(0.6 g, 5.08 mmol) in dimethylformamide (5 ml). The reaction mixture was poured onto crushed ice, stirred for 5 min and the resulting solid filtered and dried *in vacuo*. Column chromatography on silica with CH_2Cl_2/CH_3OH as eluant gave the product as a brown powder in 66% yield. ^{1}H NMR ($CDCl_3$): δ 8.65 (2H, *d*), 8.31 (2H, *d*), 7.86–7.60 (6H, *m*). Pale-yellow truncated octahedral crystals were obtained from CH_2Cl_2/hexane solution.

Crystal data

$C_{19}H_{10}N_2O_2$	Mo $K\alpha$ radiation
M_r = 298.29	λ = 0.71073 Å
Orthorhombic	Cell parameters from 25 reflections
Pbcn	θ = 12.05–17.43°
a = 14.997 (6) Å	μ = 0.092 mm^{-1}
b = 12.898 (9) Å	T = 293 (2) K
c = 14.743 (14) Å	Truncated octahedron
V = 2852 (4) Å^3	0.46 × 0.46 × 0.40 mm
Z = 8	Pale yellow
D_x = 1.390 Mg m^{-3}	
D_m not measured	

Data collection

Siemens *P*4 diffractometer	θ_{max} = 25.05°
ω scans	$h = 0 \rightarrow 17$
Absorption correction: none	$k = 0 \rightarrow 15$
2520 measured reflections	$l = 0 \rightarrow 17$
2520 independent reflections	3 standard reflections every 97 reflections intensity decay: 2%
1162 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0693P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.068	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.163	$\Delta\rho_{max}$ = 0.176 e Å^{-3}
S = 0.926	$\Delta\rho_{min}$ = −0.258 e Å^{-3}
2520 reflections	Extinction correction: none
208 parameters	Scattering factors from *International Tables for Crystallography* (Vol. C)
H atoms riding using *AFIX* in *SHELXL*93 (Sheldrick, 1993)	

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.216 (4)	C7—C8	1.351 (5)
C1—N1	1.405 (5)	C8—C9	1.401 (5)
C1—C2	1.471 (5)	C9—C10	1.357 (6)
C2—C3	1.375 (5)	C10—C11	1.414 (5)
C2—C11	1.409 (5)	C10—C12	1.470 (5)
C3—C4	1.400 (5)	C12—O2	1.219 (4)
C4—C5	1.367 (6)	C12—N1	1.403 (5)
C5—C6	1.409 (5)	N1—C13	1.448 (4)
C6—C7	1.411 (5)	C15—C19	1.444 (6)
C6—C11	1.416 (5)	C19—N2	1.138 (5)
O1—C1—N1	119.6 (4)	N1—C12—C10	117.0 (3)
O1—C1—C2	123.8 (4)	C12—N1—C1	125.0 (3)
N1—C1—C2	116.6 (4)	C12—N1—C13	117.1 (3)
C11—C2—C1	120.3 (3)	C1—N1—C13	117.8 (3)
C11—C10—C12	119.9 (4)	C14—C13—N1	120.4 (3)
C2—C11—C10	121.1 (3)	C18—C13—N1	119.1 (3)
O2—C12—N1	119.8 (3)	C16—C15—C19	119.3 (3)
O2—C12—C10	123.2 (4)	N2—C19—C15	178.6 (5)

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1259). Services for accessing these data are described at the back of the journal.

References

Clark, G. R. & Hall, S. B. (1989). *Acta Cryst.* C**45**, 67–71.

Easton, C. J., Gulbis, J. M., Hoskins, B. F., Scharfbillig, I. M. & Tiekink, E. R. T. (1992). *Z. Kristallogr.* **199**, 249–254.

Jazwinski, J., Blacker, A. J., Lehn, J.-M., Cesario, M., Guilhem, J. & Pascard, C. (1987). *Tetrahedron Lett.* **28**, 6057–6060.

Lindeman, S. V., Ponomarev, I. I. & Rusanov, A. L. (1995). *Acta Cryst.* C**51**, 2157–2161.

