CRUICKSHANK, D. W. J. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis.* p. 41. Oxford: Pergamon Press.

CRUICKSHANK, D. W. J. (1962). *Tetrahedron,* **17**, 155.

CRUICKSHANK, D. W. J. & SPARKS, R. A. (1960). *Proc. Roy. Soc.* A, **258**, 270.

Dictionary of Values of Molecular Constants (1955). Vol. II. Centre National de la Recherche Scientifique, and I. C. I. Ltd.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

ROBERTSON, J. M. & WHITE, J. G. (1947). *J. Chem. Soc.* p. 358.

ROLLETT, J. S. & DAVIES, D. R. (1955). *Acta Cryst.* **8**, 125.

SPARKS, R. A. (1958). *Ph. D. Thesis,* University of California, Los Angeles.

TROTTER, J. (1960). *Acta Cryst.* **13**, 86.

Acta Cryst. (1965). **18**, 643

The Crystal Structure of PNb_9O_{25}, ($P_2O_5 . 9Nb_2O_5$)

BY R. S. ROTH* AND A. D. WADSLEY
Division of Mineral Chemistry, C.S.I.R.O., Melbourne, Australia

AND STEN ANDERSSON
Research Institute of National Defence, Department 4, Stockholm, and Institute of Inorganic Chemistry, Stockholm, Sweden

(*Received* 5 *May* 1964)

PNb_9O_{25} crystallizes in the tetragonal system, with the lattice parameters $a = 15·60$, $c = 3·828$ Å and the space group $I\bar{4}$ or possibly $I4/m$. The structure, predicted from crystallochemical principles and refined by Fourier and least-squares methods, contains blocks of the ReO_3-type structure, three octahedra wide, three long and infinite in the third dimension. These blocks are joined to similar blocks at different levels along c by having octahedral edges in common, and the tetrahedral positions at the junctions are occupied in part by the phosphorus atoms, which may or may not be ordered.

Introduction

There has been a good deal of recent attention given to the compounds made by reacting niobium pentoxide with the oxides of uni-, di-, tri-, and quadrivalent elements at high temperatures. In most cases the ionic radii of these elements are equal to or greater than that of Nb^{5+} itself, and the wide variety of compounds that are formed fall into a number of different structural types which have been of independent interest to us for some little time.

Waring & Roth (1964) recently showed that both Nb_2O_5 and Ta_2O_5 form a number of isostructural compounds ANb_9O_{25} and ATa_9O_{25}, where A is one or another of the small pentavalent ions As, V, and P. The presence of isolated tetrahedrally coordinated Nb atoms in the crystal structure of the high temperature form of Nb_2O_5 (Gatehouse & Wadsley, 1964) has prompted us to examine PNb_9O_{25}, a representative member of this new group, where phosphorus might be expected to adopt positions of a similar kind in a structure related to Nb_2O_5 in some close way.

Experimental

The original specimen of PNb_9O_{25}, made in the United States by Waring & Roth (1964), was fine-grained and no single crystal could be isolated from it. A microchemical analysis of this material, kindly made by E. S. Pilkington and P. R. Smith, C.S.I.R.O. Division of Mineral Chemistry, proved that combined phosphorus is present in the correct order of magnitude. The exact composition can be inferred from the isostructural relationship with the As and V compounds, as both of these can be prepared by standard ceramic techniques as single phases with the exact formulae ANb_9O_{25}.

At the University of Stockholm low temperature Nb_2O_5 was treated with an excess of phosphoric acid in a gold capsule under hydrothermal conditions at 750 °C and 20,000 p.s.i. A number of fine needles, present in a matrix of another phase, proved to be single crystals of PNb_9O_{25} and were used for the structure determination, undertaken cooperatively in Stockholm and in Melbourne.

The crystal data are summarized in Table 1, the unit-cell dimensions being derived from a powder diffractometer pattern. Zero, first and second level

---

* On leave from National Bureau of Standards, Washington, D.C., U.S.A.

integrated Weissenberg photographs were taken with filtered copper radiation around c, the axis of elongation of the needles. The multiple film technique was used and intensities were estimated visually with a standard scale. The scattering curve for Nb^{5+} was derived from Thomas & Umeda's (1957) table, that of O^{2-} from Suzuki (1960), and the P values from *International Tables for X-ray Crystallography* (1962).

