

SHORT STRUCTURAL PAPERS

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2-Oxo-2,7-diphenyl-4,5-dimethyl-1-aza-2-phosphacyclohepta-4,6-diene (*P2₁/c* Modification)

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Abstract. C₁₉H₂₀NOP, monoclinic, *P2₁/c*, $a = 11.307$ (6), $b = 22.981$ (9), $c = 6.983$ (2) Å, $\beta = 95.47$ (3)°, $M = 309.35$, $Z = 4$, $D_x = 1.14$ g cm⁻³. The molecules are linked into chains in the [001] direction by N-H...O hydrogen bonds of length 2.787 (5) Å, which are significantly shorter than those of 2.889 (5) Å observed for the dimers in the *C2/c* modification [Lampin, Mathey & Sheldrick, *Acta Cryst.* (1974). B30, 1626–1628]. The bond lengths to P are P=O 1.479 (3); P–N 1.661 (3); P–C(ar) 1.794 (4) and P–C(alk) 1.786 (4) Å.

Introduction. Cell dimensions were determined by a least-squares fit to the settings for 15 reflexions ($\pm hkl$) on a Syntex *P2₁* four-circle diffractometer (Mo *K* α , 0.71069 Å). Intensities from a prismatic crystal, elongated *c*, recrystallized from ethanol, with approximate dimensions 0.18 × 0.24 × 0.56 mm, were collected on the diffractometer with graphite-monochromated Mo *K* α radiation. Measurements were carried out in the θ – 2θ mode ($3.0 \leq 2\theta \leq 50.0^\circ$) at scan speeds varying linearly between 2.93° min⁻¹ (150 c.p.s. and below) and 9.77° min⁻¹ (5000 c.p.s. and above). Scan and background times were equal. Three standard reflexions, monitored at regular intervals, did not display any significant variations. Lorentz and polarization but no absorption [$\mu(\text{Mo } K\alpha) = 1.17$ cm⁻¹] corrections were applied. From the 3378 reflexions recorded (one quadrant of reciprocal space), 2199 were

retained for use in the structure analysis, after application of the criterion $F \geq 2.5\sigma(F)$ and averaging [internal consistency index, $R = 0.046$], where $\sigma(F)$ is based on the counting statistics.

The structure was solved by a multisolution technique (Sheldrick, 1975, to be published) in which 2¹⁴ sign permutations were expanded by the \sum_2 formula. In this method a permutation is rejected at any stage if its internal consistency falls below a preset value. Additionally, a similarity test is applied to avoid the calculation of too many closely similar *E* maps. Here, only two *E* maps were computed, of which the second best (in terms of \sum_2 consistency) revealed the positions of all atoms in the seven-membered ring, the O atom, and five of the atoms [C(61)–C(63), C(65), C(66)] in one benzene ring (Fig. 1). The positional parameters of the remaining nine C atoms were located from subsequent difference syntheses. The structure was refined by full-matrix least-squares calculations, $\sum w\Delta^2$ being minimized; anisotropic temperature factors were introduced for all atoms. At this stage of the refinement, a difference synthesis revealed the positions of all the H atoms, which were included, with group isotropic temperature factors for the benzene ring and methyl H atoms, in the final cycles of refinement. Although reasonable positional parameters for the two C(2) H atoms were extracted from this and later difference syntheses, all attempts to include them as variables in the least-squares refinement led to unreasonably short C–H distances. The coordinates of these H atoms were, therefore, fixed with a joint isotropic temperature factor as variable. The final value of $R_G = [\sum w\Delta^2 / \sum wF_o^2]^{1/2}$ was 0.072, with $R_w = \sum w^{1/2}\Delta / \sum w^{1/2}F_o = 0.072$ and $R = 0.081$. The weights were $w = k / [\sigma^2(F_o) + gF_o^2]$ where k and g refined to 1.6795 and 0.001516 respectively. In the final cycle the largest observed shift/e.s.d. was –0.040. A final difference synthesis displayed no peaks or troughs > 0.28 e Å⁻³. Complex neutral-atom scattering factors (Cromer & Waber, 1965; Cromer & Liberman, 1970) were employed.* The heavy-atom coordinates are listed in

