2) and there was no indication of any deviation of the benzene ring from exact perpendicularity to c. (F_o-F_c) syntheses were computed for both zones and the oxygen atoms shifted by small amounts. Observed and calculated structure amplitudes and calculated phase angles are included in Table 2, the value of R for all the observed $0kl$ and $h0l$ planes being 9·0%.

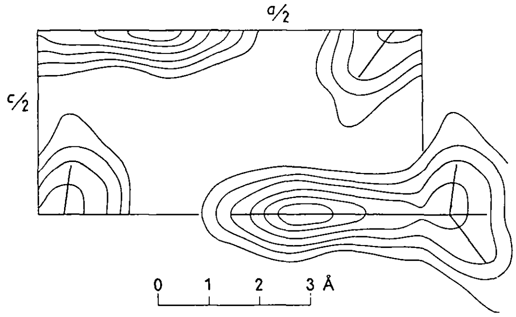

Fig. 2. Electron-density projection along [010]. Contours at intervals of 2 e.Å^{-2}.

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. 1(b). All the carbon and nitrogen atoms lie on the plane $Z = 0$, while the equation of the nitro group plane is

$$0{\cdot}6464X-0{\cdot}6500Y+0{\cdot}3995Z+1{\cdot}2719 = 0$$

where X, Y, Z are coordinates expressed in Å units. The angle between these planes is 66·4°.

Table 1. *Coordinates of the atoms*

Atom	x/a	y/b	z/c
C1	−0·1222	+0·2377	0
C2	−0·0407	+0·1734	0
C3	−0·0145	+0·0159	0
C4	−0·0884	−0·0814	0
C5	−0·1756	−0·0386	0
C6	−0·1926	+0·1221	0
C7	−0·1493	+0·4109	0
C8	+0·0797	−0·0431	0
C9	−0·2500	−0·1568	0
N	+0·0321	+0·2903	0
O_1	+0·0429	+0·3790	+0·1308
O_2	+0·0810	+0·3084	−0·1308

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. The distances between the oxygen atoms and the carbon atoms of the neighbouring methyl groups are 3·09 Å, and the closest approaches of the methyl hydrogen atoms to the oxygens (assuming C–H =