Table 1. *Crystallographic data for* PNb_9O_{25}

System: tetragonal

Unit-cell dimensions	$a=15{\cdot}60$, $c=3{\cdot}828$ Å
Systematically absent reflexions:	hkl with $h+k+l\neq 2n$
Possible space groups*:	$I4$ (No. 79), $I\bar{4}$ (No. 82), $I4/m$ (No. 87)
D_x(g.cm^{-3}), $Z=2$:	4·52.

* The relationship $F(hkl)\neq F(\bar{h}kl)$ eliminated the space groups $I4/mmm$, $I\bar{4}2m$, $I\bar{4}m2$, $I4mm$ and $I422$ with the same systematically absent reflexions.

Calculations were made on the C.S.I.R.O. Elliott 803 computer, except for the least-squares refinement which was made on the FACIT machine at the University of Stockholm.

Structure determination

The length of the c axis, ~3·8 Å, is common to many oxide structures, where it usually corresponds to the length of an octahedral body diagonal. The intensity data showed a prominent pseudocubic sub-cell, also with a side of 3·8 Å, oriented in the [120] and [$2\bar{1}0$] directions, from which we can infer that some of the octahedra are joined by corners. The presence in the unit cell of two P, eighteen Nb and fifty O atoms requires three sets of twofold special positions if the structure is an ordered one, and these can be provided by the space group $I\bar{4}$, but not by the possible alternatives $I4$ and $I4/m$. In the former case two Nb and two O can occupy the special positions (0, 0, 0) and (0, 0, $\frac{1}{2}$) b. c., with two P at the faces (0, $\frac{1}{2}$, $\frac{1}{4}$) or (0, $\frac{1}{2}$, $\frac{3}{4}$) b. c.

With one of the Nb atoms "anchored" at the origin, the other two, both present in eightfold positions, will fall along the sub-cell directions, and by assuming that they are all in octahedral coordination with oxygen, and can share edges as well as corners with each other, a model of the idealized structure [Fig. 1(a)] could readily be drawn out on squared paper. This contained blocks of octahedra, three wide and three long sharing corners [Fig. 1(b)] and joined to identical blocks at different levels by edge-sharing, the junctions of the neighbouring blocks constituting tetrahedral positions in which the phosphorus atoms were located.

The model fulfils the three criteria which a structure of this kind must satisfy (Andersson & Wadsley, 1962):

(a) The unit cell must have the correct size and symmetry,

(b) It must contain the correct numbers of atoms of each kind.

(c) The positions of the atoms must correspond with the correct sub-cell orientation.

The positions of the atoms in a real structure differ from those of an ideal one, and it is necessary to know the directions in which they shall be moved if their coordinates will refine. By analogy with Nb_2O_5, to which the present structure bears some similarities, we can assume that the distances between niobium atoms at the same level are about 3·8 Å, while those at different levels along c will be 2·8 Å in projection on to (001), the atom fixed by the origin providing the reference point.

No Patterson function was necessary, as the parameters refined rapidly by successive Fourier and difference syntheses. Further treatment of the data, however, posed additional problems. Firstly, there are *two* tetrahedral positions for each phosphorus atom (Fig. 2). The structure can be either polar, with the phosphorus ordered in the space group $I\bar{4}$, or non-polar in $I4/m$ when two of these atoms will statistically occupy the fourfold positions 4(d), perhaps with the limitation of local ordering customarily found in non-stoichiometric tunnel structures of a related kind (Wadsley, 1964). With $I4/m$ the atoms in the eightfold positions are in 8(h), where z is either 0 or $\frac{1}{2}$, while in $I\bar{4}$ the 8(g) position includes z as an additional variable.

