seems to be the pervasive molecular origin of CO semibridging in this kind of molecules.[47]

There is yet another criterion which favors this interpretation: if simple steric reasons were to force the unique CO group toward the Nb(1) and Nb(2) centers, then one should anticipate the Nb(3)–C(33)–O(33) functionality would bend away from them. As can be seen from the drawing in Figure 4, the bridging carbonyl group is leaning toward the Nb(1)–Nb(2) vector, with the Nb(3),C(33),O(33) angle amounting to 169.6 (11)°. An on-scale model demonstrates that the CpNb(CO)$_3$ unit [Nb(3)] could (from a steric point of view) as well be oriented within the cluster in such a way that no semibridging CO is generated. In addition, the finding that the angles Nb(1)–C(33)–Nb(2) and Nb(1)–O(33)–Nb(2) approach orthogonality (Table IV) does certainly not occur by accident and suggests the CO ligand interacts to equal extent with Nb(1) and Nb(2) via its two orthogonal π systems.

Acknowledgment. Our research on "Coordinatively Unsaturated Metal Carbonyls" is funded by the Deutsche Forschungsgemeinschaft (Grant He 954/6). We furthermore express our thanks to the Fonds der Chemischen Industrie, to the Hoechst Aktiengesellschaft, to the Degussa Hanau, and to the BASF Aktiengesellschaft for generous support of this work. Continued assistance by Dr. K. K. Mayer and Mr. E. Fischer (mass spectra), Ms. I. Esprester (elemental analyses), Dr. Th. Burgemeister (NMR spectra), and Ms. B. Reiter (synthetic work) is gratefully acknowledged. We are indebted to Professor F. A. Cotton for valuable hints concerning the nomenclature of metal carbonyls.

---

(47) This interpretation has first been stressed by Cotton et al. for rationalizing the structure of $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$[8,9] and is in agreement with the high reactivity of the latter compound toward thermal dismutation.[10] Remember in this context that **4** can be converted to its precursor **3** under the same conditions as $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$ *cleanly* degrades to $(\eta^5\text{-}C_5H_5)V(CO)_4$.

Crystal Structure and Low-Temperature ^{1}H NMR Spectrum of Tetramesityldiphosphine. Evidence for the Anti-Conformational Preference in Tetraaryldiphosphines

S. G. Baxter, Alan H. Cowley,* Raymond E. Davis,* and Paul E. Riley

Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received July 25, 1980*

Abstract: The structure of tetramesityldiphosphine (**1**) has been determined by single-crystal X-ray diffraction techniques with data collected at −35 °C by counter methods. Clear colorless crystals of **1** form in tetragonal space group $P4_12_12$ with $a = 8.873$ (4) and $c = 39.272$ (16) Å at −35 °C. The calculated density of 1.157 g cm^{-3}, assuming 4 molecules of **1** per unit cell, agrees with the measured value of 1.15 g cm^{-3}. The structure was solved by direct methods and refined by full-matrix least-squares procedures using the 1533 reflections with $I_0/\sigma(I_0) > 2.0$. At convergence, the conventional R index is 0.050. The molecule possesses rigorous C_2 symmetry and exhibits on anti conformation. The slow-exchange limit 200-MHz ^{1}H NMR spectrum of **1** has been recorded and is consistent with a C_2 structure in solution. The molecular structure of **1** is compared to that of 1,1,2,2-tetramesityldisilane, and in most respects the structures are very similar. It is thus concluded that the same factors which dictate the conformational preference in the disilane are also dominant in **1**. Conjugation between the lone pair on phosphorus and the aryl π system does not appear to play a major role in determining the ground-state geometry of **1**.

