

Although the association of P and Nb in a mixed oxide is unusual, there is some evidence for it in the chemical literature (Hahn, 1951), and it is well known that small quantities of phosphate ion are almost quantitatively removed from solution by co-precipitation with  $\text{Nb}_2\text{O}_5$  (Schoeller & Webb, 1936). Two questions arise out of the present study. Firstly, is there a possible tetragonal polymorph of  $\text{Nb}_2\text{O}_5$  with the same structure as  $\text{PNb}_9\text{O}_{25}$ , where the phosphorus is replaced by Nb? Secondly, could a solid solution also exist between  $\text{Nb}_2\text{O}_5$  and some hitherto unsuspected phase  $\text{PNb}_{27}\text{O}_{70}$ , with the same structure and essentially identical unit cell dimensions, where once again P and Nb are interchangeable?

There is still considerable work apart from this to be done on phases known to be related to  $\text{PNb}_9\text{O}_{25}$ . Mohanty, Fiegel & Healy (1962) showed that the high temperature compound  $\text{Ta}_2\text{O}_5 \cdot 2\text{Nb}_2\text{O}_5$ , originally found to have little or no variability of composition by Holtzberg & Reisman (1961), has a body-centred tetragonal unit cell with dimensions near enough to those of the present compound to assure a close, if not isostructural relationship. All we can conclude at this stage is that Nb and Ta cannot adopt completely ordered positions of their own without a change of symmetry group.

Waring & Roth (1964) showed that the compound  $\text{GeNb}_{18}\text{O}_{47}$  (*i.e.*  $\text{GeO}_2 \cdot 9\text{Nb}_2\text{O}_5$ ) has a similar body-centred tetragonal unit cell. There is no good reason to suppose that three oxygen atoms can be absent from this structure, and we will attempt in due course to prove that its unit cell has a full complement of

fifty oxygen atoms with some additional ions present in the empty tetrahedral interstices.

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## The Crystal Structure of 1,5-Dimethylnaphthalene

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The crystal structure of 1,5-dimethylnaphthalene was determined in order to ascertain whether distortion of the molecule due to steric effects could be detected. The result obtained by refinement of the projections along two crystallographic axes showed that the C-C bond distances in the naphthalene nucleus do not differ significantly from those in unsubstituted naphthalene. The bond angles, on the other hand, were slightly different, but the distortion of the molecule is near the level of detectability. The hydrogen atoms showed up sufficiently clearly in a difference Fourier map to exclude free rotation of the methyl groups.

### Introduction

Some years ago an investigation was carried out in this laboratory on the redistribution of charge in naphthalene caused by methyl substitution (Dallinga, Smit & Mackor, 1960; Maclean & Mackor, 1960).

Hydrogen-deuterium exchange in  $\alpha,\alpha$ - and in  $\beta,\beta$ -dimethylnaphthalene was measured and the nuclear magnetic resonance spectra were recorded. A satisfactory semi-quantitative interpretation of the results could be given. The occurrence of steric effects, however, could not be excluded, nor could their influence

be estimated. An accurate determination of the shape of the molecules of these compounds by X-ray analysis of their crystals seemed to be a rational complement to these investigations.

The first compound whose crystal structure was determined was 1,5-dimethylnaphthalene. Here a steric interaction of the methyl groups and the neighbouring  $\alpha$ -hydrogen atoms might be supposed. The principal aims were to determine:

- Whether the steric interaction influences the positions of the methyl groups, and
- Whether the C-C bond distances in the naphthalene nucleus and the angles between these bonds are affected by the methyl substitution.

### Cell dimensions and space group

Crystals were available in the form of thin platelets, elongated in one direction which was chosen as the  $a$  axis. The dimensions of the monoclinic unit cell are:

$$a = 6.18 \pm 0.01, b = 8.91 \pm 0.01, c = 16.77 \pm 0.02 \text{ \AA};$$

$$\beta = 101^\circ 4 \pm 0^\circ 05.$$

With four molecules per unit cell the X-ray density is  $1.145 \text{ g.cm}^{-3}$ .

The systematic absences ( $h0l$  if  $l \neq 2n$  and  $0k0$  if  $k \neq 2n$ ) pointed to the space group  $P2_1/c$  ( $C_{2h}^5$ ).

### Experimental

Weissenberg diagrams were taken with Cu  $K\alpha$  radiation. The zero-layer lines with both the  $a$  and the  $b$  axis as the oscillation axis were investigated. The intensities were estimated visually with the multiple-film technique. The relatively high volatility of the compound made it necessary to enclose the crystals in a sealed glass capillary during the exposures.

Because of their shape, the crystals could be mounted more easily with the  $a$  axis as oscillation axis than with the  $b$  axis, which was perpendicular to the crystal platelets. Accordingly the quality of the diagrams obtained with the former orientation was better than with the latter. The intensities were corrected for Lorentz and polarization factors. In view of the small size of the crystals and the absence of heavy atoms no correction for absorption was applied.