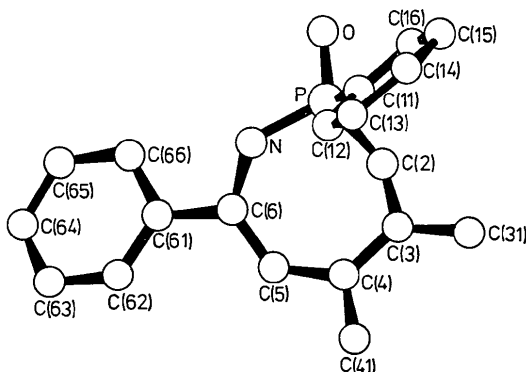


Fig. 1. Atom numbering in the molecule.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31122 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1 and their anisotropic temperature factor components in Table 2; H atom positional parameters and isotropic temperature factors are 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 1. Atom positional parameters ($\times 10^4$)

	x	y	z
P	2464 (1)	1900 (1)	4842 (1)
O	2252 (2)	2531 (1)	4584 (3)
N	1843 (3)	1630 (1)	6713 (4)
C(2)	1891 (4)	1440 (2)	2896 (5)
C(3)	2360 (4)	836 (2)	3145 (6)
C(4)	1979 (4)	482 (2)	4490 (6)
C(5)	1125 (4)	670 (2)	5839 (6)
C(6)	1063 (3)	1166 (2)	6829 (5)
C(31)	3267 (6)	662 (3)	1789 (9)
C(41)	2393 (7)	-141 (2)	4755 (9)
C(11)	4024 (4)	1770 (2)	5249 (5)
C(12)	4536 (5)	1415 (2)	6674 (7)
C(13)	5755 (6)	1344 (3)	6958 (9)
C(14)	6472 (6)	1631 (3)	5801 (12)
C(15)	5983 (6)	1982 (3)	4414 (11)
C(16)	4788 (5)	2062 (2)	4115 (8)
C(61)	149 (3)	1258 (2)	8208 (5)
C(62)	-284 (5)	796 (3)	9245 (8)
C(63)	-1132 (6)	881 (4)	504 (9)
C(64)	-1552 (6)	1419 (5)	800 (10)
C(65)	-1153 (5)	1884 (3)	9838 (9)
C(66)	-293 (4)	1809 (2)	8526 (7)

Table 2. Anisotropic temperature factors ($\text{\AA}^2 \times 10^3$)

The anisotropic temperature factor takes the form

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}lhc^*a^* + 2U_{12}hka^*b^*)].$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P	66 (1)	48 (1)	41 (1)	2 (1)	8 (1)	5 (1)
O	89 (2)	57 (2)	51 (2)	9 (1)	14 (1)	12 (2)
N	65 (2)	54 (2)	41 (2)	-9 (2)	11 (2)	-7 (2)
C(2)	91 (3)	67 (3)	44 (2)	-3 (2)	4 (2)	1 (2)
C(3)	88 (3)	69 (3)	54 (2)	-16 (2)	14 (2)	-2 (2)
C(4)	95 (3)	56 (3)	62 (3)	-14 (2)	20 (2)	-5 (2)
C(5)	77 (3)	59 (3)	64 (3)	-7 (2)	15 (2)	-15 (3)
C(6)	59 (2)	51 (2)	52 (2)	-7 (2)	6 (2)	-7 (2)
C(31)	133 (6)	93 (4)	86 (4)	-22 (3)	49 (4)	4 (4)
C(32)	158 (6)	60 (3)	103 (4)	-9 (3)	46 (4)	7 (4)
C(11)	69 (3)	47 (2)	52 (2)	-1 (2)	13 (2)	3 (2)
C(12)	75 (4)	75 (3)	72 (3)	9 (3)	8 (3)	14 (3)
C(13)	86 (4)	110 (5)	99 (4)	4 (3)	-1 (3)	25 (4)
C(14)	59 (4)	108 (5)	155 (6)	-24 (5)	10 (4)	10 (4)
C(15)	79 (5)	114 (5)	154 (6)	14 (5)	42 (4)	-10 (4)
C(16)	75 (4)	90 (4)	101 (4)	25 (3)	31 (3)	7 (3)
C(61)	58 (3)	73 (3)	52 (2)	-12 (2)	8 (2)	-9 (2)
C(62)	108 (4)	88 (4)	85 (3)	-4 (3)	45 (3)	-13 (3)
C(63)	114 (5)	146 (7)	100 (4)	-5 (4)	55 (4)	-35 (5)
C(64)	78 (4)	174 (8)	102 (5)	-40 (5)	33 (3)	-6 (5)
C(65)	65 (3)	115 (5)	109 (4)	-29 (4)	6 (3)	14 (4)
C(66)	50 (3)	93 (4)	84 (3)	-18 (3)	4 (2)	8 (3)

