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Molecular Structure of Sterically Crowded Bis(2,2'-biphenylylene)spirophosphoranes. Distortion toward Apical-Basal Ring Placement in a Rectangular Pyramid[1]

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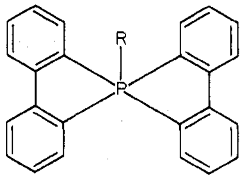
Single-crystal X-ray studies were performed on [8-(dimethylamino)-1-naphthyl]bis(2,2'-biphenylylene)phosphorane, $(C_{12}H_8)_2P(C_{10}H_6NMe_2)$ (V) and (1-naphthyl)bis(2,2'-biphenylylene)phosphorane, $(C_{12}H_8)_2P(C_{10}H_7)$ (VI). The structures of V and VI are located about 64% and 25%, respectively, along a coordinate leading to a rectangular pyramid which has one of the biphenylylene rings in an apical-basal orientation. The structures are a result of steric crowding between the α-naphthyl groups and the biphenylylene rings. V crystallizes in the monoclinic space group $P2_1/c$, with $a = 9.265$ (4) Å, $b = 13.266$ (8) Å, $c = 21.580$ (9) Å, $\beta = 95.50$ (3)°, and $Z = 4$. VI crystallizes in the monoclinic space group $P2_1/n$, with $a = 16.033$ (6) Å, $b = 9.345$ (3) Å, $c = 18.765$ (5) Å, $\beta = 98.68$ (3)°, and $Z = 4$. For VI, solution and refinement included an acetone molecule corresponding to the one to one solvate formula $(C_{12}H_8)_2P(C_{10}H_7)\cdot(CH_3)_2CO$. Data for both compounds were collected, by using an automated Enraf-Nonius CAD4 diffractometer, out to a maximum $2\theta_{Mo\,K\alpha}$ of 55°. Full-matrix least-squares refinement techniques led to the final agreement factors of $R = 0.047$, $R_w = 0.049$ for V on the basis of 3452 reflections having $I \geq 2\sigma_I$ and $R = 0.094$, $R_w = 0.093$ for VI on the basis of 2860 reflections having $I \geq \sigma_I$. On the basis of these structures, implications regarding ligand exchange mechanisms are discussed.

Introduction

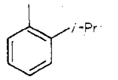
Although the molecular structures of a large assortment of cyclic phosphoranes have been elucidated,[2,3] no examples involving the interesting bis(biphenylylene) series have been studied. The structure of PPh_5,[4] an example of a derivative containing five directly bonded carbon atoms, shows only modest distortion from a regular trigonal bipyramid. In solution, the NMR behavior of PPh_5[5] is indicative of ligands undergoing rapid intramolecular exchange at all temperatures studied. By way of contrast, exchange barriers ranging from 12 to 28 kcal/mol have been determined from NMR studies on spirocyclic pentaorganyl derivatives incorporating a bis(biphenylylene) framework and a fifth ligand that varies in steric properties.[6-12] For all of these derivatives, a ground-state trigonal-bipyramidal structure is consistent with the NMR patterns obtained at temperatures where the exchange process has been slowed sufficiently.

For many cyclic phosphoranes,[13] two intramolecular exchange processes are evident, a lower energy process that presumes a square, or more precisely, a rectangular-pyramidal transition state with ring placement in the basal plane and a higher energy process that suggests diequatorial ring placement in an intervening trigonal bipyramid. The lower energy process corresponds to a Berry pseudorotation[14] with the unique ligand as the pivotal group; the higher energy process corresponds to a related pseudorotation in which one of the ring atoms bonded to phosphorus acts as the pivotal ligand. Usually rotation of the unique ligand about the attached phosphorus bond is required to accompany the exchange process. In the higher energy process it is conceivable that a "square" pyramidal transition state also is involved.[13]

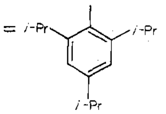
In a detailed study of the temperature dependence of the proton NMR spectra of (2-isopropylphenyl)bis(4,4'-dimethyl-2,2'-biphenylylene)phosphorane (I) and the corresponding 2,4,6-triisopropylphenyl derivative (II), Whitesides et al.[12] interpreted the exchange mechanism for I to involve a Berry permutation integrally coupled with a rotation of the isopropylphenyl moving around the P-aryl bond. For II, axial placement of the triisopropylphenyl ligand in an intermediate trigonal bipyramid is supported. The exchange barriers were $\Delta G^{\ddagger} = 17.8 \pm 0.3$ kcal/mol (56 °C) for I and 26.0 ± 1.2 kcal/mol (202 °C) for II.



I, R =



II, R =



Hellwinkel and co-workers conducted NMR studies[6-8,10,11] on a more extensive series of pentaorganyl compounds containing bis(biphenylylene) units. Their studies indicated the presence of these general processes. More often the lower energy process is detected. Usually, when the higher energy process is indicated, more bulky substituents are present. Occasionally though, each of these processes is consistent with NMR data when very similar compounds are involved. For example, equilibration of the four proton methyl signals above 20 °C for the 2-biphenylyl derivative of the chiral bis(biphenylylene) III is consistent with passage through a rectangular-pyramidal transition state having a basal orientation of the biphenylylene ring network,[6] $\Delta G^{\ddagger} = 15.7$ kcal/mol (20 °C). In contrast, racemization of the related optically active spirocyclic IV is proposed[11] to occur by way of a trigonal-bipyramidal transition state with a diequatorial 2,2'-biphenylylene group, $\Delta G^{\ddagger} = 27.6 \pm 1$ kcal/mol (30 °C).

With the quantitative NMR studies of these bis(biphenylylene) derivatives at hand, it is important to establish

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(1) Pentacoordinated Molecules. 36. Previous paper in the series: Day, R. O.; Sau, A. C.; Holmes, R. R. *J. Am Chem. Soc.* **1979**, *101*, 3790.

(2) Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257.

(3) Holmes, R. R. "Pentacoordinated Phosphorus Compounds, Spectroscopy and Structure"; *ACS Monogr., No. 175*, in press, and references cited therein.

(4) Wheatley, P. J. *J. Chem. Soc.* **1964**, 2206.

(5) Luckenbach, R. "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements"; G. Thieme: Stuttgart, 1973.

(6) Hellwinkel, D. *Chimia* **1968**, *22*, 488.

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(8) Hellwinkel, D.; Wilfinger, H.-J. *Tetrahedron Lett.* **1969**, 3423.

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(10) Hellwinkel, D.; Lindner, W.; Schmidt, W. *Chem. Ber.* **1979**, *112*, 281.

(11) Hellwinkel, D.; Krapp, W. *Chem. Ber.* **1979**, *112*, 292.

(12) Whitesides, G. M.; Eisenhut, M.; Bunting, W. M. *J. Am. Chem. Soc.* **1974**, *96*, 5398.

(13) Holmes, R. R. *J. Am Chem. Soc.* **1978**, *100*, 433 and references in Table IV cited therein.

(14) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

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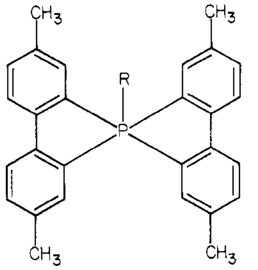
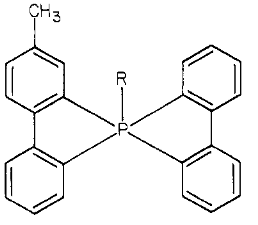
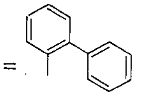


III



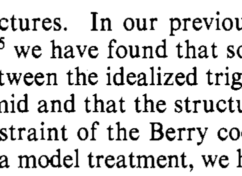
IV

R =



ground-state structures. In our previous work with cyclic phosphoranes,[2,3,15] we have found that solid-state structures span the range between the idealized trigonal bipyramid and rectangular pyramid and that the structural displacement is along the C_{2v} constraint of the Berry coordinate.

