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2-Oxo-2,7-diphenyl-4,5-dimethyl-1-aza-2-phosphacyclohepta-4,6-diene

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Abstract. $C_{19}H_{20}NOP$, monoclinic, $C2/c$, $a=23{\cdot}529$ (5), $b=17{\cdot}736$ (4), $c=8{\cdot}099$ (1) Å, $\beta=98{\cdot}42$ (1)°, $M=309{\cdot}35$, $Z=8$, $D_x=1{\cdot}23$ g cm^{-3}. The molecules are linked into dimers by N–H···O hydrogen bonds of length 2·889 (5) Å. The short N–C bond length of 1·412 (6) Å is indicative of a strong interaction between the nitrogen lone pair and the dienic system. The bond lengths to phosphorus are P=O, 1·476 (3); P–N, 1·664 (4); P–C(ar), 1·803 (5) and P–C(alk), 1·808 (5) Å.

Introduction. Cell dimensions were determined from measurements of 16 high 2θ-angle reflexions with Mo $K\alpha_1$ ($\lambda=0{\cdot}70926$ Å) radiation. The intensities from a prismatic crystal with approximate dimensions $0{\cdot}15\times0{\cdot}15\times0{\cdot}50$ mm were collected on a Stoe 4-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Measurements were carried out with standard background counts and a θ–2θ scan of fixed range for $2\theta\le45°$. Three standard reflexions, which were monitored at regular intervals, did not display any significant variations due to crystal deterioration. 2456 reflexions were recorded of which 659 were rejected because the net count was less than $2{\cdot}5\sigma$ based on counting statistics. Lorentz and polarization but no absorption [μ(Mo $K\alpha$) $=1{\cdot}7$ cm^{-1}] corrections were applied. When equivalent reflexions had been averaged, 1652 unique reflexions were obtained.

The systematic absences hkl ($h+k$ odd) and $h0l$ (l odd) gave Cc or $C2/c$ as possible space groups. The centrosymmetric $C2/c$ was indicated by the intensity statistics and confirmed by the successful refinement of the structure. A Patterson synthesis was interpreted to yield coordinates for the phosphorus, and the remaining heavy atoms were located from difference syntheses. Their positional and anisotropic temperature factor parameters were refined by full-matrix least-squares methods until $R_G=[\sum w\Delta^2/\sum wF_o^2]^{1/2}$ had converged to 0·096 and $R_w=\sum w^{1/2}\Delta/\sum w^{1/2}F_o$ to 0·092. A difference synthesis revealed the positions of all the hydrogen atoms. The phenyl hydrogen atoms were defined for inclusion in the least-squares refinement by $x_H=1{\cdot}776x_C-x_O$, where x_C and x_O are fractional coordinates of the carbon atom to which the hydrogen is bonded, and of the centroid of the ring, respectively. The remaining hydrogen atom positional parameters were allowed to refine freely with isotropic temperature factors, with the exception of those for the methyl hydrogen atoms where it was found necessary to introduce the constraint of an overall factor. The terminal value of R_G was 0·059 with R_W 0·061 and R_x 0·068.* A final difference synthesis revealed no peaks of density higher than 0·3 e Å^{-3}. The weights adopted were those obtained from counting statistics where a standard deviation $\sigma(I)=[N_S+N_B+(0{\cdot}01N_P)^2]^{1/2}$ was assigned to each net intensity I, N_S being the gross count, N_B the background count corrected to cover the same time span as N_S, and $N_P=N_S-N_B$. Complex neutral atom scattering factors (Cromer, 1965; Cromer & Waber, 1965) were employed for all atoms. The heavy-atom coordinates are listed in Table 1 and their anisotropic temperature-factor components in Table 2; hydrogen atom positional parameters and isotropic

Table 1. *Atom positional parameters* ($\times10^4$)