Merlino, S. & Sartori, F. (1982). *Acta Cryst.* B**38**, 1476–1480.

Mocharla, R., Powell, D. R. & van der Helm, D. (1984). *Acta Cryst.* C**40**, 1369–1371.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1990). *SHELXTL/PC*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Siemens (1994). *XSCANS Users Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Spek, A. L. (1995). *PLATON. Molecular Geometry Program*. University of Utrecht, The Netherlands.

Whitlock, H. W. & Sheridan, R. E. (1988). *J. Am. Chem. Soc.* **110**, 4071–4073.

Zimmerman, S. C. & van Zyl, C. M. (1987). *J. Am. Chem. Soc.* **109**, 7894–7896.

Acta Cryst. (1997). C**53**, 1119–1122

1,8-Bis(dimethylphosphino)naphthalene: an Unusual Case of Pseudosymmetry

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Abstract

The title compound, $C_{14}H_{18}P_2$, crystallizes in the rare tetragonal space group $P4_2bc$ with two independent mol-

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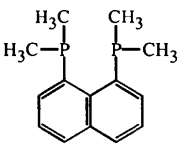
ecules, each of which displays crystallographic twofold symmetry. In both molecules, the proximity of the PMe_2 groups leads to distortion, the main feature of which is the out-of-plane displacement of the P atom [by 0.378 (5) and 0.297 (6) Å]. The structure displays a marked pseudosymmetry, with local inversion centres each relating four pairs of molecules.

Comment

We are interested in the structure and properties of 1,8-diphosphine-substituted naphthalenes. We present here the first in a series of structure determinations, that of 1,8-bis(dimethylphosphino)naphthalene, (I).



(I)

The compound crystallizes in the rare space group $P4_2bc$ (No. 106). A recent paper (Utz, Geib & Cooper, 1996) described the centrosymmetric counterpart, $P4_2/mbc$, as rare, because it occurs only 13 times in the Cambridge database (Allen & Kennard, 1993); $P4_2bc$ is represented 12 times. Our structure displays unusual pseudosymmetry, as discussed below.

The structure (Fig. 1) consists of two independent molecules, each with crystallographic twofold symmetry; the central bond of the naphthalene moiety, C5—C6, lies along the twofold axes 1,0,z (molecule 1) and 0.5,0,z (molecule 2).

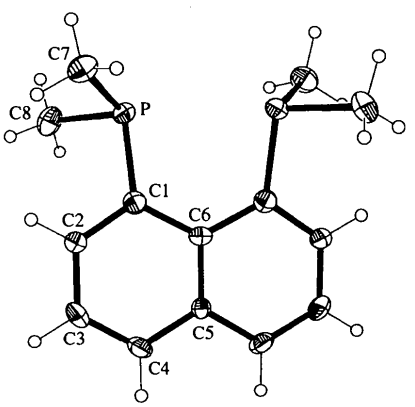


Fig. 1. One of two independent molecules of the title compound in the crystal. Ellipsoids represent 50% probability levels. Only the asymmetric unit is numbered.

The two bulky PMe_2 groups necessarily lie close to each other, with P···P distances of 3.070 (1) and 3.036 (1) Å, much less than the double van der Waals radius of 3.8 Å for phosphorus (*cf.* 3.052 Å in the diphenylphosphino analogue; Jackson, James, Orpen & Pringle, 1993). This leads, as expected, to steric distortions in the molecule. The main distortions involve a twisting of the molecule such that the torsion angles P—C1···C1#—P# are 30.7 (2) and 20.0 (2)°. In each of the independent rings, the atoms C1–C4 are essentially coplanar (mean deviations 0.010 and <0.001 Å), with small displacements of C5 [0.042 (6) and 0.049 (5) Å] and C6 [0.139 (5) and 0.077 (5) Å], and a much larger displacement of the P atom in the opposite direction [0.378 (5), 0.297 (6) Å]. It is surprising that the extent of this distortion is appreciably different in the two molecules; the in-plane distortions are, however, slightly greater for molecule (2) [C6—C1—P 121.6 (4) and 123.1 (3)°; additionally, the bonds C1—C6 and C5—C6 are slightly longer than the standard naphthalene values of 1.420 and 1.422 Å; Allen *et al.*, 1987]. Table 2 shows associated molecular dimensions; our recent more extensive discussions of distortions in 1,8-disubstituted naphthalene systems can be found in Bahl, Grahn & Jones (1996*a*,*b*). The methyl substituents show an approximately 'bisecting' conformation with respect to the ring plane, whereby the torsion angles X—P—C1—C2 are 15 and 24° (X is the centre of gravity of the three atoms bonded to phosphorus). For a detailed discussion, see Heinicke *et al.* (1996).