On the basis of a model treatment, we have proposed[13] that a changeover in mechanism from the lower to the higher energy process is likely as the steric requirements of the unique ligand are progressively increased for bis(biphenylylenes). It is felt that the determination of the structures of a series of this type might provide evidence for the proposed intermediary of pentacoordinated forms corresponding to that in the aforementioned higher energy process for II. Accordingly, we carried out X-ray structural investigations of the series of bis(2,2′-biphenylylene)spirophosphoranes (kindly supplied by Professor D. Hellwinkel, Institut für Organische Chemie der Universität Heidelberg) in which the fifth ligand R varies in size as methyl, phenyl, 1-naphthyl, and 8-(dimethylamino)-1-naphthyl. The structures of the α-naphthyl compounds V and VI are reported in this paper while the structural study of the methyl VII and phenyl derivative VIII forms the topic of the succeeding paper along with supporting conformational calculations.[16]



V, R = 8-$(CH_3)_2$N-1-Np
VI, R = 1-Np
VII, R = CH_3
VIII, R = Ph
Np = naphthyl

Experimental Section

Space Group Determination and Data Collection for [8-(Dimethylamino)-1-naphthyl]bis(2,2′-biphenylylene)phosphorane (V). Crystals suitable for X-ray diffraction analysis were obtained by recrystallization from acetone. A crystal having dimensions of 0.35 × 0.35 × 0.40 mm was cut from a larger crystalline mass and mounted in a thin-walled glass capillary. Preliminary investigations using an Enraf-Nonius CAD4 automated diffractometer and graphite-monochromated Mo Kα radiation (fine-focus tube, 45 kV, 20 mA, takeoff angle 3.1°, λ($K\alpha_1$) 0.709 30 Å, λ($K\alpha_2$) 0.713 59 Å) indicated monoclinic (2/*m*) symmetry. From the observed extinctions 0*k*0, $k = 2n + 1$, and *h*0*l*, $l = 2n + 1$, the space group was uniquely determined as $P2_1/c$-C_{2h}^5.[17] The lattice constants as determined by the least-squares refinement of the diffraction geometry for 25 reflections having $10.09° \leq \theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 15.75°$ as measured at an ambient temperature of 24 ± 2 °C are $a = 9.265$ (4) Å, $b = 13.266$ (8) Å, $c = 21.580$ (9) Å, and $\beta = 95.50$ (3)°. A unit cell content of four molecules gives a calculated volume of 17.4 Å^3 per nonhydrogen atom, which is in the range to be expected for such molecules. The assignment of $Z = 4$ was confirmed by all subsequent stages of solution and refinement.

Data were collected by using the θ–2θ scan mode, with a θ scan range of (0.65 + 0.35 tan θ)° centered about the calculated Mo K$\bar{\alpha}$ peak position, and scan rates that varied from 0.59 to 4.0°/min. Background counts were measured for half of the total scan time by extending the scan range 25% on either side of the aforementioned limits. The intensity, *I*, for each reflection is then given by $I = (\mathrm{FF}/S)(P - 2(B_1 + B_2))$ where *P* is the counts accumulated during the peak scan, B_1 and B_2 are the left and right background counts, *S* is an integer which is inversely proportional to the scan rate, and FF is either unity or a multiplier to account for the occasional attenuation of the diffracted beam. The standard deviations in the intensities, σ_I, were computed as $\sigma_I^2 = ((\mathrm{FF})^2/S^2)(P + 4(B_1 + B_2)) + 0.002I^2$.

A total of 6013 independent reflections (+*h*, +*k*, ±*l*) having $2° \leq 2\theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 55°$ was measured. Five standard reflections, monitored after every 12 000 s of X-ray exposure time, gave no indication of crystal deterioration or loss of alignment. No corrections were made for absorption ($\mu_{\mathrm{Mo}\,K\bar{\alpha}} = 0.136$ mm^{-1}), and the intensities were reduced to relative amplitudes by means of standard Lorentz and polarization corrections, including corrections for the monochromator.

Solution and Refinement for V. Initial coordinates for the 38 independent nonhydrogen atoms were determined by a combination of direct methods (MULTAN) and standard Fourier difference techniques. Isotropic unit-weighted full-matrix least-squares refinement[18] of the structural parameters for these atoms and a scale factor gave a conventional residual $R = \sum||F_o| - |F_c||/\sum|F_o|$ of 0.104 and a weighted residual $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ of 0.106 for the 2171 reflections having $I \geq 3\sigma_I$ and $(\sin\theta)/\lambda \leq 0.52$ Å^{-1}. Anisotropic refinement led to $R = 0.080$ and $R_w = 0.085$ for the 2310 low-angle reflections having $I \geq 2\sigma_I$. Initial coordinates for the 22 aromatic hydrogen atoms were then inferred from the required geometry of the molecule, while initial coordinates for the 6 methyl hydrogen atoms were obtained from a difference Fourier synthesis. Inclusion of the 28 hydrogen atoms (isotropic) in subsequent refinement led to $R = 0.034$ and $R_w = 0.040$. The final cycles of refinement including the high-angle data and using variable weights ($w^{1/2} = 2(Lp)F_o/\sigma_I$) led to $R = 0.047$, $R_w = 0.049$, and GOF[19] = 1.27 for the 3452 reflections having $I \geq 2\sigma_I$. During the final cycle of refinement the largest shift in any parameter was 0.08 times its estimated standard deviation. A final difference Fourier synthesis showed a maximum density of 0.22 e/Å^3.

Space Group Determination and Data Collection for (1-Naphthyl)bis(2,2′-biphenylylene)phosphorane (VI). Experimental conditions were the same as described for V, unless otherwise noted. The best crystals for X-ray diffraction analysis were obtained by recrystallization from acetone, although these diffracted poorly. A crystal having dimensions of 0.17 × 0.20 × 0.40 mm was mounted on the tip of a glass fiber. Preliminary diffractometric investigations indicated monoclinic (2/*m*) symmetry. From the observed extinctions 0*k*0, $k = 2n + 1$, and *h*0*l*, $h + l = 2n + 1$, the space group was uniquely determined as $P2_1/n$ (alternate setting of $P2_1/c$[17]). The lattice constants based on 25 reflections having $11.00° \leq \theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 13.75°$ are $a = 16.033$ (6) Å, $b = 9.345$ (3) Å, $c = 18.765$ (5) Å, and $\beta = 98.68$ (3)°. A unit cell content of four nonsolvated molecules gives a calculated volume of 19.9 Å^3 per nonhydrogen atom. Solution and refinement of the structure disclosed four acetone molecules per unit cell, as well. The assignment is thus $Z = 4$, for the one to one solvate $(C_{12}H_8)_2P(C_{10}H_7)\cdot(CH_3)_2CO$.

Data were collected and reduced as for V, except that the scan range was (0.85 + 0.35 tan θ)°, the scan rates varied from 0.87 to 4.0°/min, and three standard reflections were monitored. A total of 4880 independent reflections having $2° \leq 2\theta_{\mathrm{Mo}\,K\bar{\alpha}} \leq 50°$ was measured.

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(15) Holmes, R. R; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

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(17) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I; p 99.

(18) The function minimized was $\sum w(|F_o| - |F_c|)^2$. Mean atomic scattering factors were taken from ref 17, Vol. IV, 1974, pp 72–98. Real and imaginary dispersion corrections for P and O were taken from the same source, pp 149–150.

(19) Goodness of fit, GOF = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$. N_o = number of observations = 3452; N_v = number of variables = 455.