Table 1. Projection along the  $a$  axis  
Comparison of calculated  
and observed structure amplitudes  $0kl$

h	k	l	$F_c$	$F_o$	h	k	l	$F_c$	$F_o$
0	0	0	+336.0	-	0	2	11	+ 0.5	-
		2	- 58.9	55.6			12	- 7.1	7.4
		4	- 41.3	42.2			13	+ 1.4	2.0
		6	- 18.7	21.6			14	+ 0.5	-
		8	- 3.7	4.6			15	- 6.3	7.4
		10	+ 1.4	1.6			16	- 1.0	-
		12	- 0.5	2.8			17	+ 4.3	5.0
		14	- 9.1	7.6			18	- 0.3	-
		16	+ 18.4	17.6			19	+ 1.1	-
		18	- 0.2	-			20	- 0.6	-
		20	- 1.1	1.2					
0	1	1	- 18.5	19.2	C	3	1	- 0.5	1.0
		2	- 14.5	15.2			2	- 2.1	1.5
		3	- 3.6	4.2			3	+ 2.0	2.8
		4	- 36.8	40.4			4	+ 1.6	2.0
		5	- 5.9	8.5			5	- 3.0	2.8
		6	- 28.2	30.0			6	+ 2.2	2.4
		7	+ 30.2	36.2			7	- 0.2	-
		8	+ 32.5	33.4			8	+ 2.6	3.2
		9	- 14.6	16.4			9	+ 3.5	4.2
		10	- 5.7	6.2			10	+ 0.6	-
		11	- 7.9	9.6			11	+ 1.0	-
		12	+ 5.9	5.0			12	- 0.5	-
		13	+ 3.6	3.6			13	- 1.3	-
		14	+ 1.9	2.0			14	- 1.0	-
		15	+ 0.4	-			15	- 0.6	2.0
		16	+ 1.5	-			16	- 1.5	-
		17	- 1.0	-			17	+ 0.4	-
		18	- 0.8	-			18	- 1.5	3.2
		19	- 1.7	1.6			19	+ 0.4	-
		20	- 1.0	1.2			20	+ 1.0	1.2
		21	- 2.3	2.0					
0	2	0	- 10.6	11.6	C	4	0	+ 28.5	26.0
		1	+ 69.2	65.6			1	+ 4.6	4.4
		2	+ 4.7	4.0			2	- 5.1	4.6
		3	+ 12.1	13.6			3	- 7.6	7.6
		4	- 19.6	21.0			4	- 5.4	5.4
		5	- 3.6	3.6			5	+ 13.9	16.0
		6	+ 1.4	1.2			6	- 0.8	1.6
		7	- 4.5	3.6			7	+ 5.1	5.4
		8	+ 8.2	9.6			8	+ 1.1	1.5
		9	- 3.4	4.2			9	+ 0.5	-
		10	+ 10.2	11.2			10	+ 2.6	2.4

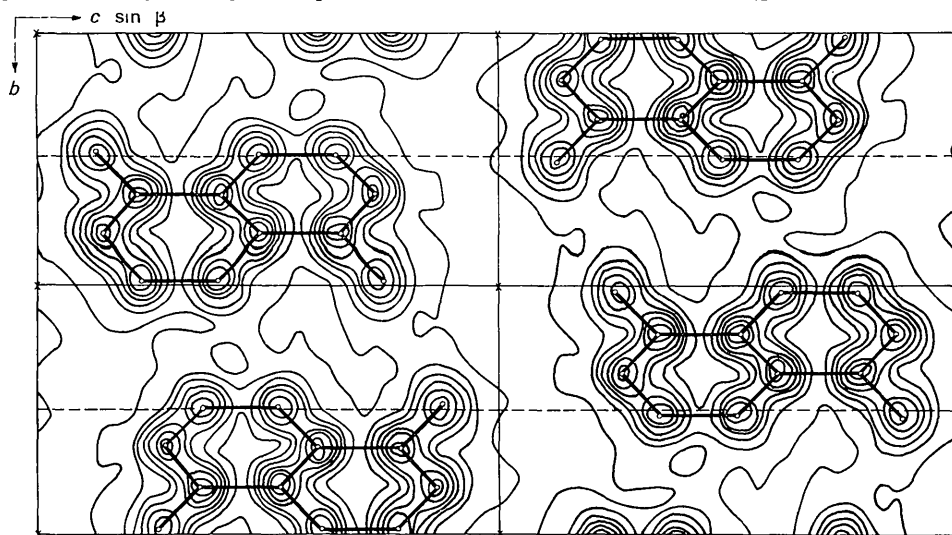


Fig. 1. Projection of the electron density along the  $a$  axis. Contours at intervals of  $1 \text{ e.\AA}^{-2}$ .

Table 1 (cont.)