Introduction

Tetraalkyldiphosphines and 1,1,2,2-tetraalkyldisilanes exhibit remarkably similar stereochemistries, thus leading Mislow and co-workers[1] to conclude that the electronic gauche effect[2] plays a negligible role in regard to the ground-state preference of tetraalkyldiphosphines. Specifically, the gauche ground-state preference of both R_2P-PR_2[3–5] and $R_2HSi-SiHR_2$[1] compounds was found to increase as the steric bulk of the alkyl moiety increased from Me to *t*-Bu. In sharp contrast to the 1,1,2,2-tetraalkyldisilanes, the 1,1,2,2-tetraaryldisilanes were found to exhibit a preference for the anti ground state which increased with the steric demands of the aryl group.[6] Thus, both 1,1,2,2-tetraphenyl- and 1,1,2,2-tetramesityldisilane have been found to adopt the anti conformation in the solid state.[6,7] However, it was not clear that this anti preference would persist in the tetraaryldiphosphines, because the conformational behavior of these compounds could be influenced by conjugation between the phosphorus lone pair and the aryl π system. Accordingly, we have performed a single-crystal X-ray diffraction analysis of tetramesityldiphosphine (**1**), the first such study of a tetraaryldiphosphine. Compound **1**[8] was chosen primarily because definitive structural data already exist for its disilane counterpart.[6] We have also recorded the slow-exchange limit ^{1}H NMR spectrum of **1** in an effort to probe its structure in solution.

Results and Discussion

Crystals of **1** form in space group $P4_12_12$, with four molecules per unit cell. Thus, the molecules possess rigorous C_2 symmetry.

---

(1) Baxter, S. G.; Dougherty, D. A.; Hummel, J. P.; Blount, J. F.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 7795.

(2) For a discussion of the gauche effect, see: (a) Wolfe, S. *Acc. Chem. Res.* **1972**, *5*, 102. (b) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371. (c) Epiotis, N. D. *Ibid.* **1973**, *95*, 3087.

(3) (a) Durig, J. R.; DiYorio, J. S. *Inorg. Chem.* **1969**, *8*, 2796. (b) McAdam, A.; Beagley, B.; Hewitt, T. G. *Trans. Faraday Soc.* **1970**, *66*, 2732. (c) Durig, J. R.; MacNamee, R. W. *J. Mol. Struct.* **1973**, *17*, 426. (d) Cowley, A. H.; Dewar, M. J. S.; Goodman, D. W.; Padolina, M. C. *J. Am. Chem. Soc.* **1974**, *96*, 2648. (e) Ames, D. L.; Turner, D. W. *J. Chem. Soc., Chem. Commun.* **1975**, 179. (f) Elbel, S.; Dieck, H. tom; Becker, G.; Ensslin, W. *Inorg. Chem.* **1976**, *15*, 1235. (g) Schweig, A.; Thon, N.; Vermeer, H. *J. Am. Chem. Soc.* **1979**, *101*, 80. (h) *J. Electron Spectrosc. Relat. Phenom.* **1979**, *15*, 65.

(4) Richter, R.; Kaiser, J.; Sieler, J.; Hartung, H.; Peter, C. *Acta Crystallogr., Sect. B* **1977**, *B33*, 1887.

(5) (a) Brunelle, J. A.; Bushweller, C. H.; English, A. D. *J. Phys. Chem.* **1976**, *80*, 2598. (b) Aime, S.; Harris, R. K.; McVicker, E. M.; Fild, M. *J. Chem. Soc., Chem. Commun.* **1974**, 426.

(6) Baxter, S. G.; Mislow, K.; Blount, J. F. *Tetrahedron* **1980**, *36*, 605.

(7) However, empirical force field (EFF) calculations indicate that the energies of the gauche and anti conformers of 1,1,2,2-tetraphenyldisilane are very close.[6] According to EFF calculations[6] the anti conformer of 1,1,2,2-tetramesityldisilane is more stable than the gauche form by 3 kcal/mol.

(8) Stepanov, B. I.; Karpova, E. N.; Bokanov, A. I. *Zh. Obshch. Khim.* **1969**, *39*, 1544.