Table I. Bond Lengths (Å) for Nonhydrogen Atoms in $(C_{12}H_8)_2P(C_{10}H_6NMe_2)$ (V)[a]

type[b]	bond length	type[b]	bond length
P-C1	1.941 (3)	C4′-C5′	1.373 (4)
P-C1′	1.909 (2)	C5′-C6′	1.385 (4)
P-C2	1.846 (3)	C6′-C12′	1.383 (3)
P-C2′	1.886 (2)	C11′-C7′	1.395 (3)
P-CN1	1.892 (2)	C7′-C8′	1.378 (4)
C11-C12	1.465 (4)	C8′-C9′	1.385 (4)
C1-C11	1.400 (3)	C9′-C10′	1.385 (4)
C2-C12	1.401 (3)	C10′-C1′	1.390 (3)
C2-C3	1.385 (4)	CN1-CN9	1.433 (3)
C3-C4	1.395 (4)	CN1-CN2	1.373 (3)
C4-C5	1.366 (5)	CN2-CN3	1.405 (4)
C5-C6	1.373 (5)	CN3-CN4	1.354 (4)
C6-C12	1.392 (4)	CN4-CN10	1.410 (4)
C11-C7	1.404 (4)	CN10-CN9	1.430 (3)
C7-C8	1.365 (4)	CN10-CN5	1.418 (4)
C8-C9	1.376 (4)	CN5-CN6	1.346 (5)
C9-C10	1.395 (4)	CN6-CN7	1.403 (4)
C10-C1	1.394 (3)	CN7-CN8	1.374 (4)
C11′-C12′	1.479 (3)	CN8-CN9	1.432 (4)
C1′-C11′	1.391 (3)	CN8-N	1.441 (3)
C2′-C12′	1.396 (3)	N-CM1	1.479 (3)
C2′-C3′	1.388 (3)	N-CM2	1.471 (4)
C3′-C4′	1.393 (4)		

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Atoms are labeled to agree with Figure 1.

No corrections were made for absorption ($\mu_{\mathrm{Mo}\,K\alpha} = 0.133$ mm^{-1}).

Solution and Refinement for VI. Initial coordinates for the 35 nonhydrogen atoms of the phosphorane were obtained by direct methods (MULTAN). Unit-weighted isotropic refinement of the structural parameters for these atoms and a scale factor gave $R = 0.182$ and $R_w = 0.250$ for the 2276 reflections having $I \geq \sigma_I$ and $(\sin \theta)/\lambda \leq 0.52$ Å^{-1}. Anisotropic refinement gave $R = 0.167$ and $R_w = 0.234$. A difference Fourier synthesis at this point showed four independent peaks (~2 e/Å^3), which were consonant with the geometry expected for an acetone molecule.

Initial coordinates for the 23 independent hydrogen atoms of the phosphorane molecule were calculated, but since attempts to vary the parameters for these atoms proved unsuccessful, they were included in all subsequent refinement as fixed isotropic scatterers. Their positional parameters, however, were updated as refinement converged, so that the final C–H bond lengths were 0.98 Å. No attempt was made to include the hydrogen atoms of the acetone moiety.

Subsequent refinement using variable weights, and including the atoms of the acetone molecule as isotropic scatterers, gave $R = 0.088$ and $R_w = 0.099$. Inclusion of the high-angle data in the refinement gave $R = 0.100$ and $R_w = 0.103$ for the 2860 reflections having $I \geq \sigma_I$. The final cycles of refinement treated the atoms of the acetone molecule as anisotropic scatterers and led to the final values of $R = 0.094$, $R_w = 0.093$, and GOF[20] = 1.96. During the last cycle of refinement the largest shift in any parameter was 0.07 times its estimated standard deviation. A final difference Fourier synthesis showed a maximum density of 0.553 e/Å^3.

Computations were done on a CDC CYBER 175 computer by using the direct-methods program MULTAN, by Main, Germain, and Woolfson; Johnson's thermal ellipsoid plot program, ORTEP; JIMDAP, a modified version of Zalkin's Fourier program, FORDAP; LINEX, a modified version of the Oak Ridge full-matrix least-squares program ORTEP; and several locally written programs.

Table II. Bond Angles (Deg) for Nonhydrogen Atoms in $(C_{12}H_8)_2P(C_{10}H_6NMe_2)$ (V)[a]

type	bond angle	type	bond angle
C1-P-C1′	175.5 (1)	C12′-C11′-C1′	113.1 (2)
C1-P-CN1	85.8 (1)	C12′-C11′-C7′	125.9 (2)
C1-P-C2	87.4 (1)	C12′-C2′-C3′	119.0 (2)
C1-P-C2′	92.5 (1)	C2′-C3′-C4′	120.0 (2)
C2-P-CN1	106.1 (1)	C3′-C4′-C5′	120.5 (2)
C2-P-C1′	97.1 (1)	C4′-C5′-C6′	119.9 (3)
C2-P-C2′	101.8 (1)	C5′-C6′-C12′	120.0 (3)
CN1-P-C1′	93.6 (1)	C6′-C12′-C2′	120.6 (2)
CN1-P-C2′	151.9 (1)	C11′-C7′-C8′	119.9 (3)
C1′-P-C2′	85.9 (1)	C7′-C8′-C9′	119.3 (3)
P-C1-C11	110.9 (2)	C8′-C9′-C10′	120.9 (3)
P-C1-C10	130.9 (2)	C9′-C10′-C1′	120.5 (3)
P-C2-C12	113.2 (2)	C10′-C1′-C11′	118.3 (2)
P-C2-C3	126.9 (2)	C1′-C11′-C7′	121.1 (2)
C12-C11-C1	113.6 (2)	P-CN1-CN9	123.2 (2)
C12-C11-C7	125.8 (2)	P-CN1-CN2	117.4 (2)
C11-C12-C2	114.9 (2)	CN9-CN1-CN2	118.6 (2)
C11-C12-C6	125.5 (3)	CN1-CN2-CN3	121.9 (3)
C12-C2-C3	119.9 (2)	CN2-CN3-CN4	120.2 (3)
C2-C3-C4	119.4 (3)	CN3-CN4-CN10	120.7 (3)
C3-C4-C5	120.5 (3)	CN4-CN10-CN9	119.3 (2)
C4-C5-C6	120.8 (3)	CN4-CN10-CN5	121.9 (3)
C5-C6-C12	119.9 (3)	CN9-CN10-CN5	118.8 (3)
C6-C12-C2	119.5 (3)	CN10-CN5-CN6	121.3 (3)
C11-C7-C8	119.8 (3)	CN5-CN6-CN7	120.6 (3)
C7-C8-C9	120.7 (3)	CN6-CN7-CN8	120.7 (3)
C8-C9-C10	120.1 (3)	CN7-CN8-CN9	120.0 (3)
C9-C10-C1	120.6 (3)	CN7-CN8-N	123.2 (3)
C10-C1-C11	118.2 (2)	N-CN8-CN9	116.7 (2)
C1-C11-C7	120.6 (3)	CN8-CN9-CN10	118.0 (2)
P-C1′-C11′	113.6 (2)	CN8-CN9-CN1	123.3 (2)
P-C1′-C10′	128.1 (2)	CN8-N-CM1	108.6 (2)
P-C2′-C12′	113.8 (2)	CN8-N-CM2	115.4 (2)
P-C2′-C3′	127.1 (2)	CM1-N-CM2	108.4 (3)
C11′-C12′-C2′	113.7 (2)		
C11′-C12′-C6′	125.7 (2)		

[a] See footnotes to Table I.