	x	y	z
P	506 (1)	2088 (1)	−47 (2)
O	−120 (1)	1975 (2)	−482 (4)
N	798 (2)	2542 (2)	−1512 (6)
C(2)	713 (2)	2647 (3)	1810 (7)
C(3)	1357 (2)	2614 (3)	2372 (6)
C(4)	1720 (2)	2979 (3)	1528 (7)
C(31)	1519 (3)	2147 (4)	3893 (7)
C(41)	2360 (2)	3033 (4)	2186 (9)
C(5)	1555 (2)	3362 (3)	−56 (7)
C(6)	1170 (2)	3171 (3)	−1403 (7)
C(11)	866 (2)	1192 (3)	291 (6)
C(12)	579 (3)	581 (3)	848 (7)
C(13)	864 (3)	−110 (4)	1194 (9)
C(14)	1425 (3)	−183 (4)	977 (8)
C(15)	1714 (3)	412 (4)	447 (9)
C(16)	1442 (2)	1098 (3)	90 (7)
C(61)	1136 (2)	3627 (3)	−2950 (7)
C(62)	603 (3)	3784 (3)	−3925 (7)
C(63)	566 (3)	4237 (3)	−5341 (7)
C(64)	1059 (4)	4514 (4)	−5851 (9)
C(65)	1585 (4)	4352 (4)	−4894 (10)
C(66)	1627 (3)	3916 (3)	−3494 (8)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30410 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Anisotropic temperature factors* (Å^2 × 10^3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	33 (7)	41 (8)	35 (8)	3 (1)	3 (1)	−1 (1)
O	41 (2)	57 (2)	48 (2)	7 (2)	0 (2)	−4 (2)
N	44 (3)	44 (3)	33 (3)	−2 (2)	0 (2)	−10 (2)
C(2)	44 (3)	49 (4)	41 (3)	0 (3)	4 (3)	4 (3)
C(3)	46 (3)	55 (4)	38 (3)	−8 (3)	−10 (3)	3 (3)
C(4)	43 (3)	54 (4)	45 (3)	0 (3)	−4 (3)	−7 (3)
C(31)	81 (4)	82 (5)	45 (4)	10 (4)	−12 (3)	3 (4)
C(41)	48 (4)	118 (6)	84 (5)	−3 (5)	−14 (4)	−18 (4)
C(5)	41 (3)	45 (3)	65 (4)	−5 (3)	9 (3)	−10 (3)
C(6)	38 (3)	39 (3)	48 (4)	−4 (3)	3 (3)	−4 (3)
C(11)	50 (3)	41 (3)	39 (3)	−2 (3)	0 (3)	−6 (3)
C(12)	76 (4)	49 (4)	69 (5)	6 (3)	3 (4)	−11 (3)
C(13)	106 (6)	48 (4)	90 (6)	21 (4)	−5 (5)	−7 (4)
C(14)	100 (6)	59 (5)	75 (5)	−4 (4)	−22 (5)	30 (5)
C(15)	77 (5)	65 (5)	97 (6)	−7 (4)	6 (4)	27 (4)
C(16)	58 (4)	56 (4)	77 (5)	−1 (4)	16 (4)	11 (3)
C(61)	60 (4)	35 (3)	41 (3)	−2 (3)	7 (3)	−9 (3)
C(62)	76 (4)	43 (3)	44 (4)	0 (3)	16 (3)	−6 (3)
C(63)	101 (5)	50 (4)	47 (4)	9 (3)	0 (4)	−2 (4)
C(64)	141 (7)	56 (4)	64 (5)	12 (4)	20 (5)	−22 (5)
C(65)	109 (6)	68 (5)	88 (6)	8 (5)	45 (5)	−29 (5)
C(66)	71 (4)	51 (4)	66 (4)	8 (4)	22 (4)	−17 (3)

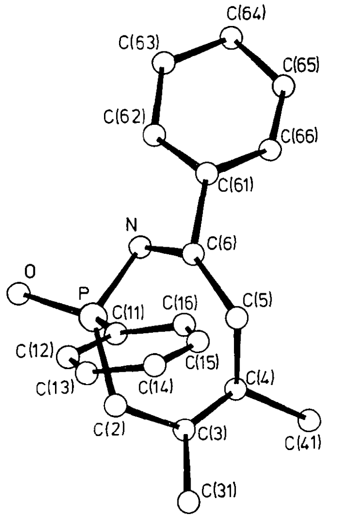

Fig. 1. Atom numbering in the molecule.

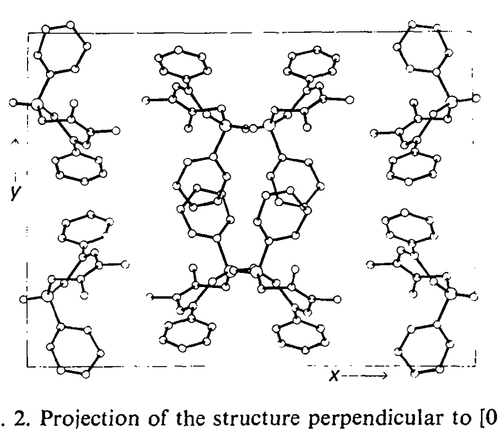

Fig. 2. Projection of the structure perpendicular to [001].

temperature factors are summarized in Table 3. The full covariance matrix was used in the estimation of the bond lengths and selected bond angles presented in Tables 4 and 5.