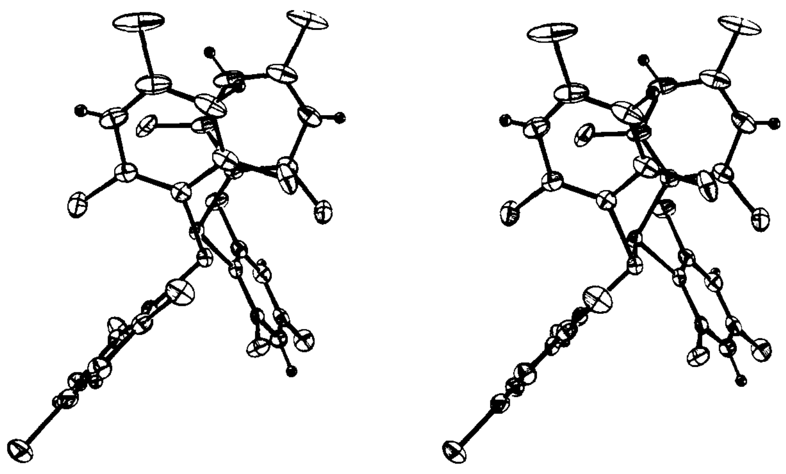

Figure 1. Stereoscopic view of the molecular structure of tetramesityldiphosphine (**1**) as determined by X-ray diffraction.

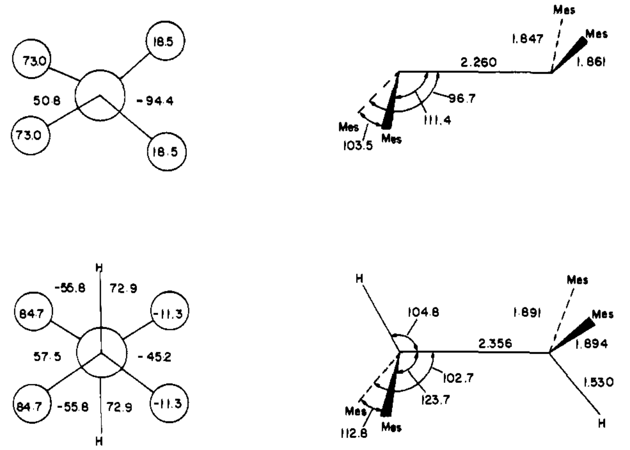

Figure 2. Structural details of the crystal structures of tetramesityldiphosphine (**1**) and 1,1,2,2-tetramesityldisilane[6] (top and bottom rows, respectively). The numbers for the disilane are averages of the values for the two symmetry-independent molecules in the unit cell. In the Newman projections, the numbers in the circles are the P-P-C-C (or Si-Si-C-C) torsion angles, and the other numbers are the torsion angles about the central bond. In the sawhorse figures, the numbers on the left are bond angles and those on the right are bond lengths (Å).

Table I. Bond Lengths (Å), Bond Angles (Deg), and Torsion Angles (Deg) for Tetramesityldiphosphine (**1**)[a]

	Bond Lengths		
P-P′	2.260 (1)	C(6)-C(9)	1.505 (6)
P-C(1)	1.861 (3)	C(10)-C(11)	1.409 (5)
P-C(10)	1.847 (4)	C(10)-C(15)	1.426 (5)
C(1)-C(2)	1.416 (5)	C(11)-C(12)	1.409 (6)
C(1)-C(6)	1.411 (5)	C(11)-C(16)	1.491 (6)
C(2)-C(3)	1.395 (5)	C(12)-C(13)	1.363 (7)
C(2)-C(7)	1.513 (5)	C(12)-H(12)	0.85 (5)
C(3)-C(4)	1.378 (6)	C(13)-C(14)	1.377 (7)
C(3)-H(3)	0.95 (4)	C(13)-C(17)	1.506 (7)
C(4)-C(5)	1.379 (6)	C(14)-C(15)	1.391 (6)
C(4)-C(8)	1.506 (5)	C(14)-H(14)	1.02 (5)
C(5)-C(6)	1.392 (5)	C(15)-C(18)	1.505 (6)
C(5)-H(5)	0.88 (4)		
	Bond Angles		
P′-P-C(1)	111.4 (1)	P-C(10)-C(11)	125.5 (3)
P′-P-C(10)	96.7 (1)	P-C(10)-C(15)	115.3 (3)
C(1)-P-C(10)	103.5 (2)	C(11)-C(10)-C(15)	119.2 (3)
P-C(1)-C(2)	128.1 (3)	C(10)-C(11)-C(12)	118.0 (4)
P-C(1)-C(6)	114.0 (3)	C(10)-C(11)-C(16)	123.7 (3)
C(2)-C(1)-C(6)	117.6 (3)	C(12)-C(11)-C(16)	118.3 (4)
C(1)-C(2)-C(3)	119.6 (3)	C(11)-C(12)-C(13)	123.5 (4)
C(1)-C(2)-C(7)	124.5 (3)	C(11)-C(12)-H(12)	114 (4)
C(3)-C(2)-C(7)	116.0 (3)	C(13)-C(12)-H(12)	122 (4)
C(2)-C(3)-C(4)	122.9 (4)	C(12)-C(13)-C(14)	117.6 (4)
C(2)-C(3)-H(3)	116 (2)	C(12)-C(13)-C(17)	122.2 (5)
C(4)-C(3)-H(3)	120 (2)	C(14)-C(13)-C(17)	120.2 (5)
C(3)-C(4)-C(5)	117.3 (3)	C(13)-C(14)-C(15)	122.9 (4)
C(3)-C(4)-C(8)	121.0 (4)	C(13)-C(14)-H(14)	121 (2)
C(5)-C(4)-C(8)	121.7 (4)	C(15)-C(14)-H(14)	116 (2)
C(4)-C(5)-C(6)	122.5 (4)	C(14)-C(15)-C(10)	118.7 (4)
C(4)-C(5)-H(5)	121 (3)	C(14)-C(15)-C(18)	118.4 (4)
C(6)-C(5)-H(5)	117 (3)	C(10)-C(15)-C(18)	122.9 (3)
C(5)-C(6)-C(1)	120.1 (4)		
C(5)-C(6)-C(9)	117.0 (4)		
C(1)-C(6)-C(9)	122.8 (3)		
	Torsion Angles		
C(1)-P-P′-C(1)′	−94.4	P′-P-C(1)-C(2)	18.5
C(10)-P-P′-C(10)′	50.8	P′-P-C(10)-C(11)	73.0