Table III. Bond Lengths (Å) for Nonhydrogen Atoms in $(C_{12}H_8)_2P(C_{10}H_7)\cdot(CH_3)_2CO$ (VI)[a]

type[b]	bond length	type[b]	bond length
P-C1	1.910 (5)	C6′-C12′	1.381 (7)
P-C1′	1.936 (6)	C12′-C2′	1.435 (7)
P-C2	1.852 (5)	C1′-C11′	1.383 (7)
P-C2′	1.875 (5)	C11′-C7′	1.416 (8)
P-CN1	1.866 (6)	C7′-C8′	1.397 (8)
C11-C12	1.469 (7)	C8′-C9′	1.361 (8)
C11′-C12′	1.474 (7)	C9′-C10′	1.405 (8)
C2-C3	1.408 (7)	C10′-C1′	1.385 (7)
C3-C4	1.399 (8)	CN1-CN2	1.359 (7)
C4-C5	1.377 (8)	CN2-CN3	1.401 (8)
C5-C6	1.400 (8)	CN3-CN4	1.361 (9)
C6-C12	1.404 (7)	CN4-CN10	1.393 (8)
C12-C2	1.396 (7)	CN10-CN5	1.444 (9)
C1-C11	1.388 (7)	CN5-CN6	1.383 (9)
C11-C7	1.387 (7)	CN6-CN7	1.384 (9)
C7-C8	1.398 (8)	CN7-CN8	1.412 (8)
C8-C9	1.375 (8)	CN8-CN9	1.429 (8)
C9-C10	1.396 (7)	CN9-CN10	1.415 (8)
C10-C1	1.409 (7)	CN9-CN1	1.437 (8)
C2′-C3′	1.385 (7)	CA1-CA2	1.47 (2)[c]
C3′-C4′	1.381 (7)	CA1-CA3	1.54 (1)[c]
C4′-C5′	1.396 (8)	CA1-OA	1.13 (1)[c]
C5′-C6′	1.364 (8)		

[a] See footnote *a* to Table I. [b] Atoms are labeled to agree with Figure 3. [c] Values for acetone.

Results and Discussion

Bond lengths and angles for nonhydrogen atoms of [8-(dimethylamino)-1-naphthyl]bis(2,2′-biphenylylene)phosphorane (V) are listed in Tables I and II, respectively. Similar bond parameter data for (1-naphthyl)bis(2,2′-biphenylylene)phosphorane (VI) are given in Tables III and IV. An ORTEP drawing in Figure 1 indicates the general geometrical configuration for V. A schematic representation of pertinent bond parameters for V is illustrated in Figure 2. The related ORTEP and schematic representation for VI is presented in Figures 3 and 4, respectively. Atomic coordinates are given in Tables V and VI for V and in Tables VII and VIII for VI. Thermal parameters and bond lengths and angles involving

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[20] As defined in ref 19, but with $N_o = 2860$ and $N_v = 352$.

Table IV. Bond Angles (Deg) for Nonhydrogen Atoms in $(C_{12}H_8)_2P(C_{10}H_7)\cdot(CH_3)_2CO$ (VI)[a]

type[b]	bond angle	type[b]	bond angle
C1-P-C1′	177.4 (2)	C7′-C11′-C12′	124.3 (5)
CN1-P-C2	116.4 (2)	C2′-C12′-C11′	113.2 (5)
CN1-P-C2′	132.6 (2)	C6′-C12′-C11′	127.4 (5)
C2-P-C2′	110.9 (2)	C12′-C2′-C3′	118.2 (5)
C1-P-CN1	87.7 (2)	C2′-C3′-C4′	121.3 (5)
C1-P-C2	86.2 (2)	C3′-C4′-C5′	119.6 (6)
C1-P-C2′	94.2 (2)	C4′-C5′-C6′	120.4 (6)
C1′-P-CN1	90.0 (3)	C5′-C6′-C12′	121.0 (6)
C1′-P-C2	95.9 (2)	C6′-C12′-C2′	119.4 (5)
C1′-P-C2′	86.6 (2)	C11′-C7′-C8′	116.7 (6)
P-C1-C11	113.5 (4)	C7′-C8′-C9′	122.5 (6)
P-C1-C10	128.7 (4)	C8′-C9′-C10′	120.2 (6)
P-C2-C12	113.6 (4)	C9′-C10′-C1′	119.0 (6)
P-C2-C3	125.7 (4)	C10′-C1′-C11′	120.4 (5)
C1-C11-C12	112.0 (4)	C1′-C11′-C7′	121.2 (6)
C7-C11-C12	125.7 (5)	P-CN1-CN2	119.7 (4)
C2-C12-C11	114.6 (4)	P-CN1-CN9	124.4 (4)
C6-C12-C11	125.9 (5)	CN1-CN2-CN3	124.5 (6)
C12-C2-C3	120.6 (5)	CN2-CN3-CN4	119.9 (6)
C2-C3-C4	118.8 (5)	CN3-CN4-CN10	118.7 (6)
C3-C4-C5	121.0 (5)	CN4-CN10-CN9	121.4 (6)
C4-C5-C6	120.4 (6)	CN4-CN10-CN5	120.1 (6)
C5-C6-C12	119.7 (5)	CN9-CN10-CN5	118.5 (6)
C6-C12-C2	119.5 (5)	CN10-CN5-CN6	120.0 (7)
C11-C7-C8	119.3 (5)	CN5-CN6-CN7	122.0 (7)
C7-C8-C9	119.9 (5)	CN6-CN7-CN8	119.6 (6)
C8-C9-C10	120.6 (5)	CN7-CN8-CN9	120.0 (6)
C9-C10-C1	120.3 (5)	CN8-CN9-CN10	119.9 (6)
C10-C1-C11	117.8 (5)	CN8-CN9-CN1	120.6 (6)
C1-C11-C7	122.0 (5)	CN10-CN9-CN1	119.5 (5)
P-C1′-C11′	112.5 (4)	CN9-CN1-CN2	115.8 (5)
P-C1′-C10′	127.1 (4)	OA-CA1-CA2	125 (2)[c]
P-C2′-C12′	113.0 (4)	OA-CA1-CA3	119 (2)[c]
P-C2′-C3′	128.4 (4)	CA2-CA1-CA3	116 (1)[c]
C1′-C11′-C12′	114.4 (5)		

[a] See footnote *a* to Table I. [b] See footnote *b* to Table III. [c] Values for acetone.

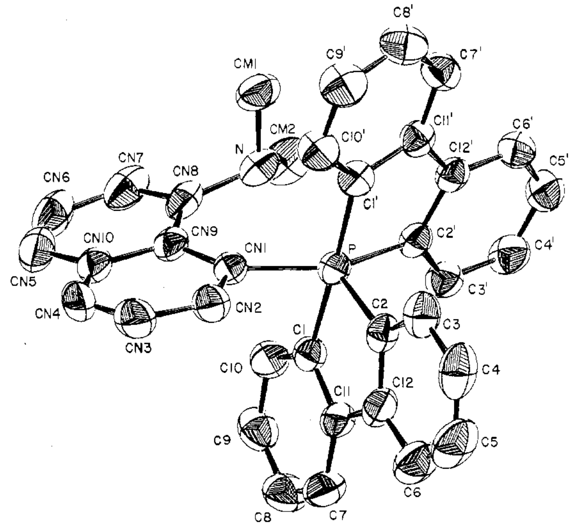

Figure 1. ORTEP plot of the $(C_{12}H_8)_2P(C_{10}H_6NMe_2)$ molecule (V) with thermal ellipsoids at the 50% probability level.

hydrogen atoms are provided as supplementary material (refer to the end of this article).