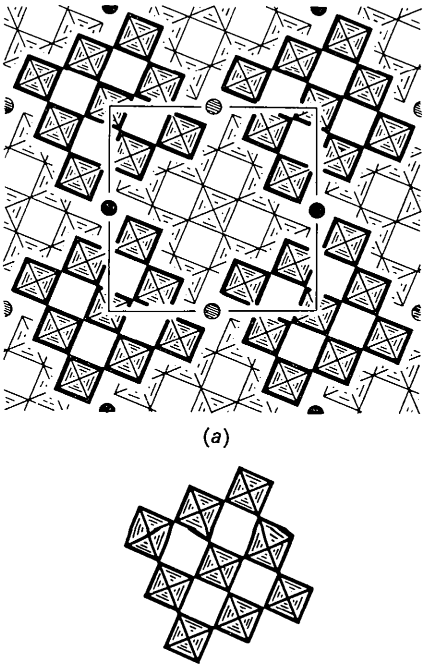

Fig. 1. (a) Idealized octahedral structure of PNb_9O_{25}, the heavier and lighter being at two levels along c. The phosphorus atoms are drawn as circles, and the unit cell is shown in projection on to (001). (b) A block of 3×3 octahedra, infinite out of the plane of the paper. Fig. 1 (a) is made up by the union of these blocks.

Table 2. *Fractional atomic parameters for two alternative space groups*

I$\bar{4}$

Atom	Point position	*x*	σ*x*	*y*	σ*y*	*z*	B_{iso}	σ*B*
P	2(*c*)	0		½		¼	2·6	1·1
Nb(1)	2(*a*)	0		0		0	1·3	0·2
Nb(2)	8(*g*)	0·2188	0·0005	0·1094	0·0005	0	1·0	0·1
Nb(3)	8(*g*)	0·1142	0·0005	0·3310	0·0005	0	0·9	0·1
O(1)	2(*b*)	0		0	0	½	0·9	1·7
O(2)	8(*g*)	0·2488	0·0032	0·3917	0·0032	0	0**	0·8
O(3)	8(*g*)	0·1121	0·0039	0·0521	0·0037	0	0**	0·7
O(4)	8(*g*)	0·1755	0·0041	0·2212	0·0040	0	1·4	1·4
O(5)	8(*g*)	0·0175	0·0050	0·2729	0·0050	0	2·3	1·5
O(6)	8(*g*)	0·0722	0·0050	0·4531	0·0050	0	2·3	1·6
O(7)	8(*g*)	−0·1461	0·0034	0·3536	0·0034	0	0	1·0

*I*4/*m*

Atom	Point position	*x*	σ*x*	*y*	σ*y*	*z*	B_{iso}	σ*B*
P	4(*d*)*	0		½	¼	¼	2·4	2·2
Nb(1)	2(*a*)	0		0		0	1·2	0·2
Nb(2)	8(*h*)	0·2186	0·0005	0·1093	0·0005	0	1·0	0·1
Nb(3)	8(*h*)	0·1143	0·0005	0·3311	0·0005	0	0·9	0·1
O(1)	2(*b*)	0		0		½	0·5	1·5
O(2)	8(*h*)	0·2500	0·0031	0·3901	0·0030	0	0**	0·8
O(3)	8(*h*)	0·1141	0·0038	0·0508	0·0037	0	0**	0·7
O(4)	8(*h*)	0·1748	0·0042	0·2197	0·0042	0	1·6	1·5
O(5)	8(*h*)	0·0138	0·0050	0·2767	0·0050	0	2·4	1·6
O(6)	8(*h*)	0·0707	0·0054	0·4537	0·0054	0	2·9	1·7
O(7)	8(*h*)	−0·1460	0·0032	0·3528	0·0033	0	0**	1·0

* Two phosphorus atoms statistically occupying the fourfold positions.