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits. As stated in the text, the methyl hydrogen atoms were constrained to idealized positions with C-H distances of 0.95 Å.

A stereoview and structural details of **1** are presented in Figures 1 and 2, respectively, and a summary of bond lengths, angles, and torsion angles appears in Table I. Inspection of these data reveals that **1** adopts the anti conformation and as such represents the first case of a diphosphine with four hydrocarbon substituents which prefers the anti ground state. The molecule possesses two pairs of symmetry-related rings; one (the A rings) has ring planes that are nearly parallel to the P-P bond, and the other (the B rings) has ring planes that are almost perpendicular to the central bond. The steric congestion present in the molecule is manifested in the elongation of the P-P bond, which, although within the range of reported values,[9] is quite long for a diphosphine.[3-5] The Ar-P bonds are also slightly longer than those in trimesitylphosphine,[10] and one pair of P-P-C angles is somewhat larger than those usually encountered in tricoordinate phosphorus compounds.[11] It is not surprising that the A rings (those with ortho methyl groups pointing toward the other half of the molecule) possess the larger P-P-C angles and are thus bent away from the central bond or that the A rings possess the longer P-C bonds.

It is also possible to invoke electronic effects to explain the trends in the P-P and P-C bond lengths. Through-bond coupling[12,13]

---

[9] For a collection of P-P bond lengths, see: Cowley, A. H. "Compounds Containing Phosphorus-Phosphorus Bonds"; Dowden, Hutchinson and Ross, Inc.: Stroudsburg, Pa., 1973; p 6.

[10] Blount, J. F.; Maryanoff, C. A.; Mislow, K. *Tetrahedron Lett.* **1975**, 913.

[11] (a) Spencer, C. J.; Lipscomb, W. N. *Acta Crystallogr.* **1961**, *14*, 250. (b) Palenik, G. J.; Donohue, J. *Ibid.* **1962**, *15*, 564. (c) Daly, J. J. *J. Chem. Soc.* **1964**, 6147. (d) *Ibid.* **1965**, 4789. (e) *J. Chem. Soc. A* **1966**, 428. (f) *Ibid.* **1966**, 1020. (g) Bart, J. C. J. *Acta Crystallogr., Sect. B* **1969**, *B25*, 762. (h) Sanz, F.; Daly, J. J. *J. Chem. Soc. A* **1971**, 1083. (i) Calhoun, H. P.; Trotter, J. *J. Chem. Soc. Dalton, Trans.* **1974**, 386. (j) Lex, J.; Baudler, M. *Z. Anorg. Allg. Chem.* **1977**, *431*, 49.

