Outstanding Steric Hindrance: Structure of Bis(2,4,6-tri-*tert*-butylphenylphosphinoyl)-methane

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Abstract. $C_{37}H_{62}O_2P_2$, $M_r = 600.85$, monoclinic, $P2_1/n$, $a = 10.104$ (2), $b = 22.381$ (5), $c = 16.186$ (3) Å, $\beta = 91.93$ (2)°, $V = 3658.19$ Å^3, $Z = 4$, $D_x = 1.091$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, μ(Mo $K\alpha$) = 1.43 cm^{-1}, $F(000) = 1320$, $T = 233$ K, $wR = 0.070$, $w = 1/\sigma^2(F_o)$ for 392 refined parameters and 3428 unique, observed reflections with $I \geq 2.0\sigma(I)$. The bonding of two 2,4,6-tri-*tert*-butylphenylphosphinoyl substituents to a common methylene group results in a very crowded molecule whose steric strain is mainly relieved by a boat distortion of the phenyl rings. Bond lengths and angles do not show major deviations from standard values nor does the compound isomerize to the *P*-hydroxo isomer.

Introduction. Stable compounds containing multiple bonds involving heavier main-group elements have recently attracted considerable attention. Interest focused mainly on silicon–silicon (Fink, Michalczyk, Haller, West & Michl, 1984) and silicon–carbon double bonds (Brook *et al.*, 1982; Wiberg & Wagner, 1983; Wiberg, Wagner & Müller, 1985), and on systems containing unsaturated Group V*b* elements, in particular P, As and Sb (Cowley, 1984*a,b*; Becker, Becker & Mundt, 1983; Appel, Knoll & Ruppert, 1981).

Structure determinations laid the ground for a description of the bonding in these novel unsaturated systems. This was hampered, however, by the fact that extremely bulky substituents were generally necessary for a successful stabilization, thus giving rise to the question whether the observed highly hindered multiple bond geometries represented true 'standard' cases, or whether they were distorted by substituent effects. As a case in point, the first experimentally determined silicon–carbon double bond length (Brook *et al.*, 1982) was found to be drastically longer than values proposed on the basis of highly accurate *ab initio* calculations (Schaefer, 1982); this was explained by steric and electronic substituent effects (Apeloig & Karni, 1984). A subsequent structure determination on a silaethene containing less-demanding and electronic-

ally indifferent substituents gave values virtually identical to the theoretical figures (Wiberg *et al.*, 1985).

Though highly desirable, similar assessments of the substituent effect on the multiple bond geometry of other heavy main-group elements have not yet been made, however.

We report here on the structure determination of the highly hindered bis(2,4,6-tri-*tert*-butylphenylphosphinoyl)methane (BPM) which contains the very bulky 2,4,6-tri-*tert*-butylphenyl (Ar*) substituent. It was prepared by addition of two moles of H_2O to the parent diphosphaallene Ar*P=C=PAr* (DPA) (Karsch, Köhler & Reisacher, 1984; Appel, Fölling, Josten, Siray, Winkhaus & Knoch, 1984; Yoshifuji, Toyota & Inamoto, 1984) under forced conditions (Karsch & Reisacher, 1985, unpublished observations). Comparison of the pertinent structural parameters with those of other compounds containing Ar* substituents allows conclusions about the geometrical effects induced by Ar*. This is important as Ar* has been shown to be a superior substituent for the stabilization of a wide variety of other unsaturated Group V*b* compounds.

BPM

DPA
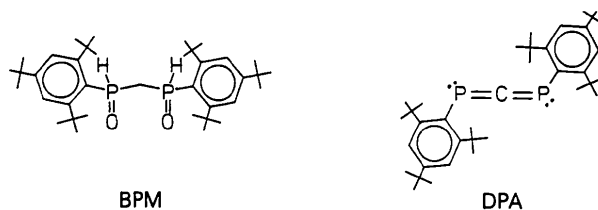
Experimental. Colorless, plate-like crystals (0.4 × 0.4 × 0.1 mm) grown from toluene; Syntex $P2_1$ diffractometer equipped with a monochromator; cell dimensions and their e.s.d.'s obtained by least squares from setting angles of 15 high-angle reflections from various parts of reciprocal space accurately centered on the diffractometer; no indication for symmetry higher than monoclinic by reduced-cell calculations and axial photographs; 5206 measured reflections [scan mode: ω, scan width: 0.7°, scan speed: 0.9–29.3° min^{-1}, (sinλ/λ)$_{max}$ = 0.538 Å^{-1}, *hkl* range: +10,+24,±17] merged