h	k	l	F <sub>c</sub>	F <sub>o</sub>	h	k	l	F <sub>c</sub>	F <sub>o</sub>
0	4	11	-14.0	14.0	0	7	8	-0.4	-
		12	-4.9	5.4			9	-0.3	-
		13	+4.6	5.4			10	+6.7	7.0
		14	+3.8	3.6			11	+5.0	5.0
		15	-1.0	1.8			12	-16.9	16.0
		16	+4.4	3.2			13	+4.7	3.6
		17	+0.2	-			14	+2.6	2.4
		18	+0.6	-			15	+1.0	1.4
		19	+3.4	1.2			16	+1.8	1.4
0	5	1	+0.7	2.0	0	8	0	+3.9	7.2
		2	+2.6	3.2			1	+3.3	3.2
		3	+17.0	19.4			2	-3.0	3.2
		4	-14.1	14.0			3	+4.6	4.2
		5	-12.4	12.8			4	+1.9	3.2
		6	-1.3	1.2			5	-5.7	6.2
		7	+0.4	-			6	-1.7	2.0
		8	+2.0	1.8			7	-1.9	2.0
		9	-0.3	-			8	-1.0	-
		10	-5.5	5.4			9	-1.0	-
		11	-17.5	15.3			10	-2.3	2.6
		12	+11.9	12.0			11	+8.4	9.6
		13	+13.2	15.2			12	+2.5	2.4
		14	-0.4	-			13	-3.0	3.2
		15	+3.4	4.6			14	-2.5	1.6
		16	-1.0	-	0	9	1	+1.0	-
		17	+1.9	-			2	+0.5	-
		18	-2.1	2.8			3	-0.9	-
		19	-4.5	4.6			4	+0.3	-
0	6	0	-0.0	1.6			5	+0.3	-
		1	+0.1	-			6	+0.8	-
		2	+2.6	3.2			7	-0.3	-
		3	+4.8	5.8			8	-0.3	-
		4	-23.9	24.8			9	-0.9	-
		5	-8.5	8.6			10	-0.9	-
		6	+7.1	7.4			11	+1.3	1.6
		7	-2.4	1.8			12	-0.3	-
		8	+10.5	10.0			13	-1.7	1.4
		9	-1.0	-	0	10	0	+5.0	4.2
		10	+18.0	17.5			1	-5.9	6.2
		11	+8.8	8.4			2	-1.1	-
		12	-19.1	18.4			3	-0.7	-
		13	-2.3	1.8			4	-2.1	1.6
		14	+1.0	-			5	-1.0	-
		15	+0.1	-			6	-0.5	-
		16	-0.2	-			7	-0.0	-
		17	-0.3	1.2			8	+0.5	-
		18	-2.9	3.6			9	+0.1	-
0	7	1	-1.6	1.8	0	11	1	-2.4	1.6
		2	-4.2	5.0			2	-0.7	-
		3	+4.2	5.2			3	-0.5	1.4
		4	+15.4	16.0			4	+1.5	1.2
		5	-3.8	3.6					
		6	-0.9	-					
		7	+3.1	2.0					

Determination of the crystal structure

Projection along [100]

The partly sharpened Patterson projection along the *a* axis showed a strikingly regular pattern. Round the origin all peaks were arranged on the points of a pattern of squares with sides of about 1 Å, the diagonal being parallel to the *b* axis and the projection of the *c* axis. This suggested an orientation of the molecules in the crystal lattice such that in projection the C-C bonds were either parallel to the *a* axis or formed angles of about 45° with it.

Actually in this way a trial (projected) structure could be found, from which intensities of the *0k*l reflexions could be calculated that were reasonably similar to those observed. From a Fourier electron-density projection, using the calculated signs of the structure amplitudes, the assumed atomic coordinates of the carbon atoms could be readjusted. This resulted in an inversion of the signs of only a few of the weaker reflexions. The final electron-density projection along this axis is shown in Fig. 1. Calculated and observed structure amplitudes are given in Table 1.

Projection along [010]

The projection along [100] being known, the interpretation of the partly sharpened Patterson projection along the *b* axis gave no difficulties. After some refinement a final set of signs could be attributed to all *h0l* reflexions observed. This resulted in the final electron-density projection along the *b* axis, shown in Fig. 2. In this projection a serious overlap of some of the atoms is obvious. Apart from the lesser accuracy of the intensity data this is another reason why the atomic coordinates derived from this projection may be expected to be less accurate. Calculated and observed structure amplitudes are given in Table 2.

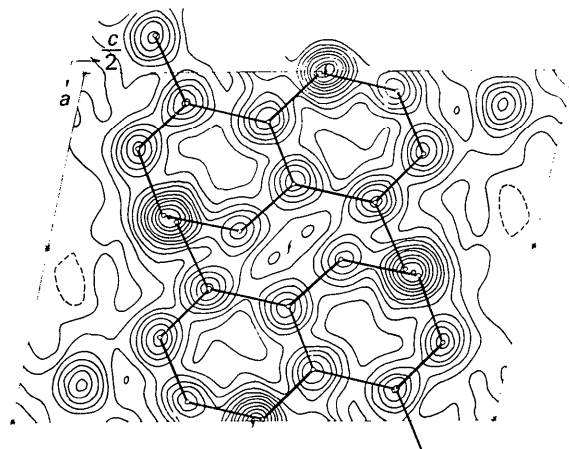


Fig. 2. Projection of the electron density along the *b* axis. Contours at intervals of 1 e.A<sup>-2</sup>; zero line dotted.

Table 2. Projection along the *b* axis  
Comparison of calculated  
and observed structure amplitudes *h0l*