The basic structural representation of the 1-naphthyl derivative VI, which is apparent from examination of the angles at phosphorus in Figure 4, is that of a trigonal bipyramid. However, for the 8-$(CH_3)_2$N-1-Np derivative V, the structural type is more nearly a rectangular pyramid[21] with trans basal

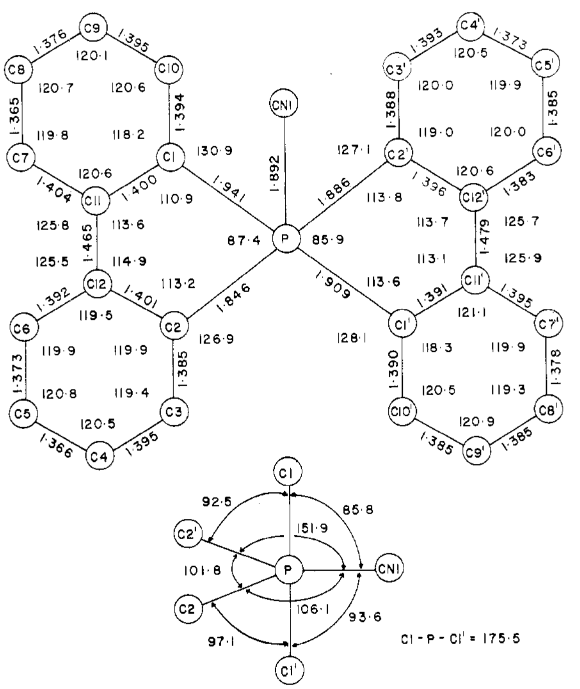

Figure 2. Schematic drawing of $(C_{12}H_8)_2P(C_{10}H_6NMe_2)$ (V) showing pertinent bond parameters for the bis(biphenylylene) network.

Table V. Atomic Coordinates in Crystalline $(C_{12}H_8)_2P(C_{10}H_6NMe_2)$ (V)[a]

atom type[b]	coordinates		
	10^4x	10^4y	10^4z
P	2273.0 (6)	8148.3 (5)	5975.5 (3)
N	1126 (2)	6262 (2)	6262 (1)
C1	3104 (2)	8386 (2)	6823 (1)
C2	2975 (2)	9399 (2)	5779 (1)
C3	2874 (3)	9848 (2)	5197 (1)
C4	3523 (3)	10785 (2)	5126 (2)
C5	4253 (4)	11256 (2)	5624 (2)
C6	4362 (3)	10820 (2)	6204 (2)
C7	4420 (3)	9672 (2)	7455 (1)
C8	4415 (3)	9069 (3)	7967 (1)
C9	3767 (3)	8135 (2)	7926 (1)
C10	3102 (3)	7794 (2)	7356 (1)
C11	3780 (2)	9330 (2)	6877 (1)
C12	3727 (3)	9885 (2)	6288 (1)
C1′	1427 (2)	7807 (2)	5161 (1)
C2′	3813 (2)	7295 (2)	5803 (1)
C3′	5079 (3)	7107 (2)	6184 (1)
C4′	6175 (3)	6527 (2)	5964 (1)
C5′	6018 (3)	6139 (2)	5372 (1)
C6′	4756 (3)	6316 (2)	4990 (1)
C7′	1825 (3)	6840 (2)	4239 (1)
C8′	520 (3)	7169 (2)	3949 (1)
C9′	−326 (3)	7821 (2)	4262 (1)
C10′	108 (3)	8126 (2)	4865 (1)
C11′	2282 (2)	7165 (2)	4841 (1)
C12′	3659 (2)	6888 (2)	5204 (1)
CN1	459 (2)	8382 (2)	6284 (1)
CN2	−105 (3)	9338 (2)	6223 (1)
CN3	−1307 (3)	9639 (2)	6528 (1)
CN4	−1897 (3)	8999 (2)	6923 (1)
CN5	−1916 (3)	7338 (3)	7442 (1)
CN6	−1404 (3)	6393 (3)	7518 (1)
CN7	−376 (3)	6019 (2)	7139 (1)
CN8	184 (2)	6628 (2)	6706 (1)
CN9	−230 (2)	7667 (2)	6657 (1)
CN10	−1367 (3)	8007 (2)	7009 (1)
CM1	221 (3)	5871 (2)	5713 (1)
CM2	2151 (4)	5469 (3)	6491 (2)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Atoms are labeled to agree with Figure 1.

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(21) In ref 2, footnote 59 should be adjusted to take account of the fact that V does not have a TP structure.

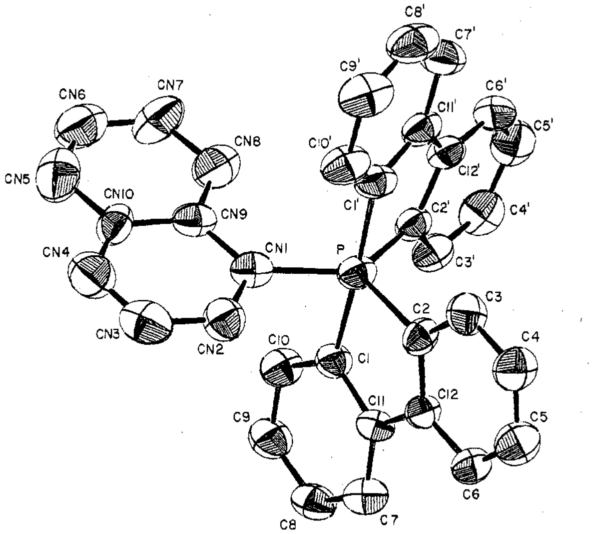


Figure 3. ORTEP plot of the $(C_{12}H_8)_2P(C_{10}H_7)\cdot(CH_3)_2CO$ system (VI) with thermal ellipsoids at the 50% probability level.

Table VI. Refined Parameters for Hydrogen Atoms in Crystalline $(C_{12}H_8)_2P(C_{10}H_6NMe_2)$ (V)[a]

	coordinates			
atom type[b]	10^3x	10^3y	10^3z	B_{iso}, Å^2
H3	239 (2)	951 (2)	483 (1)	3.0 (5)
H4	343 (2)	1102 (2)	471 (1)	4.0 (5)
H5	469 (3)	1190 (2)	557 (1)	5.9 (6)
H6	487 (3)	1116 (2)	658 (1)	6.4 (7)
H7	486 (3)	1031 (2)	747 (1)	4.7 (6)
H8	486 (3)	932 (2)	836 (1)	5.0 (6)
H9	373 (3)	770 (2)	828 (1)	5.5 (6)
H10	266 (3)	714 (2)	733 (1)	4.4 (5)
H3′	520 (2)	738 (2)	660 (1)	3.9 (5)
H4′	710 (3)	641 (2)	623 (1)	5.4 (6)
H5′	677 (2)	575 (2)	521 (1)	3.7 (5)
H6′	462 (3)	606 (2)	458 (1)	4.4 (5)
H7′	243 (2)	637 (2)	404 (1)	3.7 (5)
H8′	20 (3)	695 (2)	353 (1)	4.3 (5)
H9′	−123 (3)	806 (2)	407 (1)	5.1 (6)
H10′	−49 (3)	852 (2)	508 (1)	4.5 (6)
HN2	37 (2)	984 (2)	598 (1)	3.6 (5)
HN3	−167 (3)	1035 (2)	647 (1)	5.8 (7)
HN4	−268 (2)	918 (2)	712 (1)	3.4 (5)
NH5	−269 (3)	761 (2)	767 (1)	5.5 (6)
HN6	−174 (3)	596 (2)	782 (1)	5.6 (6)
HN7	−11 (3)	528 (2)	715 (1)	5.6 (6)
HM11	−28 (3)	526 (2)	582 (1)	3.8 (5)
HM12	86 (3)	564 (2)	539 (1)	5.4 (6)
HM13	−50 (3)	640 (2)	554 (1)	5.6 (6)
HM21	269 (3)	568 (2)	687 (1)	6.5 (7)
HM22	287 (3)	530 (2)	616 (1)	7.3 (7)
HM23	164 (3)	484 (2)	659 (1)	5.1 (6)

[a] See footnote *a* to Table V. [b] Hydrogen atoms are labeled according to the carbon atom to which they are bonded.

angles of 151.9 and 175.5°. More quantitatively, application of the dihedral angle method, previously outlined for phosphoranes,[15] gives the extent of structural change from the idealized geometries. These results (Table IX) show that the displacement from the trigonal bipyramid toward an idealized rectangular pyramid is 24.8% for VI and 64.0% for V on the basis of unit bond distances. The near equality of the terms labeled *B* and *C* means that the structural displacement follows the C_{2v} constraint of the Berry coordinate. Adherence to the latter constraint also is seen from the dihedral angle of 86.1° between planes X and XIV for V (Table X) and 86.8° between planes X and XIII for VI (Table XI). For displacement along this coordinate, this angle ranges from 90 to 85.9°. Atom deviations from these planes are very small.