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to give 4778 unique data ($R_{int} = 0.042$) of which 1350 with $I \le 2.0\sigma(I)$ deemed unobserved; orientation and intensity control by means of one standard reflection (202) repeated every 50 reflections; only random intensity fluctuations; Lp but no absorption correction; solution by direct methods and location of remaining atoms by difference Fourier syntheses; treatment of one disordered *tert*-butyl group [at C(5)] as two sets of three half-occupancy C atoms refined in two different blocks (five of these C atoms refined with anisotropic, one with isotropic thermal parameters); all other non-H atoms refined with anisotropic thermal parameters (full matrix); all H atoms located in difference maps with the exception of H(743) which was calculated at its idealized position, and those at the disordered *tert*-butyl group which were not included; H atoms kept fixed with $U_{iso} = 0.05$ Å² in final refinement cycles; function minimized: $\sum w(|F_o| - |F_c|)^2$, unobserved reflections not included in refinement; $R = 0.068$, $wR = 0.070$, $w = 1/\sigma^2(F_o)$; maximum ratio of shift to e.s.d. in last cycle less than 0.02 (0.2 for the disordered methyl groups); final difference map qualitatively featureless, max. residual electron density: +0.46 and −0.35 e Å⁻³ with the highest peaks near the disordered C atoms; computing procedures and programs as described elsewhere (Karsch, Appelt & Müller, 1985); scattering factors for neutral isolated atoms (except for H) from Cromer & Waber (1965), those for H based on a bonded spherical atom model as given by Stewart, Davidson & Simpson (1965), corrections for f' and f'' (Mo $K\alpha$) applied for all atoms (*International Tables for X-ray Crystallography*, 1974).

Discussion. Table 1 contains the final atomic parameters, and Table 2 gives selected interatomic distances and angles.† Table 3 summarizes some deformation parameters for the substituents Ar* in BPM and DPA. Fig. 1 gives a view of the molecule together with the numbering scheme used. Fig. 2 sketches approximate 'side on' views of the two substituents Ar* in order to visualize their distortions.

BPM exists as a discrete monomer in the solid state. No abnormally short intermolecular contacts are observed. Two tetrahedral Ar*P(O)H groups are bonded to a common CH₂ group. Thus any isomerization to the *P*-hydroxo isomer can be excluded for the solid state. One of the P—Ar* bonds [P(1)—C(2)] is nearly antiperiplanar with respect to the central P—C—P skeleton as shown by a torsion angle C(2)—P(1)—C(1)—P(2) of 170.9 (4)°, whereas the other

† Lists of additional crystal structure data, observed and calculated structure factor amplitudes, anisotropic thermal parameters for the non-H atoms, and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42999 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors of the non-H atoms*