h	k	l	F <sub>c</sub>	F <sub>o</sub>	h	k	l	F <sub>c</sub>	F <sub>o</sub>
0	0	0	+336.0	-	-7	0	6	+2.7	-
1			+10.6	10.8	-6			-3.1	-
2			+24.3	25.3	-5			-0.5	-
3			+0.4	-	-4			-11.4	14.1
4			-5.6	7.4	-3			-41.5	41.9
5			+3.3	4.6	-2			+12.1	16.2
6			-6.4	5.0	-1			-8.1	7.9
7			+0.9	-	0			-18.7	20.3
-7	0	2	-2.4	-	1			-15.8	18.2
-6			-17.1	16.2	2			+0.7	-
-5			+1.2	-	3			+19.2	19.9
-4			-21.0	17.4	4			+1.2	-
-3			-0.0	-	5			+2.9	-
-2			-37.3	37.7	6			+0.8	-
-1			+20.1	20.3	7			-3.3	3.3
0			-58.9	73.3	-7	0	6	+4.6	4.6
1			-5.7	6.2	-6			-2.9	-
2			-9.2	9.1	-5			+2.6	-
3			-36.9	35.0	-4			+5.1	4.6
4			+14.6	17.0	-3			+6.6	5.8
5			-4.0	4.8	-2			+2.1	-
6			-2.3	-	-1			-35.6	41.4
7			-4.9	4.2	0			-3.7	4.6
-7	0	4	-0.1	-	1			+13.5	14.9
-6			+32.5	25.7	2			-0.9	-
-5			+2.0	-	3			+22.0	21.6
-4			+9.1	9.1	4			+6.9	7.4
-3			+8.5	9.5	5			+3.5	-
-2			-18.3	20.7	6			+0.2	-
-1			+31.8	38.9	-7	0	10	+2.1	-
0			-41.3	36.9	-6			-2.5	-
1			+15.6	16.2	-5			-3.5	-
2			+10.8	14.9	-4			+0.1	-
3			+15.9	18.2	-3			+12.8	12.0
4			+1.3	-	-2			+0.1	-
5			-8.7	5.0	-1			+2.6	-
6			+0.7	-	0			+1.4	-
7			+5.1	3.3	1			-12.9	14.1

Table 2 (cont.)

<i>h</i>	<i>k</i>	<i>l</i>	$F_c$	$F_o$	<i>h</i>	<i>k</i>	<i>l</i>	$F_c$	$F_o$
2	0	10	+ 15.3	18.0	-6	0	16	- 0.0	-
3			- 30.7	29.4	-5			+ 0.5	-
4			- 13.5	11.5	-4			- 3.1	-
5			- 0.3	-	-3			+ 0.3	-
6			- 2.1	-	-2			+ 3.7	-
-7	0	12	- 7.2	5.9	-1			+ 0.3	-
-6			- 1.5	-	0			+ 18.4	20.3
-5			+ 2.7	-	1			+ 1.3	-
-4			- 3.4	5.0	2			- 0.9	-
-3			+ 28.1	26.9	3			- 3.6	-
-2			+ 9.9	10.4	-5	0	18	- 0.3	-
-1			+ 12.6	14.1	-4			- 7.6	7.9
0			- 0.5	-	-3			- 0.2	4.2
1			+ 3.3	-	-2			- 1.7	-
2			- 7.9	10.8	-1			+ 2.0	-
3			+ 2.4	-	0			- 0.2	-
4			+ 4.9	-	1			+ 0.5	-
5			+ 0.4	-	2			+ 4.7	4.6
-6	0	14	- 1.3	-	3			+ 4.8	3.3
-5			+ 0.7	-	-4	0	20	+ 2.9	-
-4			- 2.2	-	-3			- 4.2	5.0
-3			+ 16.7	17.0	-2			+ 2.5	5.0
-2			- 22.3	21.6	-1			+ 1.5	-
-1			- 10.4	14.1	0			- 1.1	-
0			- 1.7	-	1			+ 1.0	-
1			- 9.1	7.4					
2			+ 0.9	-					
3			- 10.7	12.4					
4			- 0.4	-					
			- 2.0	-					

### Refinement of the structure. Hydrogen atoms

The coordinates of the carbon atoms in both projections were refined by the method of least squares, by minimizing  $\sum \omega(|F_o| - |F_c|)^2$ .  $\omega$  is a suitably chosen weight factor, being 1 for most reflexions and having a lower value for the stronger ones. In the first cycles the calculated structure factors  $F_c$  were based on the carbon atoms only. One overall isotropic temperature factor was used; it was found to be  $3.5 \text{ \AA}^2$ .

A difference Fourier map along [100] based on the differences between the observed structure factors,  $F_o$ ,

and those calculated from the positional parameters of the C atoms is shown in Fig. 3. As this difference projection was intended in the first place to ascertain whether any information could be gained on the positions of the hydrogen atoms, only the reflexions with diffraction angles up to about  $45^\circ$  were used.

Fig. 3 clearly shows the presence of the hydrogen atoms near the positions where they are expected. Not only those attached directly to the aromatic nucleus but also those forming part of the methyl groups can be detected. This indicates that the methyl groups do not rotate freely but have a preferred orientation.

This orientation is such that the distances of the methyl-hydrogen atoms to the nearest  $\alpha$ -hydrogen atoms of the aromatic nucleus are maximum.

Another feature of the difference projection is the negative regions enclosed by the aromatic nucleus. This was also found by Cruickshank (1956, 1957) with anthracene and naphthalene. He notes that this feature is consistent with the idea of a lateral contraction of the  $\sigma$ -electrons on the formation of the bonds.

A difference projection along [010] calculated in the same way gave hardly any evidence of the presence of the hydrogen atoms. This is presumably due to the lesser accuracy of the observed intensities of the  $h0l$  reflexions.

Though the presence and the approximate positions of the hydrogen atoms are revealed by one of the Fourier maps, one cannot expect to derive these positions with any accuracy from the available experimental data. The coordinates, therefore, were calculated assuming a C-H bond length of  $1.09 \text{ \AA}$ .