Discussion. It has been demonstrated (Lampin & Mathey, 1972) that crude 2-oxo-2,7-diphenyl-4,5-dimethyl-1-aza-2-phosphacyclohepta-4,6-diene produced by the reaction of benzonitrile with the Li

Table 3. H atom coordinates ($\times 10^4$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	x	y	z	U
H(N)	1931 (30)	1866 (15)	7625 (48)	49 (10)
H(C2)1	1015	1447	2728	90 (10)
H(C2)2	1955	1609	1604	90 (10)
H(C5)	584 (36)	400 (18)	5988 (54)	69 (13)
H(C31)1	3959 (57)	922 (27)	2034 (90)	148 (9)
H(C31)2	2979 (52)	636 (26)	411 (95)	148 (9)
H(C31)3	3637 (56)	299 (26)	2222 (89)	148 (9)
H(C41)1	1797 (54)	-409 (28)	5061 (89)	148 (9)
H(C41)2	2962 (54)	-216 (25)	5989 (89)	148 (9)
H(C41)3	2466 (57)	-294 (28)	3695 (96)	148 (9)
H(C12)	4020 (42)	1213 (20)	7431 (67)	94 (7)
H(C13)	6075 (41)	1063 (20)	8057 (67)	94 (7)
H(C14)	7305 (46)	1613 (20)	6058 (63)	94 (7)
H(C15)	6494 (44)	2239 (20)	3842 (67)	94 (7)
H(C16)	4464 (44)	2306 (21)	3329 (70)	94 (7)
H(C62)	-35 (50)	455 (24)	9040 (80)	116 (9)
H(C63)	-1449 (47)	523 (23)	1221 (76)	116 (9)
H(C64)	-2132 (50)	1460 (24)	1568 (80)	116 (9)
H(C65)	-1345 (50)	2311 (24)	9726 (76)	116 (9)
H(C66)	-18 (46)	2152 (23)	7781 (74)	116 (9)

Table 4. Bond lengths (\AA)

P—O	1.479 (3)	P—N	1.661 (3)
P—C(2)	1.794 (4)	P—C(11)	1.786 (4)
C(2)—C(3)	1.488 (6)	C(3)—C(31)	1.515 (7)
C(3)—C(4)	1.345 (6)	C(4)—C(41)	1.511 (7)
C(4)—C(5)	1.476 (6)	C(5)—C(6)	1.338 (5)
C(6)—C(61)	1.494 (5)	C(6)—N	1.393 (5)
C(11)—C(12)	1.371 (6)	C(12)—C(13)	1.383 (7)
C(13)—C(14)	1.368 (8)	C(14)—C(15)	1.339 (9)
C(15)—C(16)	1.360 (8)	C(16)—C(11)	1.397 (6)
C(61)—C(62)	1.398 (6)	C(62)—C(63)	1.375 (8)
C(63)—C(64)	1.347 (9)	C(64)—C(65)	1.362 (9)
C(65)—C(66)	1.409 (7)	C(66)—C(61)	1.388 (6)
H(N)—N	0.83 (3)	H(C2)1—C(2)	0.99
H(C2)2—C(2)	0.99	H(C5)—C(5)	0.88 (4)
H(C31)1—C(31)	0.99 (6)	H(C31)2—C(31)	0.99 (6)
H(C31)3—C(31)	0.97 (6)	H(C41)1—C(41)	0.95 (6)
H(C41)2—C(41)	1.04 (6)	H(C41)3—C(41)	0.83 (6)
N—H(N)···O	2.787 (5)	H(N)···O	1.96 (4)

Table 5. Selected bond angles ($^\circ$)

N—P—C(2)	103.1 (2)	N—P—O	112.7 (2)
N—P—C(11)	107.3 (2)	O—P—C(2)	116.3 (2)
O—P—C(11)	109.2 (2)	C(11)—P—C(2)	107.6 (2)
P—C(2)—C(3)	111.2 (3)	C(2)—C(3)—C(4)	120.8 (4)
C(3)—C(4)—C(5)	122.7 (4)	C(4)—C(5)—C(6)	130.5 (4)
C(5)—C(6)—N	123.9 (4)	C(6)—N—P	130.5 (3)
C(31)—C(3)—C(2)	115.4 (4)	C(31)—C(3)—C(4)	123.9 (4)
C(41)—C(4)—C(3)	122.9 (4)	C(41)—C(4)—C(5)	114.4 (4)
H(N)—N—C(6)	119 (2)	H(N)—N—P	109 (2)

derivative of 1-oxo-1-phenyl-3,4-dimethyl-3-phosphalene is a mixture of two isomers, which may be distinguished by their different melting points, infrared spectra and solubilities in organic solvents. The crystal structure of the higher melting derivative (II) (m.p. 203 $^\circ$), which is also much less soluble in organic solvents than its lower melting counterpart (I) (m.p. 196 $^\circ$), showed it to be a 2-oxocycloheptadiene linked into dimers *via* two N—H···O hydrogen bonds of length 2.889 (5) \AA . Although the ^1H n.m.r. spectra of