Table VII. Atomic Coordinates in Crystalline $(C_{12}H_8)_2P(C_{10}H_7)\cdot(CH_3)_2CO$ (VI)[a]

	coordinates		
atom type[b]	10^4x	10^4y	10^4z
P	4640 (1)	6836 (1)	3256 (1)
C1	4054 (3)	8616 (5)	3112 (3)
C2	3711 (3)	6185 (6)	3640 (3)
C1′	5281 (3)	5079 (6)	3412 (3)
C2′	4533 (3)	6418 (6)	2269 (3)
C3	3605 (4)	4791 (6)	3897 (3)
C4	2844 (4)	4442 (6)	4135 (3)
C5	2210 (4)	5441 (7)	4125 (3)
C6	2316 (3)	6829 (6)	3872 (3)
C7	2731 (4)	9774 (6)	3248 (3)
C8	3014 (4)	11048 (6)	2975 (3)
C9	3814 (4)	11123 (6)	2798 (3)
C10	4328 (4)	9911 (6)	2841 (3)
C11	3251 (3)	8580 (5)	3304 (3)
C12	3069 (3)	7200 (6)	3622 (3)
C3′	4099 (3)	7176 (6)	1696 (3)
C4′	4012 (4)	6651 (7)	1001 (3)
C5′	4356 (4)	5320 (8)	871 (3)
C6′	4784 (4)	4547 (7)	1426 (3)
C7′	5756 (4)	3026 (6)	2777 (3)
C8′	6152 (4)	2525 (7)	3445 (4)
C9′	6128 (4)	3252 (7)	4070 (4)
C10′	5696 (4)	4562 (7)	4061 (3)
C11′	5318 (3)	4342 (6)	2778 (3)
C12′	4880 (3)	5052 (6)	2125 (3)
CN1	5466 (4)	7790 (6)	3888 (3)
CN2	5321 (4)	8116 (7)	4564 (3)
CN3	5895 (5)	8826 (7)	5082 (3)
CN4	6643 (5)	9295 (7)	4909 (4)
CN5	7599 (4)	9563 (7)	4009 (4)
CN6	7764 (4)	9345 (8)	3315 (4)
CN7	7220 (4)	8581 (8)	2811 (4)
CN8	6460 (4)	8039 (7)	2997 (4)
CN9	6254 (4)	8283 (6)	3701 (3)
CN10	6821 (3)	9044 (6)	4216 (3)
CA1	9001 (9)	4965 (15)	4070 (6)
CA2	8184 (9)	5714 (11)	4010 (6)
CA3	8983 (8)	3351 (12)	4233 (7)
OA	9608 (8)	5453 (14)	3947 (7)

[a] Numbers in parentheses are estimated standard deviations in the last significant figure. [b] Atoms are labeled to agree with Figure 3.

An unusual feature about the displacement coordinate followed for V and VI is that the structural distortion is toward a rectangular pyramid having one of the biphenylylene ring atoms located at the apical site. Invariably, spirocyclic phosphoranes have structures located along a coordinate connecting a rectangular pyramid that has the spirocyclic network in the basal plane.[2,3,15] This is the case for the methyl- and phenylbis(biphenylylene)phosphoranes described in the succeeding paper.[16] Relative to the latter compounds, substitution of the larger naphthyl group in VI causes a widening of the equatorial CN1–P–C2′ angle to 132.6 (2)°. For V, this angle is opened much further, to 151.9 (1)°. The C2–P–C2′ angle stays relatively constant near 111° in the methyl, phenyl, and α-naphthyl derivatives. With the attachment of the $(CH_3)_2N$ group in V, both the equatorial C2–P–C2′ and C2–P–CN1 angles decrease sharply.

In line with the distortion toward the aforementioned rectangular pyramid, the biphenylylene ring bond P–C2, which assumes the apical position, has the shortest length in both V and VI, and the trans basal distances P–CN1 and P–C2′ tend toward equality, particularly in V containing the $(CH_3)_2N$ group.

The progressive increase in the CN1–P–C2′ angle in VI and V relative to the methyl and phenyl derivatives, where this angle is about 124°, is clearly a result of a steric effect. As seen in Tables X and XI, the biphenylylene-ring systems for

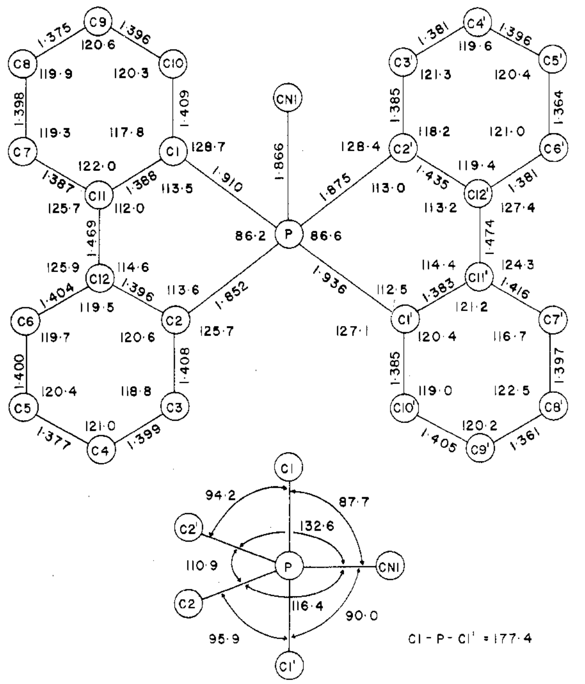


Figure 4. Schematic drawing of $(C_{12}H_8)_2P(C_{10}H_7)\cdot(CH_3)_2O$ (VI) showing pertinent bond parameters for the bis(biphenylylene) network.

Table VIII. Fixed Parameters for Hydrogen Atoms in Crystalline $(C_{12}H_8)_2P(C_{10}H_7)\cdot(CH_3)_2CO$ (VI)[a,c]

	coordinates		
atom type[b]	10^3x	10^3y	10^3z
H3	405	408	391
H4	276	347	431
H5	168	518	430
H6	187	754	387
H7	217	973	340
H8	264	1188	291
H9	403	1204	264
H10	488	996	268
H3'	385	810	178
H4'	371	721	60
H5'	429	494	38
H6'	503	362	133
H7'	578	249	233
H8'	646	162	346
H9'	641	286	453
H10'	569	510	451
HN2	478	783	470
HN3	576	899	557
HN4	705	980	527
NH5	801	1007	436
HN6	828	974	318
HN7	736	842	233
HN8	607	750	264

[a] See footnote *a* of Table VI. [b] See footnote *b* of Table VII. [c] Isotropic thermal parameters are fixed at 5 Å^2.