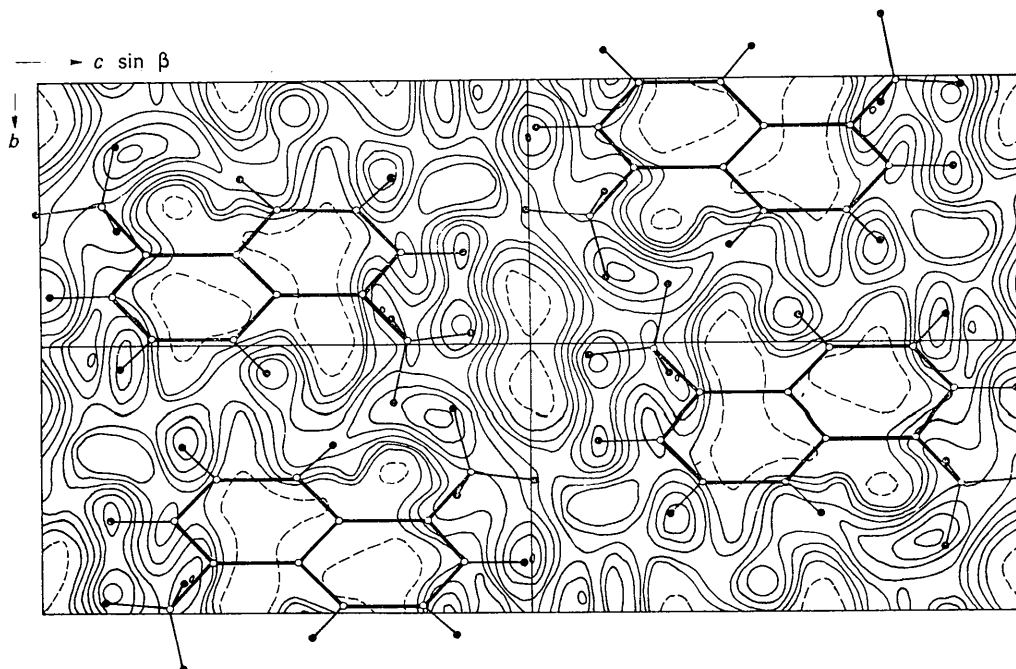


Fig. 3. Difference projection along the  $a$  axis. Calculated contribution of the C atoms subtracted. Contour lines at intervals of  $0.1 \text{ e.\AA}^{-2}$ , starting at  $0.2 \text{ e.\AA}^{-2}$ ; zero line dotted.

Table 3. Fractional coordinates of the atomic positions in 1·5-dimethylnaphthalene

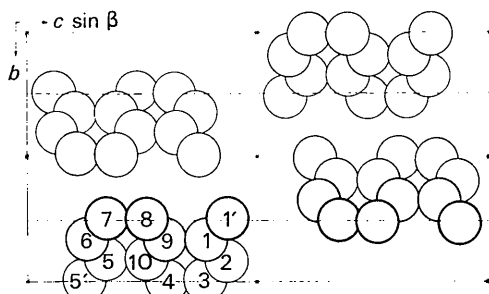
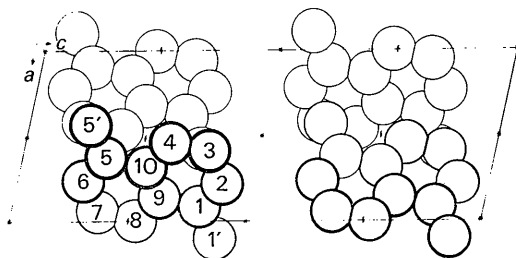
C	x	y	z	H	x	y	z
1	0·3758	0·4054	0·3264	2	0·275	0·323	0·433
2	0·2398	0·3254	0·3665	3	-0·052	0·183	0·358
3	0·0523	0·2449	0·3239	4	-0·140	0·181	0·207
4	0·0024	0·2432	0·2399	6	0·184	0·409	0·003
5	0·0898	0·3275	0·1090	7	0·514	0·549	0·077
6	0·2216	0·4070	0·0688	8	0·602	0·550	0·228
7	0·4082	0·4878	0·1106	1'(1)	0·576	0·479	0·438
8	0·4593	0·4884	0·1951	1'(2)	0·546	0·611	0·357
9	0·3209	0·4056	0·2385	1'(3)	0·720	0·452	0·357
10	0·1434	0·3256	0·1963	5'(1)	-0·112	0·252	-0·004
1'	0·5676	0·4926	0·3728	5'(2)	-0·258	0·279	0·077
5'	-0·1049	0·2381	0·0614	5'(3)	-0·084	0·119	0·077

In the last cycles of the refinement the contributions of the hydrogen atoms were included in the  $F_e$  values. A temperature factor of  $5\cdot0 \text{ \AA}^2$  for these atoms was arbitrarily chosen. Moreover four independent isotropic temperature factors were calculated for the C atoms:  $3\cdot1 \text{ \AA}^2$  for the two central C atoms,  $3\cdot6 \text{ \AA}^2$  for the four  $\alpha$ -C atoms,  $3\cdot8 \text{ \AA}^2$  for the four  $\beta$ -C atoms and  $4\cdot3 \text{ \AA}^2$  for those of the two methyl groups. As might be expected the temperature factors are found to increase with the distance from the centre of gravity of the molecule. The final value of the reliability index

$$R = \frac{\sum (F_e - F_o)}{\sum |F_o|}$$

was 9·3% for the projection along the  $a$  axis and 14·1% for the projection along the  $b$  axis. The higher value of the latter  $R$  index confirms that the intensity data of the  $h0l$  reflexions are less accurate.