[12] The authors are indebted to Professor Saul Wolfe of Queen's University, Kingston, Ontario, for suggesting this interpretation.

Table II. ^{1}H Chemical Shift Data for Tetramesityldiphosphine (**1**)[a]

proton	temp 60 °C[b]	−40 °C[c,d]
ortho methyl	2.57	1.90, 1.97, 2.15, 2.23, 2.35, 2.78
para methyl	2.10	
Ar–H	6.70	6.46, 6.54, 6.72, 6.81

[a] δ values in ppm. [b] In C_6D_6 with internal standard C_6H_6 at 60 MHz. [c] In $CDCl_3$ with internal standard $CHCl_3$ at 200 MHz. [d] No attempt was made to assign ortho and para methyl signals.

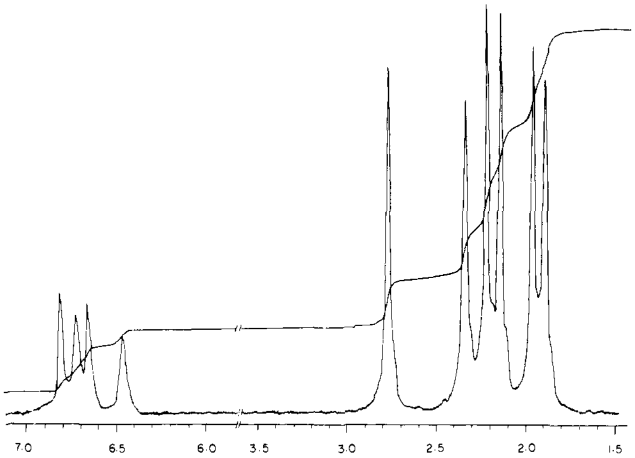

Figure 3. The 200-MHz ^{1}H NMR spectrum of tetramesityldiphosphine (**1**) in $CDCl_3$ at −40 °C.

Table III. Crystallographic Summary for Tetramesityldiphosphine (1)

Crystal Data at −35 °C[a]			
mol formula	$C_{36}H_{44}P_2$	d_{measd}, g cm^{-3} (19 °C; flotation aqueous $ZnCl_2$)	1.15
M_r	538.70		
a, Å	8.873 (4)		
c, Å	39.272 (16)	d_{calcd}, g cm^{-3}	1.157
V, Å^3	3092 (3)	cryst system	tetragonal
		space group	$P4_12_12$ (No. 92) or $P4_32_12$ (No. 96)[b]
		Z	4
		F(000), e	1160
Data Collection at −35 °C[c]			
radiation (Mo Kα), Å	0.710 69		
mode	ω scan		
scan range	symmetrically over 1.0° about $K\alpha_{1,2}$(max)		
background	offset 1.0 and −1.0° in ω from $K\alpha_{1,2}$(max)		
scan rate, deg min^{-1}	2.0–5.0		
check reflctns	4 remeasured after every 96 reflections; analysis[d] of these data indicated only random fluctuation in intensity during the 46 h of data collection with all correction factors less than 0.2σ		
2θ range, deg	4.0–50.0		
total reflctns measd	1703[e]		
data cryst dimens, mm	0.23 × 0.32 × 0.60		
abs coeff, μ(Mo Kα), cm^{-1}	1.67		

[a] Unit cell constants were obtained by least-squares refinement of the setting angles of 29 reflections with $22 < 2\theta < 25°$. [b] As discussed in the text, refinement of both enantiomers yielded no significant structural or statistical results; hence, the structure is reported in space group $P4_12_12$. [c] Syntex LT-1 inert-gas low-temperature delivery system. [d] Henslee, W. H.; Davis, R. E. *Acta Crystallogr., Sect. B* 1975, *31*, 1511. [e] Data were merged as described in text.

of vicinal aryl rings should result in an increase in the P–P bond length and a decrease in the P–C bond length. Such an interaction is maximal when the dihedral angles between the aryl rings and the central bond are 90° and inoperative when these dihedral angles are 0°. The structure of **1** is in accordance with this model. As revealed by Table I and Figure 2, the P–C bond lengths of the B rings (dihedral angle = 73.0°) are significantly shorter (0.014 Å) than those of the A rings (dihedral angle = 18.5°).