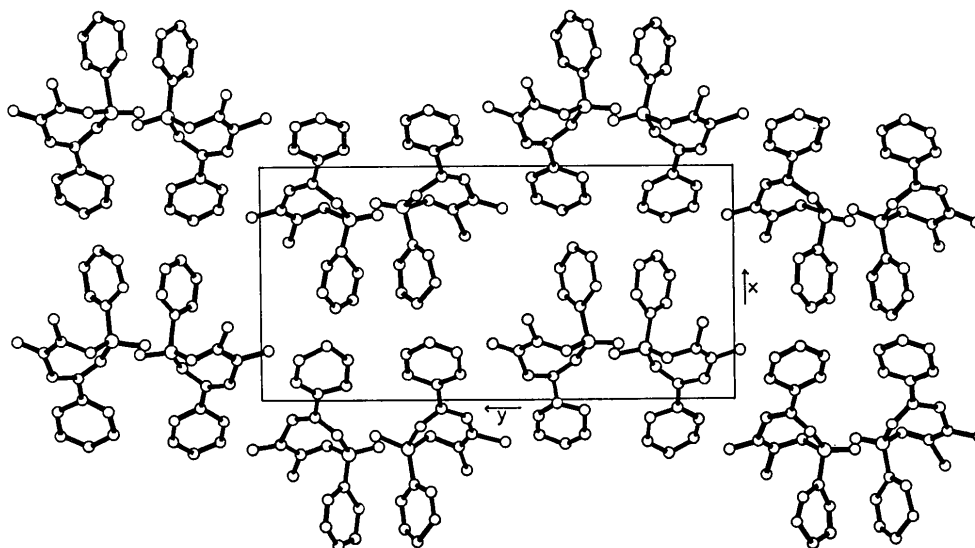


Fig. 2. Projection of the structure perpendicular to [001].

the two derivatives (in CDCl_3) were identical, small differences in the OH-NH region of the infrared spectra (in CHBr_3) allowed the inference that hydrogen bonding in (I) is stronger than in (II). On the basis of this spectral evidence and differences in the chemical properties of the two isomers, it was postulated that (I) was, in fact, a 2-hydroxycycloheptatriene displaying $\text{O-H}\cdots\text{N}$ intermolecular hydrogen bonding. This structural investigation was undertaken in order to clarify the exact nature of isomer (I).

The results show that both (I) and (II) are actually 2-oxocycloheptadienes and that the marked differences in some aspects of their spectral and chemical properties result from the nature of their association through hydrogen bonding. In (I) the molecules are linked into infinite chains in the [001] direction by linear $\text{N-H}\cdots\text{O}$ hydrogen bonds of length 2.787 (5) Å [H-N 0.83 (3), $\text{H}\cdots\text{O}$ 1.96 (4) Å]. These are much shorter and presumably stronger than those of length 2.889 (5) Å in the dimers of (II). The difference in the nature of the association and thereby the packing of the molecules in (I) (see Fig. 2) and (II) is highlighted, in addition, by the lower density of 1.14 g cm^{-3} for (I) which contrasts with 1.23 g cm^{-3} for (II). An explanation for the existence of weaker $\text{N-H}\cdots\text{O}$ hydrogen bonds in the dimer may be sought in terms

of the unavoidable steric interactions in this modification (*e.g.* $\text{O}\cdots\text{O}$ 3.40 Å). No significant differences are to be observed between the bond lengths and angles of the molecule in its two forms. Coordination at N is trigonal with a very short $\text{N-C}(6)$ distance of 1.393 (5) Å indicative of a strong interaction between the N lone pair and the dienic system of the ring.

This work was carried out within the technology programme of the Bundesministerium für Forschung und Technologie (BRD). The calculations were carried out on the institute PDP-10 computer with the crystal structure analysis program *SHELX* (G. M. Sheldrick) and ancillary programs written by myself. I am indebted to Dr F. Mathey, Institute National de Recherche Chimique Appliquee, Vert-le-Petit, France for the provision of crystals and to Frau A. Borkenstein for assistance throughout this work.

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