The differences between the  $z$  coordinates resulting from the refinement of both projections are well within the limits to be expected from the calculated standard deviations (see below). Their final values

Fig. 4. Arrangement of the molecules in the unit cell, projected along the  $a$  axis.Fig. 5. Arrangement of the molecules in the unit cell, projected along the  $b$  axis.

were obtained by averaging, using a weight factor proportional to the reciprocal value of the estimated variance.

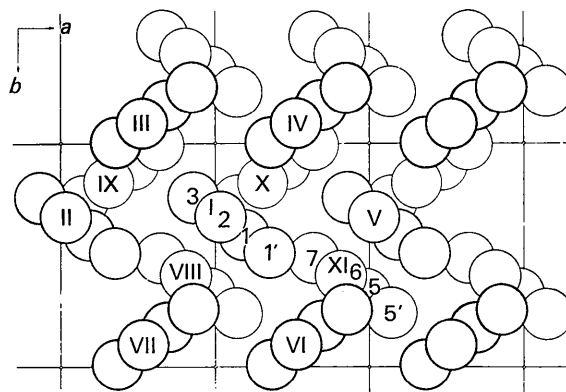
In Table 3 the final coordinates of the atoms are given. As mentioned, those of the hydrogen atoms are calculated from the assumed bond lengths and bond angles.

#### Arrangement of the molecules in the crystal lattice

The arrangement of the molecules in the crystal lattice is demonstrated more clearly in Figs. 4 and 5. These are projections of the elementary cell along the  $a$  axis and the  $b$  axis respectively. Only the carbon atoms are shown. They are represented by spheres with a diameter of about  $1\cdot5 \text{ \AA}$ .

The molecules are arranged in layers parallel to the lattice planes (001). The main plane of the carbon skeleton is nearly perpendicular to these lattice planes and forms an angle of about  $54^\circ$  with the glide planes (010). Two of these layers adjoining the plane (001) through the origin are shown projected on this plane in Fig. 6. Only four carbon atoms of each molecule are shown since the positions of the other C atoms practically coincide with those entered in the figure.

Each molecule is in contact with six molecules in the same layer and with four molecules in each of the adjacent layers, in total 14 neighbours with intermolecular atomic distances of less than  $3 \text{ \AA}$ .

Fig. 6. Arrangement of the molecules in two layers adjacent to the plane through the  $a$  and  $b$  axes.

### Accuracy

Before discussing possible distortions of the molecule one has to pay attention to the accuracy of the atomic coordinates so as to be able to decide whether any deviations found are significant.

The standard deviations in the coordinates in both projections were estimated from the differences between observed and calculated  $F$  values by the method given by Cruickshank (1949):

$$\sigma^2(x_r) = \sigma^2(F) \cdot B_{rr}/D.$$

$D$  is the determinant of the coefficients of the linear equations used in the least-square refinement.  $B_{rr}$  is the  $r$ th principal minor of  $D$ .  $\sigma(F)$  is the standard deviation of an observed  $F$  value with unit weight estimated from  $\sigma^2(F) = \sum \omega(F_o - F_c)^2 / (u - v)$ , where  $v$  is the number of unknown parameters and  $u$  the number of independent  $F$  values. The result is shown in Table 4.

Table 4. *Estimated standard deviations of the coordinates*

Projection	Coordinate	Range of est. stand. dev.	Mean value
along $a$ axis	$y$	0.00084–0.00097	0.00092 = 0.008 Å
	$z$	0.00047–0.00058	0.00053 = 0.009
along $b$ axis	$x$	0.0033–0.0053	0.0036 = 0.022
	$z$	0.00122–0.00134	0.00125 = 0.021

As expected, the coordinates derived from the projection along the  $a$  axis are more accurate than those from the projection along the  $b$  axis.

An isolated molecule of 1,5-dimethylnaphthalene may be assumed to have a centre of symmetry. In the crystal lattice this centre of symmetry is not necessarily maintained. The first question to be answered, therefore, is whether the molecule is distorted in the lattice to such an extent that any deviations from centrosymmetry can be detected. For this purpose the coordinates of the carbon atoms relative to the centre of gravity of the molecule have been calculated and compared for corresponding atom pairs. The differences of the absolute values of these coordinates are shown in Table 5.

Table 5. *Differences of the absolute values of the fractional coordinates of corresponding carbon atoms relative to the centre of gravity*

Atom pair	$\Delta x$	$\Delta y$	$\Delta z$
1–5	0.0029	0.0010	0.0005
2–6	0.0013	0.0005	0.0004
3–7	0.0022	0.0008	0.0004
4–8	0.0010	0.0003	0.0001
9–10	0.0016	0.0007	0.0001
1'–5'	0.0000	0.0012	0.0007

On comparison of these differences with the estimated standard differences of Table 4 it is obvious

that they are not significant. Any deviations from centrosymmetry are well below the level of detectability.