$$U_{eq} = \tfrac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}(Å²)
P(1)	1.0575 (2)	0.4813 (1)	0.2483 (1)	0.035
P(2)	0.9485 (2)	0.3576 (1)	0.2953 (1)	0.034
O(1)	0.9258 (4)	0.4955 (2)	0.2122 (3)	0.054
O(2)	0.9245 (4)	0.3189 (2)	0.3672 (2)	0.049
C(1)	1.0587 (6)	0.4198 (2)	0.3211 (3)	0.034
C(2)	1.1566 (6)	0.5381 (2)	0.3044 (3)	0.028
C(3)	1.1010 (5)	0.5725 (2)	0.3695 (3)	0.026
C(4)	1.1877 (6)	0.5958 (2)	0.4302 (3)	0.025
C(5)	1.3243 (5)	0.5901 (2)	0.4274 (3)	0.028
C(6)	1.3759 (5)	0.5639 (2)	0.3585 (3)	0.027
C(7)	1.2972 (6)	0.5384 (2)	0.2950 (3)	0.030
C(31)	0.9509 (6)	0.5881 (3)	0.3755 (3)	0.035
C(32)	0.9293 (6)	0.6348 (3)	0.4421 (3)	0.045
C(33)	0.8999 (6)	0.6170 (3)	0.2944 (4)	0.043
C(34)	0.8645 (6)	0.5338 (3)	0.3976 (4)	0.044
C(51)	1.4141 (6)	0.6180 (3)	0.4953 (3)	0.034
C(71)	1.3714 (6)	0.5160 (3)	0.2180 (3)	0.037
C(72)	1.3020 (6)	0.5407 (3)	0.1383 (3)	0.052
C(73)	1.3865 (6)	0.4472 (3)	0.2171 (4)	0.052
C(74)	1.5141 (6)	0.5404 (3)	0.2170 (4)	0.055
C(8)	1.0124 (6)	0.3281 (2)	0.2003 (3)	0.027
C(9)	1.1450 (6)	0.3054 (2)	0.1964 (3)	0.028
C(10)	1.2110 (5)	0.3137 (2)	0.1243 (3)	0.029
C(11)	1.1526 (6)	0.3411 (2)	0.0538 (3)	0.030
C(12)	1.0185 (6)	0.3514 (2)	0.0549 (3)	0.031
C(13)	0.9429 (5)	0.3429 (2)	0.1251 (3)	0.026
C(91)	1.2080 (6)	0.2655 (2)	0.2657 (3)	0.036
C(92)	1.2497 (6)	0.2989 (3)	0.3458 (3)	0.042
C(93)	1.3350 (6)	0.2349 (3)	0.2365 (4)	0.064
C(94)	1.1088 (6)	0.2158 (3)	0.2857 (4)	0.055
C(111)	1.2294 (6)	0.3561 (3)	−0.0235 (3)	0.041
C(112)	1.2104 (8)	0.4222 (3)	−0.0440 (4)	0.069
C(113)	1.3770 (6)	0.3428 (4)	−0.0111 (4)	0.082
C(114)	1.1771 (8)	0.3190 (3)	−0.0968 (4)	0.064
C(131)	0.7900 (6)	0.3437 (3)	0.1117 (4)	0.039
C(132)	0.7353 (6)	0.4080 (3)	0.1033 (4)	0.057
C(133)	0.7575 (6)	0.3102 (3)	0.0303 (4)	0.055
C(134)	0.7175 (6)	0.3073 (3)	0.1776 (4)	0.066
C(52)	1.3738 (11)	0.5937 (6)	0.5784 (6)	0.041
C(53)	1.5598 (11)	0.6074 (5)	0.4856 (8)	0.049
C(54)	1.3874 (13)	0.6869 (6)	0.4962 (6)	0.047
C(55)	1.4766 (18)	0.6764 (6)	0.4620 (9)	0.097
C(56)	1.5321 (15)	0.5706 (6)	0.5139 (10)	0.078
C(57)	1.3424 (15)	0.6287 (8)	0.5779 (8)	0.090

P—Ar* bond is in a synclinal (*gauche*) conformation [C(8)—P(2)—C(1)—P(1) = 63.7 (4)°]. All *ortho tert*-butyl groups are in approximate staggered conformations with respect to the P—C bonds.

Surprisingly, the P—C and P—O bonds are not elongated over standard values. The valence angle P(1)—C(1)—P(2) [116.2 (3)°] is slightly larger than the tetrahedral norm, however, thus reflecting the great steric bulk of the Ar*P(O)H groups. Peculiarities are apparent in the valence angles at the phosphorus atoms. Whereas the angles C(1)—P—O are not significantly different from the tetrahedral standard, the angles C(Ar*)—P—O are opened to more than 120°. The angles C(Ar*)—P—C(1), on the other hand, are surprisingly small [102.2 (2)°, 103.9 (3)°]. This is the more astonishing as both values are virtually identical, although Ar* bonded to P(2) should suffer from more steric strain due to its *gauche* position (see below). As steric arguments suggest an angle opening, the reason for these abnormally small valence angles is still unknown.

Table 2. *Selected interatomic distances (Å) and angles (°) including some nonbonded contacts, with e.s.d.'s in parentheses*