The pseudosymmetry of the structure is discussed in the following. Systematic absences indicated either space group $P4_2bc$ or $P4_2/mbc$. The intensity statistics were centrosymmetric ($\langle E^2 - 1 \rangle = 0.923$) and we therefore chose the latter space group. However, all attempts to solve the structure failed. For a small structure and with data of reasonable quality this is nowadays unusual.

More in hope than expectation, we then applied direct methods in $P4_2bc$, whereupon the first run yielded the complete structure (two half molecules). However, this is not definite proof that the structure is non-centrosymmetric; an old stratagem of the multisolution philosophy allowed for solving difficult centrosymmetric structures in the corresponding non-centrosymmetric space group and then transforming back to the higher symmetry. It was apparent that the coordinates of related atoms in the two molecules were closely related (indeed, correlation coefficients as high as 0.90 for the z coordinates of C6/C6′ were observed during refinement) but all attempts to transform the coordinates to the higher symmetry space group failed.

The packing diagram (Fig. 2) shows that the molecules form layers parallel to the xy plane. A more detailed analysis shows that the structure contains essentially exact local inversion centres at (0.5, 0.25, 0.5) or (0.25, 0.5, 0.5), each of which relates (a different) four pairs of molecules. Additionally, local glide planes can be identified. However, none of these symmetry elements increases the global symmetry. We are thus reasonably confident that the space group is correct.

[With hindsight, it is clear that the pairs of atoms on the twofold axes (C5, C5′; C6, C6′) can never be made equivalent, because the translation of $0.5x$ must always remain; furthermore, a referee points out that considerations of molecular size preclude molecular packing along the z axis in the higher symmetry]. Marsh (1997) has noted similar effects in non-centrosymmetric orthorhombic structures with more than one independent molecule.

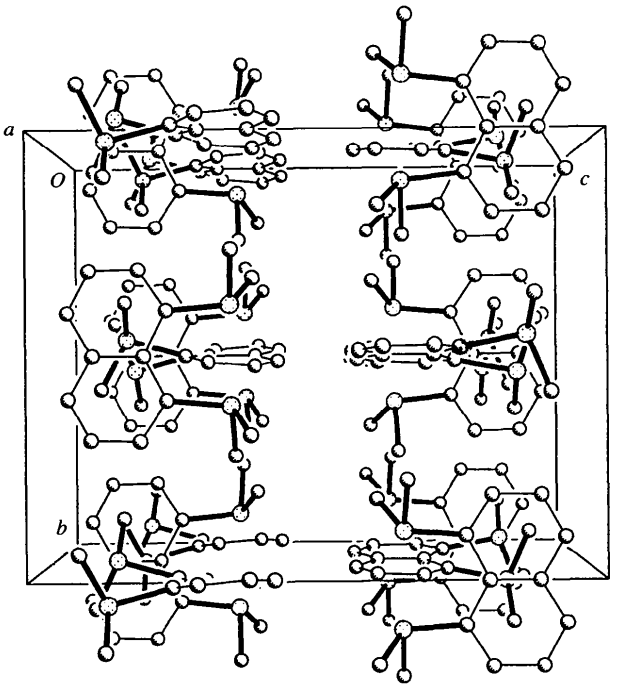


Fig. 2. Packing diagram viewed down the x axis. Radii are arbitrary. H atoms have been omitted.