Table 3. *Hydrogen atom coordinates* (× 10^4) *and isotropic temperature factors* (Å^2 × 10^3)

	x	y	z	U
H(N)	662 (14)	2419 (20)	−2392 (45)	9 (10)
H(C2)1	528 (15)	2387 (22)	2921 (50)	4 (12)
H(C2)2	611 (16)	3105 (22)	1322 (51)	7 (12)
H(C31)1	1278 (32)	1582 (42)	3729 (97)	125 (13)
H(C31)2	1906 (33)	2015 (43)	4131 (100)	125 (13)
H(C31)3	1611 (31)	2476 (42)	5254 (101)	125 (13)
H(C41)1	2483 (32)	3468 (43)	1842 (102)	125 (13)
H(C41)2	2548 (32)	2959 (41)	3503 (103)	125 (13)
H(C41)3	2482 (33)	2579 (47)	1621 (98)	125 (13)
H(C5)	1758 (16)	3833 (21)	−49 (49)	2 (11)
H(C12)	137 (5)	644 (5)	1008 (13)	32 (16)
H(C13)	643 (6)	−582 (6)	1624 (16)	82 (26)
H(C14)	1641 (6)	−711 (7)	1237 (15)	32 (16)
H(C15)	2152 (5)	345 (7)	296 (16)	87 (27)
H(C16)	1669 (4)	1564 (6)	−339 (13)	60 (22)
H(C62)	221 (5)	3650 (5)	−3550 (12)	67 (23)
H(C63)	155 (5)	4365 (5)	−6064 (13)	46 (19)
H(C64)	1031 (6)	4858 (6)	−6970 (16)	81 (24)
H(C65)	1964 (6)	4569 (7)	−5270 (17)	158 (42)
H(C66)	2039 (5)	3796 (5)	−2784 (14)	87 (27)

Table 4. *Bond lengths* (Å)

P——O	1·476 (3)	P——N	1·664 (4)
P——C(2)	1·808 (5)	P——C(11)	1·803 (5)
C(2)——C(3)	1·517 (7)	C(3)——C(31)	1·487 (7)
C(3)——C(4)	1·337 (7)	C(4)——C(41)	1·526 (7)
C(4)——C(5)	1·452 (7)	C(5)——C(6)	1·355 (7)
C(6)——C(61)	1·484 (7)	C(6)——N	1·413 (6)
C(11)——C(12)	1·387 (7)	C(12)——C(13)	1·405 (8)
C(13)——C(14)	1·364 (8)	C(14)——C(15)	1·357 (8)
C(15)——C(16)	1·386 (7)	C(16)——C(11)	1·398 (7)
C(61)——C(62)	1·408 (7)	C(62)——C(63)	1·392 (7)
C(63)——C(64)	1·379 (8)	C(64)——C(65)	1·389 (9)
C(65)——C(66)	1·363 (8)	C(66)——C(61)	1·394 (7)
H(N)——N	0·78 (4)	H(C2)1—C(2)	1·15 (4)
H(C2)2—C(2)	0·92 (4)	H(C31)1–C(31)	1·13 (8)
H(C31)2–C(31)	0·93 (8)	H(C31)3–C(31)	1·27 (8)
H(C41)1–C(41)	0·88 (8)	H(C41)2–C(41)	1·10 (8)
H(C41)3–C(41)	0·99 (8)	H(C5)——C(5)	0·97 (4)
N–H(N)···O	2·889 (5)	H(N)···O	2·14 (4)

Table 5. *Selected bond angles* (°)

N——P——C(2)	103·8 (2)	N——P——O	113·4 (2)
N——P——C(11)	107·5 (2)	O——P——C(2)	114·2 (2)
O——P——C(11)	110·5 (2)	C(11)–P——C(2)	107·9 (2)
P——C(2)–C(3)	111·4 (4)	C(2)—C(3)–C(4)	120·8 (5)
C(3)—C(4)–C(5)	124·8 (5)	C(4)—C(5)–C(6)	130·9 (5)
C(5)—C(6)–N	125·7 (5)	C(6)—N——P	130·9 (4)
C(31)–C(3)–C(2)	113·3 (5)	C(31)–C(3)–C(4)	126·0 (5)
C(41)–C(4)–C(3)	121·6 (5)	C(41)–C(4)–C(5)	113·7 (5)
H(N)–N——C(6)	117 (3)	H(N)–N——P	111 (3)