Assuming the molecule to be actually centrosymmetrical we can use this test as an independent way of estimating the accuracy by considering each difference as resulting from measurements in duplicate of the same quantity. The standard deviation then can be found from the equation:  $\sigma^2(r) = \frac{1}{2}(\Delta r)^2/(n-1)$ ,  $n$  being 6 in this case. The resulting values are:

$$\begin{aligned}\sigma(x) &= 0.0014 = 0.008 \text{ \AA} \\ \sigma(y) &= 0.0006 = 0.006 \\ \sigma(z) &= 0.0003 = 0.006\end{aligned}$$

Although the number of degrees of freedom (five) for each set of coordinates is rather small, the combined results indicate that the accuracy actually might be better than is found by Cruickshank's method.

In this connection it may be pointed out that the estimate of the standard deviation in both cases is based on the assumption that the differences entered in the calculation (*viz.* those between  $F_o$  and  $F_c$  in the first and those between the coordinates of equivalent atoms in the second case) are caused only by experimental errors. If these differences are caused partially by other factors, such as anisotropy of the temperature factors or effect of bond formation on the shape of the electron clouds of the atoms in the first case or, in the second case, actually existing minor deviations from centrosymmetry, the accuracy may be better than is indicated by the calculated standard deviations.

### Shape and dimensions of the molecule

Above it has been shown that no significant deviations from centrosymmetry could be detected in the molecule. A second question is whether the carbon skeleton is coplanar. By the method of least-squares developed by Schomaker, Waser, Marsh & Bergman (1959) with weight factors corresponding to the accuracy of the coordinates, the best plane through all carbon atoms of the molecule, and the best plane through the carbon atoms of the aromatic nucleus only were determined:

All C atoms:

$$-0.5930 X + 0.8051 Y + 0.1268 Z = 2.239 \text{ \AA}$$

Aromatic C atoms:

$$-0.5890 X + 0.8080 Y + 0.1299 Z = 2.266 \text{ \AA}$$

or with respect to orthogonal crystallographic axes ( $Z'$  axis normal to plane through  $X$  and  $Y$  axes)

$$-0.5930 X' + 0.8051 Y' + 0.0098 Z' = 2.239 \text{ \AA}$$

$$-0.5890 X' + 0.8080 Y' + 0.0137 Z' = 2.266 \text{ \AA}$$

The distances from the origin to these planes are 2.239 Å and 2.266 Å respectively. The distances of the individual carbon atoms to these planes are shown in Table 6.

Table 6. Distances to the best plane through the carbon atoms

Atom	Distance to the plane	
	All C-atoms	Aromatic C-atoms
1	-0.014 Å	-0.005 Å
2	-0.005	0.001
3	0.014	0.011
4	0.007	0.002
5	0.012	0.001
6	0.014	0.006
7	-0.001	0.000
8	-0.004	0.002
9	0.001	0.004
10	-0.012	-0.018
1'	0.006	0.024
5'	0.017	-0.037

Comparison of the deviations from the first plane with the standard deviations of Table 4 leads to the conclusion that they are not significant and that within the limits of experimental accuracy the carbon skeleton is coplanar.

If, however, the values in the last column are compared with the standard deviations estimated from the coordinates of equivalent atoms relative to the centre of gravity of the molecule, there is an indication that the methyl groups show small but probably significant departures in opposite directions from the plane of the aromatic nucleus.

The third point to be investigated is whether the lengths and the mutual angles of the carbon-carbon bonds are affected by steric effects. In Fig. 7 the bond lengths and the bond angles are given, and in Tables 7 and 8 respectively they are compared with those in naphthalene.

The aromatic bond lengths do not differ significantly from those in unsubstituted naphthalene (Cruickshank, 1957). The deviations of the bond angles

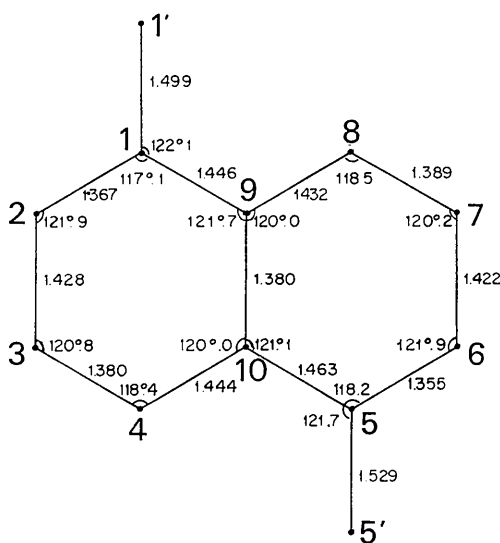


Fig. 7. Interatomic distances and bond angles in 1,5-dimethylnaphthalene.

from those in naphthalene can hardly be considered significant in view of the standard deviations derived from the  $(|F_o - F_c|)$  values.

The excellent agreement between chemically equivalent bond angles, however, indicates that it is justified to base the discussion on the smaller standard deviations of the atomic coordinates estimated from the departures from centrosymmetry. The standard deviation in all bond angles then is about  $0.5^\circ$ . One is then led to the conclusion that there is a slight but significant distortion of the aromatic nucleus, showing particularly in a decrease ( $2.3^\circ$ ) of the bond angles at the C atoms in  $\alpha$  positions and an increase ( $2.2^\circ$ ) of the angles between the central bond and the bonds connecting the central C atoms with those carrying the methyl groups.