Experimental

The title compound was obtained according to the method of Costa & Schmidbaur (1982) and recrystallized from chloroform/ethanol at 213 K.

Crystal data

$C_{14}H_{18}P_2$
M_r = 248.22
Tetragonal
$P4_2bc$
a = 12.8075 (18) Å
c = 16.419 (3) Å
V = 2693.2 (8) Å^3
Z = 8
D_x = 1.224 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 48 reflections
θ = 10.0–11.5°
μ = 0.295 mm^{-1}
T = 143 (2) K
Tablet
0.80 × 0.30 × 0.20 mm
Yellow

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: none
3208 measured reflections
3092 independent reflections
2670 reflections with $I > 2\sigma(I)$
R_{int} = 0.012

θ_{max} = 27.5°
$h = -16 \rightarrow 16$
$k = -11 \rightarrow 11$
$l = -21 \rightarrow 21$
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.101
S = 1.064
3092 reflections
151 parameters
H atoms: methyl groups rigid, others riding
$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 1.7207P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004

$\Delta\rho_{max}$ = 0.318 e Å^{-3}
$\Delta\rho_{min}$ = −0.235 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.20 (17) (based on 1696 Friedel pairs)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P	0.96206 (6)	0.11367 (5)	0.64850 (4)	0.02063 (17)
C1	1.0001 (2)	0.1000 (4)	0.7566 (3)	0.0203 (9)
C2	1.0149 (3)	0.1885 (3)	0.8020 (3)	0.0244 (8)
C3	1.0243 (3)	0.1867 (3)	0.8879 (2)	0.0263 (8)
C4	1.0133 (3)	0.0942 (4)	0.9286 (3)	0.0242 (9)
C5	1	0	0.8841 (4)	0.0166 (14)
C6	1	0	0.7968 (5)	0.0178 (14)
C7	1.0790 (3)	0.1753 (3)	0.6050 (2)	0.0312 (7)
C8	0.8765 (2)	0.2299 (2)	0.6524 (2)	0.0315 (7)
P′	0.54102 (6)	0.11119 (5)	0.35336 (5)	0.01939 (16)
C1′	0.5141 (3)	0.0989 (3)	0.2429 (2)	0.0160 (7)
C2′	0.5193 (3)	0.1886 (3)	0.1960 (3)	0.0239 (8)
C3′	0.5169 (3)	0.1862 (4)	0.1107 (3)	0.0277 (9)
C4′	0.5095 (3)	0.0946 (4)	0.0723 (3)	0.0256 (10)
C5′	1/2	0	0.1145 (4)	0.0222 (15)
C6′	1/2	0	0.2028 (5)	0.0146 (13)
C7′	0.4194 (3)	0.1729 (3)	0.3891 (2)	0.0320 (8)
C8′	0.6269 (2)	0.2269 (2)	0.3576 (2)	0.0279 (6)

Table 2. *Selected geometric parameters (Å, °)*

P—C7	1.837 (3)	P′—C7′	1.842 (3)
P—C1	1.848 (5)	P′—C8′	1.847 (3)
P—C8	1.850 (3)	P′—C1′	1.853 (4)
C1—C2	1.370 (6)	C1′—C2′	1.385 (6)
C1—C6	1.441 (6)	C1′—C6′	1.439 (5)
C2—C3	1.416 (6)	C2′—C3′	1.401 (6)
C3—C4	1.367 (7)	C3′—C4′	1.335 (7)
C4—C5	1.420 (5)	C4′—C5′	1.401 (6)
C5—C6	1.434 (10)	C5′—C6′	1.449 (10)
C7—P—C1	101.49 (15)	C7′—P′—C8′	98.47 (16)
C7—P—C8	98.67 (16)	C7′—P′—C1′	101.02 (15)
C1—P—C8	101.46 (18)	C8′—P′—C1′	102.48 (17)
C2—C1—C6	119.1 (4)	C2′—C1′—C6′	118.8 (4)
C2—C1—P	118.8 (3)	C2′—C1′—P′	117.7 (3)