** The least-squares refinement gave small negative values of *B* for these atoms.

Table 3. *Interatomic distances*

P tetrahedron

	Number	Length	Stand. Deviation
P–O(6)	4	1·65 Å	0·08 Å
O(6)–O(6)	4	2·70	0·15
O(6)–O(6)	2	2·69	0·15
O(6)–P–O(6)	2	109·2°	0·7°
O(6)–P–O(6)	2	109·6°	0·7°
	Nb(1) octahedron		
Nb(1)–O(3)	4	1·93	0·06
Nb(1)–O(1)	2	1·91	
O(1)–O(3)	4	2·72	0·06
O(3)–O(3)	4	2·73	0·06

Nb(2) octahedron

	Number	Length	Stand. Deviation
Nb(2)–O(3)	1	1·89 Å	0·06 Å
Nb(2)–O(4)	1	1·87	0·06
Nb(2)–O(7′)	1	2·18	0·05
Nb(2)–O(5′)	1	2·15	0·08
Nb(2)–O(2)	2	1·98	0·05
O(7′)–O(4)	1	3·02	0·08
O(4)–O(3)	1	2·82	0·08
O(3)–O(5′)	1	2·73	0·10
O(5′)–O(7′)	1	2·85	0·09
O(2)–O(7′)	2	2·57	0·07
O(2)–O(4)	2	2·86	0·08
O(2)–O(3)	2	3·02	0·08
O(2)–O(5′)	2	2·76	0·09

Nb(3) octahedron

	Number	Length	Stand. Deviation
Nb(3)–O(5)	1	1·76 Å	0·08 Å
Nb(3)–O(6)	1	2·01	0·08
Nb(3)–O(2′)	1	2·30	0·05
Nb(3)–O(4)	1	1·96	0·06
Nb(3)–O(7)	2	2·01	0·05
O(2′)–O(6)	1	2·92	0·09
O(6)–O(5)	1	2·94	0·10
O(5)–O(4)	1	2·59	0·10
O(4)–O(2′)	1	2·89	0·08
O(7)–O(2′)	2	2·57	0·07
O(7)–O(6)	2	2·72	0·09
O(7)–O(5)	2	3·05	0·09
O(7)–O(4)	2	2·85	0·08

The three-dimensional data, weighted by Cruickshank's scheme (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961*b*), were next refined by the method of least squares. Separate scale factors for each level and individual isotropic thermal parameters for the atoms were included as additional variables. Several cycles were run for each space group, with the assumption that in $I\bar{4}$ the z parameters for the 8(g) positions were either 0 or $\frac{1}{2}$. For $I\bar{4}$ the overall reliability factor is 9·2%, and for $I4/m$ 9·3%; the atomic parameters with temperature factors and estimated standard deviations for both space groups are given in Table 2. Although there is evidently little to choose between the two possibilities, the interatomic distances in Table 3 and the observed and calculated structure factors in Table 4 are given for the polar space group $I\bar{4}$, for which the temperature factors and their standard deviations are rather better.

Table 4. *Comparison between F_o and F_c for space group $I\bar{4}$ (observed data only)*