P(1)–C(1)	1·812(6)	P(2)–C(1)	1·824(6)
P(1)–O(1)	1·470(5)	P(2)–O(2)	1·477(4)
P(1)–C(2)	1·838(5)	P(2)–C(8)	1·814(5)
C(2)–C(3)	1·435(7)	C(8)–C(9)	1·436(8)
C(2)–C(7)	1·433(8)	C(8)–C(13)	1·423(7)
C(3)–C(4)	1·395(7)	C(9)–C(10)	1·376(8)
C(6)–C(7)	1·400(7)	C(12)–C(13)	1·404(8)
C(4)–C(5)	1·388(8)	C(10)–C(11)	1·408(7)
C(5)–C(6)	1·378(7)	C(11)–C(12)	1·375(8)
C(3)–C(31)	1·562(8)	C(9)–C(91)	1·554(7)
C(7)–C(71)	1·559(8)	C(11)–C(111)	1·532(8)
C(5)–C(51)	1·535(8)	C(13)–C(131)	1·553(8)
C(33)···P(1)	3·520(6)	C(92)···O(2)	3·345(8)
C(33)···O(1)	3·042(8)	C(94)···P(2)	3·568(6)
C(34)···P(1)	3·368(6)	C(94)···O(2)	3·271(8)
C(34)···O(1)	3·202(8)	C(132)···P(2)	3·889(6)
C(72)···P(1)	3·367(6)	C(132)···O(1)	3·228(8)
C(73)···P(1)	3·465(6)	C(134)···P(2)	3·169(6)
C(92)···P(2)	3·390(6)	C(134)···O(2)	3·665(8)
P(1)–C(1)–P(2)	116·2(3)		
C(1)–P(1)–O(1)	114·1(3)	C(1)–P(2)–O(2)	112·5(2)
C(1)–P(1)–C(2)	102·2(2)	C(1)–P(2)–C(8)	103·9(3)
O(1)–P(1)–C(2)	121·2(2)	O(2)–P(2)–C(8)	121·9(2)
P(1)–C(2)–C(3)	120·9(4)	P(2)–C(8)–C(9)	121·7(4)
P(1)–C(2)–C(7)	118·4(4)	P(2)–C(8)–C(13)	117·4(4)
C(3)–C(2)–C(7)	119·3(5)	C(9)–C(8)–C(13)	118·7(5)
C(2)–C(3)–C(31)	124·9(5)	C(8)–C(9)–C(91)	122·2(5)
C(4)–C(3)–C(31)	117·4(5)	C(10)–C(9)–C(91)	119·5(5)
C(2)–C(7)–C(71)	126·0(5)	C(8)–C(13)–C(131)	125·6(5)
C(6)–C(7)–C(71)	116·2(5)	C(12)–C(13)–C(131)	116·8(5)

Table 3. *Some deformation parameters for BPM and DPA as defined in Fig. 2*

	α (°)	β (°)	γ (°)	d(P) (Å)
DPA	8·1	5·2	5·7	0·545(9)
	8·2	4·3	6·3	0·567(9)
BPM†	10·0	4·3	11·8	0·807(8)
	15·7	7·3	14·7	1·115(8)

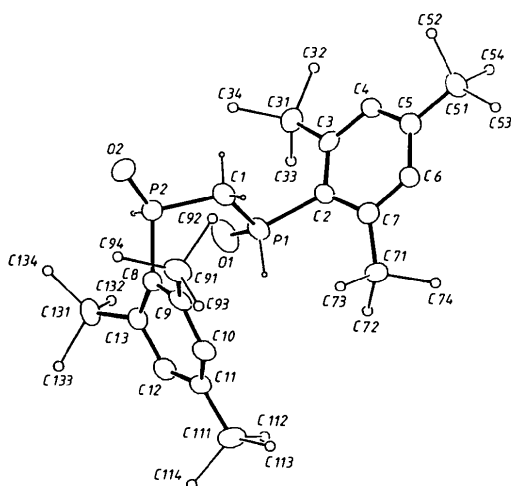† First set of values for Ar* bonded to P(1), second set for Ar* at P(2).

Fig. 1. *ORTEP* diagram (Johnson, 1976) of the molecular structure of BPM showing numbering scheme used [thermal ellipsoids at the 50% probability level; H atoms omitted for clarity except at P(1), P(2), and C(1); methyl groups with arbitrary radii].

The phenyl rings in BPM show marked deviations from planarity. Common to both rings is a distinct boat distortion which is more pronounced for Ar* bonded to P(2). As is evident from the angles listed in Table 3, the deformation is more pronounced in the part of the phenyl ring bonded to phosphorus and containing the *tert*-butyl groups *ortho* to the P—Ar* bonds (Fig. 2). Furthermore, the bonds P(1)—C(2) and P(2)—C(8) are tilted with respect to plane *A* of the phenyl rings resulting in an overall displacement of up to 1·115 (8) Å of the phosphorus atoms from the bottom plane *B* of the rings (Fig. 2). Because similar distortions are a general feature in the structural chemistry of P—Ar*-containing compounds, a comparison of their extent allows important conclusions to be drawn as to the effect of increased steric hindrance on the structural parameters of these compounds.