C6—C1—P	121.6 (4)	C6′—C1′—P′	123.1 (3)
C5—C6—C1^{i}	117.3 (3)	C1′—C6′—C1′^{ii}	125.5 (6)
C5—C6—C1	117.3 (3)	C1′—C6′—C5′	117.3 (3)
C1^{i}—C6—C1	125.5 (6)	C1′^{ii}—C6′—C5′	117.3 (3)
P—C1—C2—C3	167.6 (3)	P′—C1′—C2′—C3′	169.6 (3)
P—C1—C6—C5	−162.00 (14)	P′—C1′—C6′—C1′^{ii}	11.88 (15)
P—C1—C6—C1^{i}	18.00 (14)	P′—C1′—C6′—C5′	−168.12 (15)

Symmetry codes: (i) $2-x, -y, z$; (ii) $1-x, -y, z$.

The absolute structure was determined by the method of Flack (1983) and the origin was fixed by the method of Flack & Schwarzenbach (1988).

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1288). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–S19.

Bahl, A., Grahn, W. & Jones, P. G. (1996*a*). *Acta Cryst.* C**52**, 2014–2017.

Bahl, A., Grahn, W. & Jones, P. G. (1996*b*). *Acta Cryst.* C**52**, 2017–2020.

Costa, T. & Schmidbaur, H. (1982). *Chem. Ber.* **115**, 1374–1378.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* A**44**, 499–506.

Heinicke, J., Kadyrov, R., Kindermann, M. K., Kloss, M., Fischer, A. & Jones, P. G. (1996). *Chem. Ber.* **129**, 1061–1071.

Jackson, R. D., James, S., Orpen, A. G. & Pringle, P. G. (1993). *J. Organomet. Chem.* **458**, C3–C4.

Marsh, R. E. (1997). Personal communication and publication in preparation.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Siemens (1994). *XP. Interactive Molecular Graphics Program*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Stoe & Cie (1992*a*). *DIF*4. *Diffractometer Control Program*. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1992*b*). *REDU*4. *Data Reduction Program*. Stoe & Cie, Darmstadt, Germany.

Utz, T. L., Geib, S. J. & Cooper, N. J. (1996). *Acta Cryst.* C**52**, 2992–2994.

Acta Cryst. (1997). C**53**, 1122–1124

Methyl 8-Hydroxy-1,2,3,4-tetrahydronaphthalene-5-carboxylate

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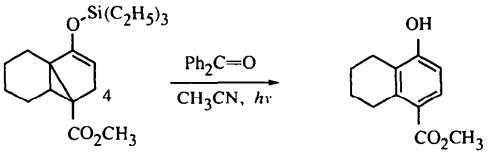
Abstract

All non-H atoms in the two identical molecules of the title compound, $C_{12}H_{14}O_3$, lie on a crystallographic mirror plane, except for C2 and C3, which lie equally above and below the plane by approximately 0.4 Å. Intermolecular hydrogen bonds between the phenol group and the carboxylate O atom link the molecules into chains which lie along the *a* axis.

Comment

During the course of our studies of the photochemical [2+2] cycloaddition of carbonyl compounds with cyclopropyl-substituted silyl enol ethers, a mixture of the tricyclic silyl enol ether, (1), and benzophenone were subjected to UV irradiation. Only one product of this type, (2), in 28% yield, was isolated from the reaction mixture. The ^{1}H and ^{13}C NMR spectra were insufficient for unequivocal structural assignment of this material and so an X-ray structural analysis was carried out on (2).



(1) (2)

Compound (2) was formed from initial H4-atom abstraction by photoexcited triplet biradical benzophenone, followed by cyclopropylmethyl radical fragmentation; this gave a radical intermediate that underwent subsequent oxidation and hydrolysis. This product is unusual, since such reactions normally result in an oxetane product by way of the well known Paterno–Büchi reaction (Porco & Schreiber, 1991).

Essentially, there are two identical molecules in the asymmetric unit. For both molecules, all of the non-H atoms lie on a mirror plane, except for C2 and

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