V and VI are very close to planarity. Similarly for VI, the α-naphthyl group is planar. Introduction of the $(CH_3)_2N$ group in V causes a doubling of the atom deviations from the least-squares plane of the naphthyl group (plane VII, Table X). Further, this plane is tilted downward as one proceeds to the left from the phosphorus atom in Figure 1. The dihedral angle between this plane and the equatorial plane (with reference to the trigonal-bipyramidal end of the distortion coordinate, plane X of Table X) is 21.1°. The related dihedral angle in the α-naphthyl derivative, VI, is 5.8°. The downward tilt and reduction in planarity of the naphthyl group in V seem to result from an effort of the $(CH_3)_2N$ group to minimize repulsions with the biphenylylene system. As a consequence, the nitrogen atom is displaced upward (Figure 1) from the equatorial plane (plane X, Table X). In both structures V and VI, the sum of the equatorial angles at phosphorus is 360°.

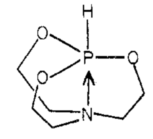
Table IX. Calculation of Percent Displacement from the Idealized Trigonal Bipyramid (TP) toward the Idealized Rectangular Pyramid (RP)[a,b]

	V	VI
A (deg) = $\Sigma_i|\delta i(C) - \delta i(RP)|$	78.3 (77.3)[d]	164.2 (163.7)[d]
B (deg) = $\Sigma_i|\delta i(C) - \delta i(TP)|$	139.4 (140.4)	54.2 (54.0)
C (deg) = 217.7° − A	139.4 (140.4)	53.5 (54.0)
D = %(TP → RP)[c]	64.0 (64.5)	24.8 (24.8)

[a] Based on the dihedral angle method cited in ref 15. The pivotal ligand is C2 for both V and VI. [b] A is the sum of the dihedral angles calculated from the positions of the atoms attached to phosphorus relative to those for an idealized RP containing the carbon atom of the 1-Np ligand in a basal position. B is a similar sum relative to a TP containing the carbon atom of the 1-Np ligand in an equatorial position. The value 217.7° is the difference in the dihedral angle summation between the idealized geometries, RP and TP. [c] $D = (B + C)/2(217.7)$. [d] Unparenthesized values refer to use of unit bond distances. Parenthesized values refer to use of observed bond distances.

Examination of the number of close intramolecular vs. intermolecular contacts, in the range 2.5–2.7 Å for C- - -H nonbonding interactions, supports intramolecular repulsions as the principal feature leading to the large CN1–P–C2' angle in V. The ratio of intra- to intermolecular contacts of this type is 4:2 for VI and 7:2 for V.

The P–N distance in V is 2.810 Å. While this is shorter than the van der Waals sum of 3.4 Å, it is not indicative of a bonding interaction of any appreciable magnitude. P–N bonding distances for phosphoranes containing five-membered rings are in the range 1.64–1.70 Å for equatorial P–N bonds and 1.74–1.82 Å for axial nitrogen atoms with reference to a trigonal-bipyramidal geometry.[3] For phosphoranes containing $(CH_3)_2N$ groups the P–N bond length is in the range 1.65–1.67 Å.[3,22,23] The $(CH_3)_2N$ group has been observed only at the equatorial position. An intramolecular donor–acceptor P–N bond is present in a compound studied by Verkade et al.,[24] i.e., IX. The bond length here is somewhat longer: 1.986 (5) Å. Even at this length the bond strength should be considerably reduced.



IX

The sum of the angles at nitrogen is 332.4°, indicative of its pyramidal character. In all cases, when $(CH_3)_2N$ groups are attached to pentacoordinated phosphorus, the geometry at nitrogen is planar. The latter is attributed to P–N π bonding.[21,25]

With regard to the possibility of π bonding in the P–C bonds of the attached naphthyl groups, little evidence exists. The P–C bond length is the same in the methyl and phenyl derivative (1.859 (2) Å[16]) and rises only slightly in the Np (1.866 (6) Å) and 8-$(CH_3)_2N$-1-Np (1.892 (2) Å) derivatives. Thus,

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(23) Oberhammer, H.; Schmutzler, R. *J. Chem. Soc., Dalton Trans.* **1976**, 1454.

(24) Clardy, J. C.; Milbrath, D. S.; Springer, J. P.; Verkade, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 623.

(25) Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3047.

Table X. Deviations (Å) from Some Least-Squares Mean Planes for $(C_{12}H_8)_2P(C_{10}H_6NMe_2)$ (V)[a, b]

	I	II	III		IV	V	VI		VII
C2	0.001		0.032	C2′	-0.004		0.050	CN1	0.095
C3	0.000		0.016	C3′	0.001		0.027	CN2	0.056
C4	0.000		-0.016	C4′	0.003		-0.022	CN3	-0.058
C5	0.000		-0.032	C5′	-0.004		-0.053	CN4	-0.058
C6	0.001		-0.016	C6′	0.000		-0.023	CN5	0.054
C12	-0.002		0.013	C12′	0.003		0.031	CN6	0.090
C1		0.000	-0.015	C1′		0.000	-0.013	CN7	-0.030
C7		0.009	0.043	C7′		0.006	0.047	CN8	-0.114
C8		-0.002	0.014	C8′		0.003	0.013	CN9	-0.021
C9		-0.006	-0.022	C9′		-0.011	-0.042	CN10	-0.014
C10		0.006	-0.027	C10′		0.009	-0.034	P	(0.573)
C11		-0.008	0.012	C11′		-0.008	0.021	N	(-0.376)
P	(-0.069)	(0.032)	(0.003)	P	(-0.163)	(-0.018)	(-0.041)	C8′	(-3.756)
N	(-0.111)	(0.122)	(0.026)	N	(2.615)	(2.733)	(2.725)		

	VIII		IX		X		XI		XII	XIII		XIV
P	-0.001	P	-0.012	P	-0.028	P	-0.051	CN8	0.0	-0.328	P	0.008
C1	-0.004	C1′	0.008	CN1	0.012	CN1	0.002	CM1	0.0	0.269	C2	0.000
C2	0.006	C2′	0.020	C2	0.006	C1	0.028	CM2	0.0	-0.126	C1	-0.004
C11	0.009	C11′	0.002	C2′	0.011	C1′	0.021	N	(-0.454)	0.186	C1′	-0.004
C12	-0.010	C12′	-0.017	N	(-0.129)			P	(-3.198)		N	(0.086)
N	(0.055)			CN8	(0.476)							
				C8′	(-4.644)							

[a] Deviations in parentheses are for atoms not included in the calculation of the plane. [b] Dihedral angles (deg) between planes indicated: I and II, 2.7; III and VI, 82.2; X and XI, 85.3; IV and V, 3.9; VIII and IX, 79.7; VII and X, 21.1; X and XIV, 86.1.