h	k	l	F_o	$\|F_o\|$	h	k	l	F_o	$\|F_o\|$	h	k	l	F_o	$\|F_o\|$	h	k	l	F_o	$\|F_o\|$
4	0	0	81	116	2	10	0	122	143	10	5	1	113	112	4	2	2	466	408
8	0	0	206	212	4	10	0	325	312	12	5	1	121	125	6	2	2	110	100
10	0	0	171	168	12	10	0	100	90	1	6	1	180	185	8	2	2	147	125
18	0	0	268	257	3	11	0	249	260	11	6	1	207	235	12	2	2	160	160
3	1	0	208	250	13	11	0	258	241	13	6	1	122	133	5	3	2	108	84
9	1	0	159	156	4	12	0	141	125	6	7	1	324	309	7	3	2	440	427
11	1	0	91	96	8	12	0	179	163	14	7	1	259	238	17	3	2	100	112
13	1	0	143	129	3	13	0	102	87	5	8	1	178	203	6	4	2	81	52
2	2	0	39	51	7	13	0	253	220	4	9	1	105	134	8	4	2	197	200
4	2	0	572	587	2	14	0	312	276	10	9	1	172	136	16	4	2	151	170
6	2	0	87	103	10	14	0	89	78	3	10	1	109	101	1	5	2	197	174
8	2	0	128	130	12	14	0	105	93	9	10	1	122	118	11	5	2	307	297
12	2	0	219	209	1	15	0	102	108	11	10	1	119	105	15	5	2	105	85
5	3	0	117	142	11	15	0	179	178	13	10	1	153	132	2	6	2	283	250
7	3	0	528	544	6	16	0	182	161	4	11	1	422	396	4	6	2	141	130
17	3	0	125	111	5	17	0	118	107	8	11	1	122	112	14	6	2	79	80
2	4	0	71	37						12	11	1	155	165	1	7	2	79	94
6	4	0	95	95	1	0	1	378	286	7	12	1	172	182	5	7	2	323	329
8	4	0	273	276	5	0	1	105	125	13	12	1	92	73	15	7	2	189	220
16	4	0	234	210	9	0	1	412	412	8	13	1	167	163	6	8	2	157	165
1	5	0	154	183	13	0	1	121	90	11	14	1	242	243	14	8	2	71	70
3	5	0	58	54	19	0	1	96	107	2	15	1	265	255	1	9	2	197	195
11	5	0	377	333	2	1	1	236	203	4	15	1	115	99	5	9	2	90	90
15	5	0	99	111	4	1	1	220	229	1	16	1	111	106	9	9	2	304	259
2	6	0	330	334	3	2	1	336	347	5	16	1	149	168	2	10	2	157	136
4	6	0	117	122	13	2	1	272	269	6	17	1	122	116	4	10	2	243	235
10	6	0	94	104	15	2	1	119	91	1	18	1	151	151	3	11	2	207	234
14	6	0	102	104	4	3	1	105	103						13	11	2	203	223
1	7	0	115	135	8	3	1	238	270	2	0	2	94	84	4	12	2	91	88
5	7	0	398	387	16	3	1	190	188	4	0	2	160	131	8	12	2	121	126
15	7	0	252	244	3	4	1	75	112	8	0	2	145	143	7	13	2	220	202
6	8	0	226	231	7	4	1	430	424	10	0	2	157	120	2	14	2	213	222
14	8	0	97	93	9	4	1	105	125	18	0	2	178	239	10	14	2	58	61
1	9	0	224	220	17	4	1	136	126	3	1	2	270	215	1	15	2	115	104
5	9	0	123	136	2	5	1	203	202	9	1	2	151	144	6	16	2	121	135
9	9	0	300	286	6	5	1	128	145	13	1	2	64	127	5	17	2	87	108

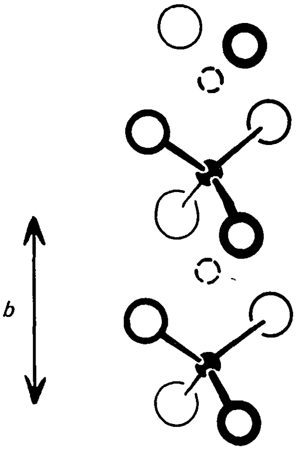

Fig. 2. Tetrahedral environment for the phosphorus atoms. Each P has two alternative positions, the black and the dotted circles.

Discussion

The structure is illustrated as an arrangement of ideal octahedra in Fig. 1(a), and as a ball-and-spoke drawing in Fig. 3. The octahedron centred around Nb(1) at the origin is virtually regular, with Nb–O bond distances averaging 1·92 ± 0·06 Å. The distances to oxygen of Nb(2) and Nb(3) vary between 1·76 and 2·30 Å with an average of 2·01 Å for the twelve independent determinations, and can be compared directly with those in Nb_2O_5 (Gatehouse & Wadsley, 1964) and in $NaNb_{13}O_{33}$ (Andersson, 1964) where similar variations occur. The four phosphorus–oxygen distances of 1·65 ± 0·08 Å are longer than is usual in most phosphates, and approach the single bond value of 1·71 Å calculated by Cruickshank (1961*a*) from the equation of Schomaker & Stephenson (1941). The size of the tetrahedron in PNb_9O_{25} is not significantly different from that in the high temperature form of Nb_2O_5, where it is occupied by niobium having bonds to oxygen averaging 1·68 Å. In both cases these sites are created by the junction of octahedral blocks, 3 × 3 in the present instance, and 3 × 4 as well as 3 × 5 in the more complicated structure, the formula for which should perhaps be written $NbNb_{27}O_{70}$, containing as it does one tetrahedral and twenty-seven octahedral niobium atoms in the unit cell.