In order to probe the solution-phase structure of **1**, we recorded the fast- and slow-exchange limit ^{1}H NMR spectra at +60 and −40 °C, respectively. The chemical shift data are collected in Table II, and the low-temperature spectrum is shown in Figure 3. The high-temperature spectrum exhibits only three signals which are attributable to the aromatic ring protons, the para and ortho methyl groups. On cooling, there are four equal intensity aromatic signals and six equal intensity methyl signals. As has been shown previously, for the tetramesityldisilane[6] and -ethane[14] analogues of **1**, such a splitting pattern is consistent only with structures of C_s, C_2, and C_i symmetry and not with those of C_{2h} and C_1 symmetry. Thus, the NMR data can be viewed as consistent with the C_2 symmetry observed crystallographically.

Direct comparison of the solid-state structure of **1** with that of the disilane analogue[6] is afforded by Figure 2. In most respects the geometries are quite similar. Most notably the conformation of both compounds is C_2 anti (the disilane possesses approximate C_2 symmetry). Another similarity between the two is that both possess two pairs of symmetry-related rings, and, as shown in Figure 2, the two structures also exhibit approximately the same degree of twist in each pair of rings. The structure of **1** also mimics that of the disilane, not only in having one pair of expanded P–P–C angles but also in the relationship between the magnitudes of these angles and the degree of twist of the aryl groups. In both structures the A rings are bent back from the other half of the molecule. There is, however, a difference between the two structures which should be addressed. In the disilane, the C–Si–Si–C torsion angle formed by the A rings is smaller than that formed by the B rings, while in **1** this relationship is reversed. In this respect the structure of **1** is directly analogous to a slightly higher energy conformation of the disilane, which is calculated to lie less than 0.5 kcal/mol above the ground state (compound **2a**$_1$ in ref 6). In light of this small energy separation between the two lowest energy conformations of the disilane (a value close to the error limits of the method[15]), the difference in the relationship between the ring twists and the torsion angles about the central bond in **1** and the disilane is not very disturbing. It is concluded that the same factors which determine the conformational preference of 1,1,2,2-tetramesityldisilane are also dominant in **1**. Thus, the striking stereochemical similarities between tetraalkyldiphosphines and 1,1,2,2-tetraalkyldisilanes are extended to the tetraaryl analogues, even though the conformational differences between the alkyl and aryl systems are pronounced. Although conjugation between the lone pair on phosphorus and the aryl rings is not precluded by the present study, it does not seem to play a major role in determining the ground-state geometry of **1**.

Experimental Section

^{1}H NMR Spectroscopy. Compound **1** was prepared and purified as described in the literature.[8] The high-temperature spectrum was recorded by cross correlation on a Varian A-60 spectrometer equipped with a Nicolet 1080 computer, using C_6D_6 as the solvent and residual C_6H_6 as the internal standard. The low-temperature spectrum was recorded on an N.T. 200 wide-bore spectrometer, operating in the Fourier transform mode. The instrument was locked on the solvent $CDCl_3$, and the residual

---

(13) (a) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. (c) Glieter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696. (d) Dougherty, D. A.; Hounshell, W. D.; Schlegel, H. B.; Bell, R. A.; Mislow, K. *Tetrahedron Lett.* **1976**, 3479.

(14) Finocchiaro, P.; Gust, D.; Hounshell, W. D.; Hummel, J. P.; Maravigna, P.; Mislow, K. *J. Am. Chem. Soc.* **1976**, *98*, 4945.

(15) (a) Dunitz, J. D.; Bürgi, H. B. *MTP Int. Rev. Sci.: Org. Chem., Ser. One* **1976**, 81. (b) Jacobus, J. *Tetrahedron Lett.* **1976**, 2927.