Table 2. *Observed and calculated structure factors*

$hk\ell$	F_o	F_c	$hk\ell$	F_o	F_c	$hk\ell$	F_o	F_c	$hk\ell$	F_o	F_c	$hk\ell$	F_o	F_c	$hk\ell$	F_o	F_c	α_c°
200	68.5	+70.7	14,1,0	7.1	- 6.7	830	2.7	+ 2.2	650	6.7	- 7.5	270	5.8	- 4.8	002	165.0	169.6	0
400	5.3	+ 5.8	15,1,0	< 2.8	+ 0.5	930	4.7	- 3.4	750	13.0	+13.0	370	< 2.9	+ 2.4	004	53.6	53.0	0
600	15.8	-12.1	16,1,0	< 2.7	- 0.4	10,3,0	2.8	- 2.6	850	3.3	- 2.3	470	10.5	+11.4	201	51.5	48.1	278
800	15.2	-16.0	17,1,0	< 2.4	+ 0.8	11,3,0	4.5	+ 6.0	950	< 2.9	- 2.6	570	6.2	+ 7.1	202	20.1	20.9	21
10,0,0	6.1	- 6.7	18,1,0	< 2.0	+ 1.0	12,3,0	< 2.9	- 1.5	10,5,0	4.4	+ 3.9	670	2.6	+ 5.5	203	57.4	57.1	274
12,0,0	3.4	+ 3.1	19,1,0	2.1	- 2.0	13,3,0	5.7	+ 5.7	11,5,0	7.1	- 6.9	770	3.4	+ 2.8	204	< 12.0	4.7	186
14,0,0	7.1	- 7.0	120	8.4	- 0.3	14,3,0	< 2.9	+ 2.7	12,5,0	4.4	- 3.4	180	< 2.9	- 2.1	205	29.2	22.7	265
16,0,0	2.4	- 1.2	220	3.5	-11.4	15,3,0	< 2.7	- 1.5	13,5,0	< 2.7	- 0.4	280	< 2.9	- 2.3	401	65.9	64.0	90
18,0,0	4.4	- 4.9	320	42.5	+46.8	16,3,0	2.8	+ 4.4	14,5,0	< 2.5	+ 0.2	380	5.2	+ 4.6	601	15.0	21.3	123
020	4.1	- 5.5	420	8.9	- 3.9	140	18.9	-18.8	15,5,0	2.3	- 0.2	480	< 2.8	+ 2.0	801	22.3	16.2	209
040	7.3	- 8.4	520	41.7	+40.5	240	10.7	+11.9	16,5,0	3.0	+ 1.8	580	< 2.7	+ 0.1	011	12.7	19.6	86
060	< 2.6	+ 1.7	620	19.8	+18.9	340	28.8	-31.1	160	2.8	- 0.4	680	< 2.7	+ 4.2	013	74.2	84.2	68
080	< 2.9	- 0.8	720	32.4	+32.1	440	10.9	- 7.5	260	3.1	+ 3.5	780	< 2.6	- 0.5	022	9.2	7.1	59
0,10,0	< 2.1	+ 0.4	820	4.2	- 6.6	540	2.4	- 0.1	360	8.8	+11.2	880	< 2.5	+ 2.2	031	28.3	34.0	238
110	33.4	+34.8	920	2.1	- 3.1	640	4.0	+ 6.2	460	17.0	+15.1	980	< 2.4	- 1.5				
210	2.0	- 1.2	10,2,0	8.9	+ 7.3	740	11.7	-10.8	560	6.6	+ 7.6	10,8,0	3.1	+ 1.1				
310	8.1	-10.5	11,2,0	9.5	+11.1	840	11.4	+ 9.1	660	< 2.8	- 1.1	190	< 2.9	- 3.1				
410	44.9	-49.2	12,2,0	10.8	+11.2	940	< 2.7	+ 1.2	760	7.6	- 7.7	290	< 2.9	+ 2.9				
510	5.6	+11.8	13,2,0	2.1	- 4.1	10,4,0	5.1	+ 6.8	860	< 2.9	- 0.6	390	< 2.8	- 2.4				
610	22.6	-24.2	14,2,0	4.9	+ 3.9	11,4,0	< 2.9	- 0.9	960	4.2	+ 3.7	490	< 2.7	+ 4.0				
710	8.8	- 9.6	130	42.1	+48.1	12,4,0	< 2.9	+ 1.6	10,6,0	< 2.9	- 2.0	590	< 2.6	+ 0.2				
810	7.1	+ 1.3	230	4.5	- 0.5	13,4,0	2.5	- 1.4	11,6,0	< 2.8	- 0.3	690	< 2.4	0				
910	2.9	+ 6.2	330	14.2	+19.2	150	4.6	+ 2.4	12,6,0	< 2.7	+ 1.1	790	< 2.2	+ 1.1				
10,1,0	7.5	+ 7.1	430	10.6	- 6.4	250	3.3	+ 4.4	13,6,0	< 2.4	+ 0.9	890	3.6	- 3.2				
11,1,0	19.3	+18.0	530	2.2	- 3.5	350	< 2.4	+ 2.7	14,6,0	2.5	- 1.8	990	2.6	+ 2.8				
12,1,0	< 2.8	- 1.1	630	7.3	+ 6.9	450	11.5	+12.2	15,6,0	2.9	+ 3.2	1,10,0	2.8	+ 2.3				
13,1,0	< 2.9	+ 0.7	730	2.6	- 4.2	550	6.2	+ 8.1	170	< 2.9	+ 3.6	2,10,0	1.7	+ 2.4				

1·09 Å and free rotation of the methyl groups) are 2·33 Å.