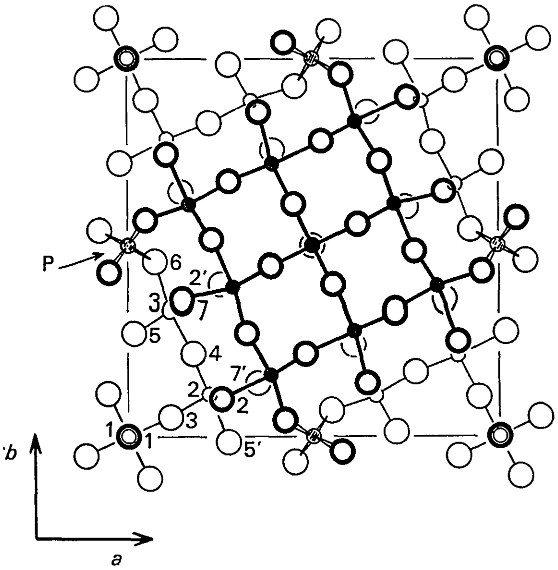

Fig. 3. Drawing of atoms in PNb_9O_{25}. Smaller circles Nb, larger ones O. The P atoms (circles) are hatched.

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 Nb_2O_5 (Schoeller & Webb, 1936). Two questions arise out of the present study. Firstly, is there a possible tetragonal polymorph of Nb_2O_5 with the same structure as PNb_9O_{25}, where the phosphorus is replaced by Nb? Secondly, could a solid solution also exist between Nb_2O_5 and some hitherto unsuspected phase $PNb_{27}O_{70}$, 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 PNb_9O_{25}. Mohanty, Fiegel & Healy (1962) showed that the high temperature compound $Ta_2O_5 . 2Nb_2O_5$, 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 $GeNb_{18}O_{47}$ (*i.e.* $GeO_2 . 9Nb_2O_5$) 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.

One of us (R.S.R.) would like to thank Professor Arne Magnéli for his hospitality at the University of Stockholm where some of this work was done.

References

Andersson, S. (1964). *Acta Chem. Scand.* In the press.

Andersson, S. & Wadsley, A. D. (1962). *Acta Cryst.* **15**, 194.

Cruickshank, D. W. J. (1961*a*). *J. Chem. Soc.*, p. 5486.

Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. & Truter, M. R. (1961*b*). *Computing Methods and the Phase Problem in X-ray Crystal Analysis,* p. 32. Symposium Publications Division, Pergamon Press.

Gatehouse, B. M. & Wadsley, A. D. (1964). *Acta Cryst.* **17**, 1545.

Hahn, R. B. (1951). *J. Amer. Chem. Soc.* **73**, 5091.

Holtzberg, F. & Reisman, A. (1961). *J. Phys. Chem.* **65**, 1192.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

Mohanty, G. P., Fiegel, L. J. & Healy, J. H. (1962). *Acta Cryst.* **15**, 1190.

Schoeller, H. R. & Webb, W. H. (1936). *Analyst,* **61**, 585.

Schomaker, V. & Stephenson, D. P. (1941). *J. Amer. Chem. Soc.* **63**, 37.

Suzuki, J. (1960). *Acta Cryst.* **13**, 279.

Thomas, L. H. & Umeda, K. (1957). *J. Chem. Phys.* **26**, 293.

Wadsley, A. D. (1964). In *Non-Stoichiometric Compounds.* Ed L. Mandelcorn, p. 98. New York: Academic Press.

Waring, J. L. & Roth, R. S. (1964). *Acta Cryst.* **17**, 455.

Acta Cryst. (1965). **18**, 647

The Crystal Structure of 1,5-Dimethylnaphthalene

By J. Beintema

Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research N.V.)

(*Received* 13 *May* 1964)

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 α,α- and in β,β-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