Table 7. Comparison of bond lengths in 1,5-dimethylnaphthalene and naphthalene

Bond	1,5-Dimethylnaphthalene		Naphthalene	
	Length (Å)	Stand. dev.*	Length (mean)	Stand. dev. of mean
1-2	1.367	0.019	1.357	0.004
5-6	1.355	0.019		
3-4	1.380	0.016		
7-8	1.389	0.015		
1-9	1.446	0.014	1.420	0.003
5-10	1.434	0.014		
8-9	1.432	0.019		
4-10	1.444	0.019		
2-3	1.428	0.032	1.416	0.006
6-7	1.422	0.028		
9-10	1.380	0.024	1.405	0.006
1-1'	1.499	0.027		
5-5'	1.529	0.024		

\* The standard deviations for 1,5-dimethylnaphthalene given in the first column are derived from the standard deviations of the atomic coordinates in Table 4. Those in the second column are based on the deviations from centrosymmetry.

Table 8. Comparison of bond angles in 1,5-dimethylnaphthalene and naphthalene

Atoms	1,5-Dimethylnaphthalene		Naphthalene	
	Angle	Stand. dev.†	Angle (mean)	Stand. dev. of mean
1-2-3	121.9°	1.0°	120.48°	0.17°
5-6-7	121.9	1.0		
2-3-4	120.8	1.8		
6-7-8	120.2	1.5		
9-1-2	117.1	1.4	120.27	0.25
10-5-6	118.2	1.4		
3-4-10	118.4	1.7		
7-8-9	118.5	1.5		
10-9-1	121.7	1.2	119.23	0.17
9-10-5	121.1	1.2		
10-9-8	120.0	0.9		
9-10-4	120.0	0.9		
9-1-1'	122.1	1.2	121.7	0.5
10-5-5'	121.7	1.2		

† See footnote to Table 7.

The intramolecular distances from the six hydrogen atoms of the methyl groups to the nearest hydrogen atoms of the aromatic nucleus were calculated to vary between 2.29 and 2.34 Å, thus being only slightly shorter than the mutual distances of neighbouring aromatic hydrogen atoms, which were calculated to vary between 2.48 and 2.50 Å.

It is concluded that the slightly distorted shape of the molecule found by this crystal structure analysis is consistent with our knowledge about the shortest possible intramolecular distances between hydrogen atoms.

Finally the shortest interatomic distances between one molecule and its neighbours have been computed. Nine of the distances between carbon atoms of a molecule and hydrogen atoms of neighbouring molecules are shorter than 3 Å, the shortest being 2.86 Å. Each molecule moreover has 37 intermolecular H-H distances representing 19 crystallographically independent distances that are smaller than 3 Å, the shortest being 2.49 Å. The shortest intermolecular distances in

anthracene (Cruickshank, 1956) and naphthalene (Cruickshank, 1957) are for C-H 2.67 and 2.82 Å and for H-H 2.50 and 2.40 Å, respectively. The intermolecular distances calculated in this investigation, therefore, agree well with those found in similar compounds.

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## The Crystal Structure of the Metastable ( $\beta$ ) Modification of *p*-Nitrophenol

BY PHILIP COPPENS AND G. M. J. SCHMIDT

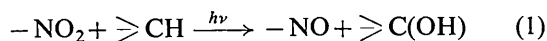
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The crystal structure of the  $\beta$  modification of *p*-nitrophenol has been refined from three-dimensional counter data to an *R* value of 6.9%. Bond lengths have been determined with an e.s.d. of better than 0.003 Å, and corrected for thermal motion, the analysis of which suggests that the molecule as a whole does not behave as a rigid body. The packing arrangements of this modification and of the previously determined  $\alpha$  form are compared; an explanation for the thermodynamic relationship of the two forms is given in terms of molecular close-packing. The photochemical behaviour of the two forms is tentatively explained in terms of the geometry of the intermolecular C-H...O-N contacts.

### Introduction

*p*-Nitrophenol undergoes a photochemical reaction in the solid state (Fritzsche, 1859) whose detailed chemical mechanism is not known but which we assume to involve in its initial stage the redox reaction



The reaction, which manifests itself in the irreversible color change of the solid from yellow to red, is topochemically controlled (Cohen & Schmidt, 1964) since it is confined to the solid state and, more specifically, to one of the two known crystalline modifications.

In order to analyze the geometric factors controlling the intermolecular redox step we have undertaken in parallel with our investigation of the *o*-nitrobenzalde-

hydes (Coppens & Schmidt, 1964) in which the redox reaction (1) takes place intramolecularly, the structure analysis of the photoactive ( $\alpha$ ) modification of *p*-nitrophenol (Coppens & Schmidt, 1965); its packing arrangement was to be compared with that of the light-stable ( $\beta$ ) form published by Toussaint (1954). A first comparison of the two structures showed a large difference in the OH...O distances:  $\alpha$ : 2.82 Å (at 90°K),  $\beta$ : 2.65 Å, which on the basis of Toussaint's estimate of a mean error of 0.04 Å would be significant. However, our measurements of the infrared spectrum of powdered  $\beta$ -nitrophenol gave the OH stretching frequency at about 3250 cm<sup>-1</sup>, very close to the corresponding band in the  $\alpha$  form. Since an OH...O distance of 2.65 Å would require this band to lie near 2750 cm<sup>-1</sup> (Nakamoto, Margoshes & Rundle, 1955)