Table IV. Fractional Coordinates and Anisotropic Thermal Parameters (×10^3) for Nonhydrogen Atoms of Tetramesityldiphosphine (1)[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P[b]	0.56460 (11)	0.60362 (10)	0.76026 (2)	338 (5)	304 (5)	257 (4)	−30 (4)	−5 (4)	14 (4)
C(1)	0.6728 (4)	0.5244 (4)	0.7967 (1)	26 (2)	39 (2)	22 (2)	0 (1)	3 (1)	−1 (1)
C(2)	0.6908 (4)	0.3712 (4)	0.8059 (1)	32 (2)	34 (2)	26 (2)	1 (1)	3 (1)	−1 (1)
C(3)	0.7886 (5)	0.3329 (5)	0.8323 (1)	40 (2)	44 (2)	33 (2)	7 (2)	3 (2)	6 (2)
C(4)	0.8701 (4)	0.4384 (5)	0.8502 (1)	33 (2)	65 (3)	25 (2)	10 (2)	0 (1)	−2 (2)
C(5)	0.8507 (4)	0.5876 (5)	0.8414 (1)	38 (2)	53 (3)	33 (2)	−7 (2)	−4 (2)	−8 (2)
C(6)	0.7564 (4)	0.6325 (4)	0.8150 (1)	34 (2)	39 (2)	35 (2)	−4 (2)	2 (2)	−5 (2)
C(7)	0.6086 (5)	0.2415 (4)	0.7891 (1)	55 (2)	31 (2)	43 (2)	−3 (2)	−14 (2)	5 (2)
C(8)	0.9735 (5)	0.3919 (6)	0.8788 (1)	50 (3)	81 (3)	40 (2)	9 (2)	−12 (2)	−2 (2)
C(9)	0.7522 (5)	0.7981 (5)	0.8068 (1)	47 (3)	44 (2)	60 (2)	−7 (2)	−13 (2)	−7 (2)
C(10)	0.4261 (4)	0.7292 (4)	0.7809 (1)	37 (2)	30 (2)	37 (2)	−1 (2)	−9 (2)	−7 (2)
C(11)	0.3461 (4)	0.6967 (4)	0.8119 (1)	33 (2)	44 (2)	36 (2)	1 (2)	−4 (2)	−12 (2)
C(12)	0.2436 (5)	0.8053 (6)	0.8231 (1)	40 (3)	63 (3)	58 (3)	−1 (2)	−1 (2)	−28 (3)
C(13)	0.2216 (5)	0.9417 (6)	0.8080 (1)	38 (2)	50 (3)	92 (3)	6 (2)	−12 (2)	−30 (3)
C(14)	0.3033 (6)	0.9729 (5)	0.7790 (1)	60 (3)	31 (2)	77 (3)	8 (2)	−34 (3)	−13 (2)
C(15)	0.4068 (5)	0.8725 (4)	0.7651 (1)	51 (2)	32 (2)	49 (2)	1 (2)	−22 (2)	−5 (2)
C(16)	0.3619 (4)	0.5529 (5)	0.8303 (1)	47 (2)	67 (3)	36 (2)	−1 (2)	12 (2)	−1 (2)
C(17)	0.1127 (6)	1.0563 (6)	0.8219 (2)	52 (3)	75 (4)	179 (6)	15 (3)	−6 (4)	−58 (4)
C(18)	0.4958 (6)	0.9216 (4)	0.7344 (1)	94 (3)	29 (2)	51 (2)	−7 (2)	−22 (2)	9 (2)

[a] Numbers in parentheses are the estimated standard deviation in the units of the least significant digits for the corresponding parameter. The U_{ij} are the mean square amplitudes of vibration in Å^2 from the general temperature factor expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. The coordinates of symmetry-related atoms not given are obtained by applying the operation $1-y$, $1-x$, $^3/_2 - z$ to the coordinates contained in the table. [b] For the P atom the anisotropic thermal parameters are given ×10^4.

$CHCl_3$ peak was used as an internal standard. Temperatures were measured by observing the spectra of external standards (ethylene glycol and methanol for the high and low temperatures, respectively).

X-ray Crystallography. Single crystals of **1** form as colorless, flattened tetragonal pyramids by slow evaporation of a benzene solution. A suitable crystal was glued to a glass fiber that was attached to the brass pin of a goniometer head. It was then transferred to a Syntex P2$_1$ diffractometer where it was maintained in a stream of cold (−35 °C), dry N_2 during the course of all subsequent crystallographic experiments. Preliminary examination of the crystal with the diffractometer indicated the tetragonal symmetry of space group $P4_12_12$ (No. 92) or $P4_32_12$ (No. 96). A summary of crystal data is given in Table III.