Standard deviations

The standard deviations of the atomic positions were calculated from Cruickshank's formulae. From the *hk*0 data, $\sigma(x) = \sigma(y) = 0{\cdot}013$ Å for carbon, 0·011 Å for nitrogen and 0·010 Å for oxygen. The standard deviations of the individual bond lengths are 0·018 Å for C–C, 0·017 Å for C–N, and 0·015 Å for N–O.

Discussion

Within the limits of experimental error all the carbon atoms and the nitrogen atom lie in one plane, but since the *z*-coordinates have been determined with less accuracy than the *x* and *y* parameters it is possible that small deviations from strict planarity have not been detected. The oxygen atoms lie one above and one below the plane of the carbon and nitrogen atoms at distances of 0·95 Å, so that the nitro group is tilted out of the aromatic plane, the angle of tilt being 66·4°. This tilt is very similar to that found in 9:10-dinitroanthracene—63·7° (Trotter, 1959*c*).

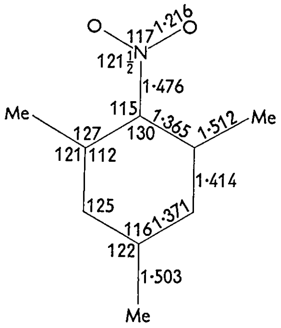

Fig. 3. Bond lengths and valency angles.

The molecular dimensions shown in Fig. 3 indicate that the repulsive forces between the oxygen atoms and the neighbouring methyl groups cause considerable distortions of the valency angles from the normal 120°, in addition to the large deviation of the nitro group from coplanarity with the aromatic ring. The mean bond lengths (with standard deviations) are

$$\begin{aligned} C_{ar}\text{–}C_{ar} &= 1{\cdot}383 \pm 0{\cdot}007 \text{ Å} \\ C_{ar}\text{–}C_{al} &= 1{\cdot}509 \pm 0{\cdot}010 \\ C_{ar}\text{–}N &= 1{\cdot}476 \pm 0{\cdot}017 \\ N\text{–}O &= 1{\cdot}216 \pm 0{\cdot}011 \end{aligned}$$

Intermolecular distances

All the intermolecular contacts correspond to normal van der Waals interactions. The shortest oxygen–oxygen distance is 3·66 Å between O_1 of the standard molecule and O_2 of the molecule with coordinates $(\bar{x}, 1-y, \frac{1}{2}+z)$. The shortest oxygen–carbon separation is between $O_2(x, y, z)$ and $C4(\bar{x}, \bar{y}, -\frac{1}{2}+z)$ where the distance is 3·29 Å, while the shortest carbon–carbon contact is 3·67 Å between $C3(x, y, z)$ and $C3(\bar{x}, \bar{y}, \frac{1}{2}+z)$. The shortest contact involving nitrogen is 4·12 Å. The perpendicular distance between the planes of the aromatic rings $= \frac{1}{2}c = 3{\cdot}63$ Å.

References

Trotter, J. (1959*a*). *Acta Cryst.* **12**, 173.
Trotter, J. (1959*b*). *Acta Cryst.* **12**, 339.
Trotter, J. (1959*c*). *Acta Cryst.* **12**, 232.

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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The structure of Au_2Mn.

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The intermetallic compound Au_2Mn possesses interesting magnetic properties which seem to require an examination of its crystal structure. The first attempt to solve this was by Raub, Zwicker & Baur (1953) in the course of their study of the gold-manganese equilibrium diagram, but their tentative assignation of the lattice gives a fractional number of molecules per unit cell. The solution of the structure was taken up in this department during resistivity studies on the alloy, and a satisfactory determination of the space lattice by one of us has been quoted previously in the paper by Smith & Street (1957). It has now proved possible to solve the structure with reasonable accuracy from powder data alone.

Samples of Au_2Mn powder were heat-treated at 660 °C. for 24 hours and quenched, and diffraction photographs taken using a Unicam evacuable 9 cm. camera and filtered Cu or Fe $K\alpha$ radiation. From the measured

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