Table XI. Deviations (Å) from Some Least-Squares Mean Planes for $(C_{12}H_8)_2P(C_{10}H_7)\cdot(CH_3)_2CO$ (VI)[a, b]

	I	II	III		IV	V	VI		VII
C2	0.002		0.018	C2′	-0.004		-0.029	CN1	-0.001
C3	0.002		0.008	C3′	0.005		-0.029	CN2	-0.041
C4	-0.004		-0.005	C4′	-0.003		-0.018	CN3	-0.001
C5	0.000		0.002	C5′	0.002		0.016	CN4	0.024
C6	0.004		0.017	C6′	-0.002		0.021	CN5	0.004
C12	-0.006		0.013	C12′	0.003		0.008	CN6	-0.038
C1		0.004	-0.032	C1′		0.011	0.061	CN7	-0.009
C7		0.006	-0.020	C7′		-0.003	-0.022	CN8	0.023
C8		-0.016	0.001	C8′		0.004	-0.035	CN9	0.023
C9		0.021	0.055	C9′		0.003	-0.013	CN10	0.017
C10		-0.014	-0.006	C10′		-0.009	0.020	P	(-0.062)
C11		0.001	-0.051	C11′		-0.006	0.020	C2	(0.042)
P	(-0.082)	(0.022)	(-0.057)	P	(0.168)	(0.011)	(0.122)	C2′	(-0.255)
								C8′	(4.468)

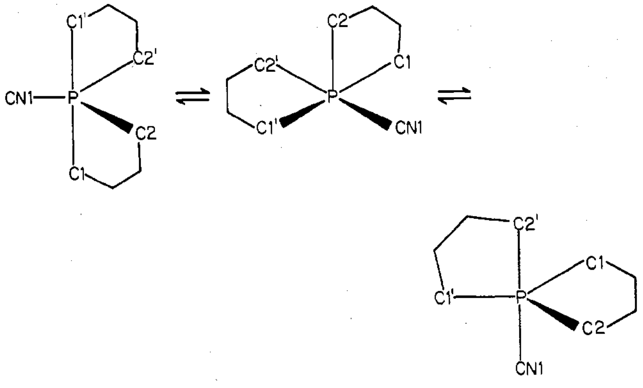
	VIII		IX		X		XI		XII		XIII
P	-0.017	P	0.036	P	0.011	P	0.013	CA1	0.034	P	0.000
C1	0.025	C1′	-0.010	CN1	-0.004	CN1	0.000	CA2	-0.011	C1	-0.017
C2	0.010	C2′	-0.046	C2	-0.003	C1	-0.007	CA3	-0.009	C1′	0.008
C11	-0.023	C11′	0.001	C2′	-0.004	C1′	-0.007	OA	-0.014	C2	0.008
C12	0.005	C12′	0.019	CN8	(0.239)						
				C8′	(4.639)						

[a] Deviations in parentheses are for atoms not included in the calculation of the plane. [b] Dihedral angles (deg) between planes indicated: I and II, 1.4; III and VI, 76.2; X and XI, 84.8; IV and V, 3.0; VIII and IX, 72.6; VII and X, 5.8; X and XIII, 86.8.

the orientation of the plane of the naphthyl groups in V and VI close to the CN1–P–C2–C2′ plane most likely is a result of steric control.

From NMR studies, Hellwinkel et al.[7] reached similar conclusions regarding positioning of the naphthyl group in a related series of bis(biphenylylene) derivatives containing a variety of groups in the 8-position. Also in agreement with our conclusion on P–N bonding, no evidence for an inner onium–ate structure was found on the basis of ^{1}H and ^{31}P NMR spectra for derivatives containing either $(CH_3)_2N$ or OCH_3 groups in the 8-position of the 1-naphthyl ligands.[7]

If one assumes that the ground-state structures determined crystallographically for V and VI are representative of their solution-state structures, facile ligand exchange would be best represented by the higher energy process, i.e., when the barrier state would involve the trigonal-bipyramidal form having a diequatorially placed biphenylylene ring. Thus, the exchange process would proceed by way of the basic transformation, illustrated for V with C2 as the pivotal ligand.



Similar permutations with simultaneous rotations of the α-naphthyl groups about their respective P-CN1 bonds (and in the case of V, rotation of $(CH_3)_2N$ group about the CN8-N bond) would provide a mechanism consistent with NMR data.[7] This exchange process follows the form of the distortion coordinate found for V and VI (Table IX).

In contrast, the X-ray study on the corresponding bis(biphenylylene) derivatives VII and VIII[16] containing substituents of lower steric requirements, methyl and phenyl, respectively, shows the distortion coordinate is not that followed for the naphthyl derivatives but is indicative of the C_{2v} pathway for the lower energy process.

It is possible then, as stated earlier,[13] that a changeover in ligand exchange mechanism takes place from the lower to the higher energy process as the steric requirements are increased for bis(biphenylylene) derivatives. This lends support to the detailed NMR line shape study of Whitesides et al.[12] which showed the lower energy process for the isopropylphenyl derivative I but the higher energy process for the more hindered triisopropylphenyl derivative II.

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Registry No. V, 52753-52-3; VI, 75082-07-4.

Supplementary Material Available: Compilations of observed and calculated structure factor amplitudes for V and VI, thermal parameters (Table XII) and bond lengths and angles involving hydrogen atoms (Table XIII) for V, and thermal parameters (Table XIV) for VI (32 pages). Ordering information is given on any current masthead page.

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Molecular Structure of the Methyl and Phenyl Derivatives of Bis(2,2'-biphenylylene)phosphorane[1]

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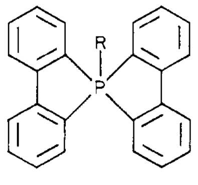
Single-crystal X-ray analysis of methylbis(2,2'-biphenylylene)phosphorane $(C_{12}H_8)_2PCH_3$ (III) and phenylbis(2,2'-biphenylylene)phosphorane $(C_{12}H_8)_2PC_6H_5$ (IV) reveals closely related structures which are nearly trigonal bipyramidal but displaced 16.9 and 15.0%, respectively, in a direction opposite to a coordinate connecting a rectangular pyramid that has the unique substituent apical. Data for both compounds were collected on an Enraf-Nonius CAD4 automated diffractometer out to a maximum $2\theta_{\mathrm{Mo}\,K\bar{\alpha}} = 55°$. III crystallizes in the monoclinic space group $C2/c$ with $a = 24.244$ (4) Å, $b = 7.138$ (3) Å, $c = 22.203$ (5) Å, $\beta = 104.08$ (2)°, and $Z = 8$ and has a pseudo-twofold axis along the phosphorus-methyl C bond. IV crystallizes as the benzene disolvate in space group $C2/c$ with $a = 16.169$ (4) Å, $b = 9.399$ (4) Å, $c = 20.961$ (8) Å, $\beta = 92.23$ (3)°, and $Z = 4$ and has a crystallographic two-fold axis along the phosphorus-phenyl C bond. Both structures were refined by full-matrix least-squares techniques: for III to final $R = 0.057$ and $R_w = 0.052$ for the 2712 reflections having $I \geq \sigma_I$; for IV to final $R = 0.051$ and $R_w = 0.053$ for the 2494 reflections having $I \geq \sigma_I$. Molecular mechanics calculations on these phosphoranes, III and IV, and the related [8-(dimethylamino)-1-naphthyl]bis(2,2'-biphenylylene)phosphorane (I) and (1-naphthyl)bis(2,2'-biphenylylene)phosphorane (II) gave reasonable agreement in reproducing structural parameters obtained in the X-ray studies. Strain energy comparisons support a changeover in intramolecular ligand-exchange mechanism as the size of the unique R group is increased.

Introduction

As shown in the preceding paper,[1b] both the 8-(dimethylamino)-1-naphthyl and the 1-naphthyl derivative of bis(2,2'-biphenylylene)phosphorane, I and II, respectively, have molecular structures displaced along a coordinate leading to a rectangular pyramid that contains the naphthyl group in a basal position. I was located about 65% along this coordinate, and II, about 25%. Usually the structures of spirocyclic phosphoranes are located along a coordinate leading to a rectangular pyramid that has the unique group in the apical position.[2-4] For PPh_5, the structure is very nearly trigonal bipyramidal.[5] Neither the presence of the unsaturated spirocyclic system nor the incorporation of five carbon atoms bonded to phosphorus then suggests the structural distortion coordinate found for I and II.



I, R = $8\text{-}(CH_3)_2N\text{-}1\text{-}Np$
II, R = 1-Np
III, R = CH_3
IV, R = Ph
Np = naphthyl

We ascribed[1b] the structural preference to steric requirements of the naphthyl group. These requirements are magnified in the $8\text{-}(CH_3)_2N\text{-}Np$ derivative I. The extensive NMR studies of Hellwinkel and co-workers[6-10] on the fluxional be-

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