The intensities (I_0) of all reflections within one octant of reciprocal space (Laue symmetry class $4/m$) were measured, as indicated in Table III, assigned standard deviations (with $p = 0.02$), and reduced as described previously.[16] The intensities and associated standard deviations were then averaged as reported elsewhere[17] to yield a symmetry-independent set of reflections of Laue symmetry $4/mmm$. The structure was readily solved in space group $P4_12_12$ by direct methods[18] and refined by full-matrix least-squares procedures.[19]

The function minimized in refinement is $\sum w(|F_o| - |F_c|)^2$, where the weight w is $\sigma(|F_o|)^{-2}$, the reciprocal square of the standard deviation of each observation, $|F_o|$. Neutral atom scattering factors for P, C,[20] and H[21] were used in these calculations, and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections[20] for anomalous scattering of Mo radiation were applied to the P scattering curve. Least-squares convergence was reached for a model in which all nonhydrogen atoms were refined anisotropically, mesityl ring hydrogen atoms isotropically, and methyl hydrogen atoms constrained to idealized positions,[22] with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.050$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.051$, and a standard deviation of an observation of unit weight = $[\sum w(||F_o| - |F_c||)^2/(m - s)]^{1/2} = 3.50$, for $m = 1533$ observations and $s = 189$ variables. Examination of the data near the conclusion of refinement indicated that several low-angle reflections were affected by secondary extinction. Hence, in the final cycles of refinement a small correction[24] (0.5 (2) × 10^{-6} e^{-2}) for this effect was applied to the data. A structure factor calculation using the atomic parameters obtained at least-squares convergence and the 1703 reflections measured during data collection gave R and R_w indices of 0.061 and 0.051, respectively.

For a determination of whether the structural model selected for this data crystal corresponds to the proper enantiomer—and hence to the proper space group—least-squares refinement of the structure was carried out, beginning with the atomic parameters obtained prior to the inclusion of the (small) imaginary corrections ($\Delta f''$) to the phosphorus scattering curve but now with the signs of these corrections reversed.[25] However, at convergence, since this model was indistinguishable from that described above (identical R indices and no significant differences in molecular geometries), the atomic parameters listed in Table IV are those of the first model.

In the final cycle of refinement no shift of an atomic parameter exceeded 0.63 of a corresponding estimated standard deviation (esd). The largest peaks on a final difference electron density map were no greater than ~1 e Å^{-3}.

Atomic positional and thermal parameters, with corresponding esd's as estimated from the least-squares inverse matrix, for the nonhydrogen atoms of **1** are presented in Table IV. Tabulations of fractional coordinates and isotropic thermal parameters for the hydrogen atoms of **1** and of the observed and calculated structure factor amplitudes are available.[26]

Acknowledgment. The authors are grateful to the National Science Foundation (Grant CHE-7910155) and the Robert A. Welch Foundation for generous financial support. We also thank the National Science Foundation for the purchase of the Syntex P2$_1$ diffractometer (Grant GP-37028).

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes and the fractional coordinates and isotropic thermal parameters for the hydrogen atoms of **1** (9 pages). Ordering information is given on any current masthead page.

---

(16) Riley, P. E.; Davis, R. E. *Acta Crystallogr., Sect. B* 1976, *B32*, 381.

(17) Riley, P. E.; Davis, R. E. *J. Organomet. Chem.* **1976**, *113*, 157.

(18) Main, P.; Woolfson, M. M.; Declerq, J. P.; Germain, G., program package MULTAN, 1974.

(19) A listing of principal computer programs used in this work is contained in ref 16.

(20) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(21) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(22) The positions of all hydrogen atoms were apparent from a difference electron density map prepared after convergence of the anisotropic model. During the final cycles of refinement the methyl hydrogen atoms were held at idealized positions.[23]

(23) Collins, R. C. HIDEAL, a local program which calculates idealized atomic coordinates.

(24) Zachariasen, W. H. *Acta Crystallogr., Sect. A* **1968**, *A24*, 212.

(25) It can be shown algebraically that this is the computational equivalent of refinement of the opposite enantiomer.

(26) See paragraph at end of paper regarding supplementary material.