As Table 3 shows, the distortions are smaller in the sterically less crowded precursor DPA where the substituents Ar* are bonded in a mutually orthogonal fashion to an almost linear P=C=P skeleton (Karsch, Reisacher & Müller, 1984). In Yoshifuji's sterically more congested Ar*$_2$P(O)Cl, however, the deformations are more pronounced than in BPM, as shown by angles $\alpha = 17\cdot8/19\cdot1$, $\beta = 9\cdot8/10\cdot8$, and $\gamma = 10\cdot9/9\cdot1°$ (Yoshifuji, Shima, Inamoto, Hirotsu & Higuchi, 1980). The validity of taking the magnitude of the boat distortion of the phenyl rings in P—Ar*-containing compounds as a measure for their steric congestion is also indicated by differently substituted diphosphenes (Yoshifuji, Inamoto, Hirotsu & Higuchi, 1985) and by BPM itself. In the latter the more distorted substituent Ar* [at P(2)] is more severely hindered because its *gauche* conformation to the P—C—P skeleton results in more sub-van-der-Waals contacts of its *tert*-butyl groups in particular with O(2) and O(1) (Table 2). As is evident from the tilt of the *ortho tert*-butyl groups away from the O atoms (Fig. 1), the repulsive interaction should thereby not be counterbalanced by possible C—H···O hydrogen bonds.
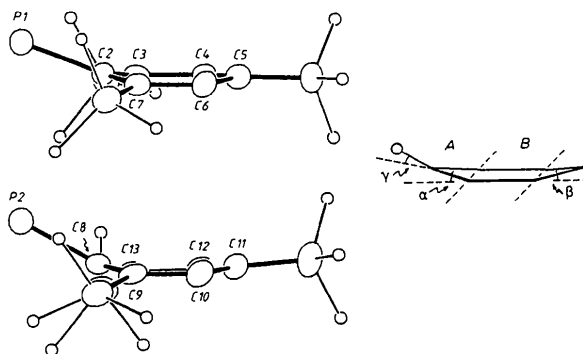

Fig. 2. 'Side on' views of groups Ar* in BPM (*ORTEP*; Johnson, 1976) and definition of deformation parameters.

The observation that the bond lengths in BPM do not show major deviations from standard values in un-hindered molecules renders these findings especially important. They imply that the steric strain in molecules containing Ar* as a stabilizing substituent is relaeved predominantly by a boat deformation of the phenyl rings. One may further conclude that sterically heavily congested molecules stabilized by Ar* should be reasonable approximations of their (unstable) homologues with sterically less demanding substituents and should yield representative structural parameters (particularly bond lengths) for the novel multiple bond geometries.

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4,4-Dinitropentanoic Acid

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Abstract. $C_5H_8N_2O_6$, $M_r = 192 \cdot 1$, monoclinic, $P2_1/n$, $a = 9 \cdot 625$ (6), $b = 9 \cdot 879$ (3), $c = 9 \cdot 875$ (4) Å, $\beta = 121 \cdot 25$ (4)°, $V = 802 \cdot 7$ Å^3, $Z = 4$, $D_x = 1 \cdot 589$ Mg m^{-3}, Cu $K\alpha$ ($\lambda = 1 \cdot 5418$ Å), $\mu = 1 \cdot 25$ mm^{-1}, $F(000) = 400$, $T = 295$ K, 1292 unique reflections, 1088 with $I > 3\sigma$ above background, final $R = 0 \cdot 041$. Bond lengths and angles are normal. The mean deviation (magnitude) of atoms C(1), C(2), C(3) and C(4) from their least-squares plane is 0·048 Å. The carboxyl group and the two nitro groups in the molecule are twisted out of this plane by 8·9, 74·9 and 75·9°, respectively. The two C—N bond distances are identical [1·539 (2) Å] and the four N—O distances of the nitro groups are within 0·005 Å of their mean value of 1·214 Å. The molecules form tight H-bonded dimers [H···O = 1·71 (3) Å] across centers of symmetry.

Introduction. We are investigating the crystal structures of a series of high-density, nitro-group-containing organic compounds as part of an overall study of the relationships between molecular structure and density in energetic materials. The title compound (I) was of interest because of the dinitroalkyl moiety.

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| \\
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NO_2
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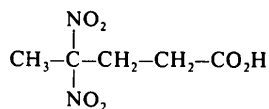
(I)

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