Discussion. The synthesis of a new class of heterocyclic phosphorus compounds, the 1-aza-2-phosphacyclohepta-4,6-dienes, from the reaction of benzonitrile with the lithium derivatives of 1-oxo-3-phospholenes, has recently been described (Mathey & Lampin, 1972). It was demonstrated (Lampin & Mathey, 1972) that crude 2-oxo-1-aza-2-phosphacyclohepta-4,6-dienes produced in this way are, in fact, mixtures of two isomers, a 2-hydroxycycloheptatriene and a 2-oxocycloheptadiene. These isomers can be distinguished by their different melting points, infrared spectra and solubilities in organic solvents. The crystal structure of the 2-oxocycloheptadiene isomer is reported in this work.

The molecules are linked into dimers by two almost linear N–H···O hydrogen bonds of length 2·889 (5) Å. The coordination at nitrogen is planar. The bond lengths within the ring are normal with the exception of the N–C(6) distance of 1·413 (6) Å which is particularly short compared with 1·474 in methylamine (Lide, 1957) or 1·498 Å in *N*,*N*-dimethyl-*p*-nitroaniline (Mak & Trotter, 1965). This phenomenon is indicative of a strong interaction between the nitrogen lone pair and the dienic system of the ring. The P–N bond length of 1·664 (4) Å is very similar to 1·656 (10) Å in $PO(NH_2)_3$ (Bullen, Stephens & Wade, 1969) and 1·647 (6) Å in $PO(NMe_2)_2C_4H_4$ (Born, 1969). The P=O distance of 1·476 (3) Å is identical with 1·476 (4) Å in the former though somewhat shorter than 1·510 (3) Å in the latter.

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References

Born, L. (1969). *Acta Cryst.* B**25**, 1460–1469.
Bullen, G. J., Stephens, F. S. & Wade, R. J. (1969). *J. Chem. Soc.* (*A*), pp. 1804–1812.
Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.
Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.
Lampin, J.-P. & Mathey, F. (1972). *Tetrahedron*, **28**, 5367–5375.
Lide, D. R. (1957). *J. Chem. Phys.* **27**, 343–352.
Mak, T. C. W. & Trotter, J. (1965). *Acta Cryst.* **18**, 68–74.
Mathey, F. & Lampin, J.-P. (1972). *Tetrahedron Lett.* **19**, 1949–1952.

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α Form of Sodium Metavanadate

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Abstract. α-$NaVO_3$, monoclinic, $C2/c$, $Z=4$, $a=10·552$ (3), $b=9·468$ (2), $c=5·879$ (2) Å, $\beta=108·47$ (3)°. $D_{calc}=2·91$ g cm^{-3}. Colourless, transparent crystals of α-$NaVO_3$ were synthesized from a 1:1 mixture of Na_2CO_3 and V_2O_5 by the Bridgman method. The structure is of the diopside type.

Introduction. The systematic absences were hkl for $h+k$ odd and $h0l$ for l odd. For intensity measurements, a crystal with dimensions of about 0·13 × 0·11 × 0·11 mm was used. Intensities were collected on a Rigaku automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite plate. The ω–2θ scan technique was employed with a scanning speed of 2° min^{-1} in ω. In all, 859 independent reflexion data, with $|F|$'s larger than $3\sigma(|F|)$, were obtained within the range $2\theta \leq 65°$. Intensities were corrected for Lorentz and polarization effects. Absorption corrections were also made assuming a sphere of 0·11 mm in diameter for the crystal shape.

Table 1. *Final atomic parameters* ($\times 10^5$) *for* α-$NaVO_3$

The thermal parameters are in the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V	29227 (3)	8979 (3)	26127 (5)	168 (2)	276 (3)	455 (8)	−35 (2)	50 (3)	26 (4)
Na(1)	50000	20571 (15)	75000	534 (13)	449 (14)	1432 (39)	0	−139 (18)	0
Na(2)	50000	41223 (13)	25000	292 (10)	371 (12)	1003 (31)	0	145 (14)	0
O(1)	12750 (14)	10125 (16)	16687 (25)	249 (11)	449 (16)	990 (38)	16 (11)	102 (17)	56 (20)
O(2)	35556 (17)	24768 (18)	32358 (29)	478 (15)	443 (16)	1433 (45)	−179 (13)	247 (21)	−148 (22)
O(3)	35245 (15)	741 (18)	3818 (26)	290 (12)	643 (17)	881 (38)	−5 (12)	124 (18)	−274 (21)