which showed large red shifts correspond to the $^1A_1(4b_1 \rightarrow 5b_1)$ and $^1B_2(4b_1 \rightarrow 4a_2)$ states of this study, and the two states which showed minor red shifts correspond to the $^1B_2(3a_2 \rightarrow 5b_1)$ and $^3B_2(3a_2 \rightarrow 5b_1)$ states of this study. Thus, the "n → π*" states show a large red shift, and the "π → π*" states show a minor red shift in hydrogen bonding solvents and upon N-alkylation.

The experimental and current theoretical results indicate that hydrogen bonding solvents and N-alkylation of carbazole have a substantial effect on the nitrogen "lone pair", but relatively little effect on the π orbitals delocalized over the biphenyl system. This suggests that increased electron density on the nitrogen destabilizes the nitrogen "lone pair", and red-shifted transitions originate from this effect. Hydrogen bonding interactions would be expected to increase the electron density on nitrogen and, through hyperconjugation, N-alkylation could have the same effect. Clearly other explanations are possible, and additional work is underway in this laboratory to characterize further the electronic states and transitions in carbazole and its derivatives.

Acknowledgment. The authors wish to express their appreciation to Dr. James A. Ryan for many helpful discussions on CI techniques and to Dr. J. L. Whitten for the use of his CI program. The authors also thank the University of Kansas for support of the computing time required for this work.

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(1) Supported in part by The Upjohn Company, Kalamazoo, Mich. 49001.

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Dimeric Structure of Di-*tert*-butylphosphinic Acid[1a]

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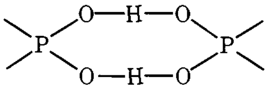
Abstract: The molecular structure of di-*tert*-butylphosphinic acid, $[(CH_3)_3C]_2PO(OH)$, as determined by single-crystal x-ray methods, is the first observed distinct dimeric $R_2PO(OH)$ compound with two acid molecules linked through a centrosymmetric configuration, **1.** The molecule crystallizes in the monoclinic space group, $P2_1/c$ with cell parameters a = 8.973 (6) Å, b = 13.130 (9) Å, c = 10.539 (7) Å, β = 117.95 (3)°, and Z = 4. The structure was solved and refined using 999 independent three-dimensional Mo Kα x-ray data collected with an automated diffractometer. Full-matrix least-squares refinement of 620 observations for which $F_o > 3\sigma(F_o)$ led to R_F = 0.059. The discrete dimer which was found contains strong, 2.506 (18) Å, hydrogen bonds, in which the oxygen atoms of O-H-O are not related by a crystallographic symmetry element. The eight-membered, hydrogen bonded ring has $\bar{1}$ site symmetry and shows a small chair-conformation distortion from planarity. The P-O bond lengths are 1.521 (8) and 1.520 (6) Å which indicates that the oxygen atoms are essentially equivalent. There appear to be weak C-H···O interactions which fix the methyl group orientations to give an overall eclipsed conformation.

Monoacidic phosphorus organic compounds of the type $(RO)_2PO(OH)$, $(R)(RO)PO(OH)$, and $R_2PO(OH)$ show association through strong hydrogen bonding forming dimers, **1,** in nonpolar solvents[2] and polymeric or helical strands, **2,** in the crystalline state.[3-5] Unlike carboxylic acids, no distinct eight-membered-ring dimers have been observed in the solid state; however, formation of eight-membered hydrogen bonded rings is not uncommon. Materials such as $K[PHO_2(OH)HF]$,[6] $SnHPO_4$,[7] β-ciliatine,[8] and 2-aminoethanol phosphate[9] have been shown to form eight-membered rings of **1,** but in each of these materials further ionic or hydrogen bonding is also present. We wish to report the existence of a distinct, eight-membered-ring, dimeric $R_2PO(OH)$ compound, di-*tert*-butylphosphinic acid, $[(CH_3)_3C]_2PO(OH)$ (H[D*t*-BP] hereafter).



1

···OPOH···OPOH···OPOH···

2

In recent years, the stereochemistry and binding affinities of organophosphorus compounds for specific ions have developed into a subject of wide chemical and biochemical interest. H[D*t*-BP] acid has acquired a special significance as an extractant in metals separations, especially the purification of

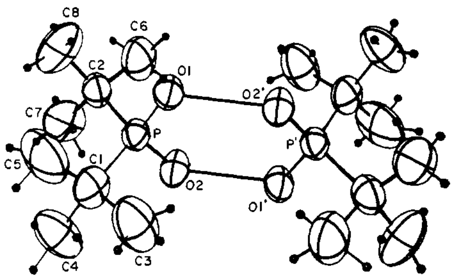


Figure 1. H[D*t*-BP] dimer showing atom labeling and 50% probability elipsoids.

Table I. Positional Parameters of H[D*t*-BP] with Estimated Standard Deviations Given in Parentheses

	x	y	z
P	0.0413 (3)	0.4044 (2)	0.6678 (2)
O_1	0.0641 (7)	0.5191 (3)	0.6872 (5)
O_2	0.0219 (6)	0.3656 (3)	0.5250 (5)
C_1	−0.1478 (10)	0.3722 (6)	0.6782 (9)
C_2	0.2350 (11)	0.3510 (6)	0.8083 (8)
C_3	−0.2896 (17)	0.4290 (9)	0.5595 (14)
C_4	−0.1968 (14)	0.2618 (8)	0.6563 (18)
C_5	−0.1448 (18)	0.4080 (11)	0.8187 (15)
C_6	0.3776 (15)	0.3834 (10)	0.7743 (12)
C_7	0.2355 (13)	0.2385 (9)	0.8108 (13)
C_8	0.2819 (15)	0.3908 (11)	0.9576 (11)
H_1	0.0040 (72)	0.5592 (43)	0.6063 (62)
H_2	0.1626 (84)	0.2083 (52)	0.8323 (71)
H_3	0.3328 (82)	0.2036 (5)	0.8670 (68)
H_4	0.1799 (81)	0.2051 (49)	0.7137 (64)
H_5	0.1804 (77)	0.3781 (47)	0.9845 (61)
H_6	0.3971 (77)	0.3667 (44)	1.0041 (65)
H_7	0.2349 (95)	0.4459 (4)	0.9480 (74)
H_8	0.3468 (92)	0.3752 (53)	0.6852 (67)
H_9	0.3718 (78)	0.4657 (45)	0.7644 (64)
H_{10}	0.4714 (78)	0.3494 (44)	0.8569 (65)
H_{11}	−0.3908 (80)	0.4352 (45)	0.5661 (64)
H_{12}	−0.2930 (94)	0.4075 (59)	0.4807 (69)
H_{13}	−0.2797 (89)	0.4848 (50)	0.5260 (71)
H_{14}	−0.1522 (94)	0.2290 (59)	0.6058 (81)
H_{15}	−0.1356 (94)	0.2128 (55)	0.7061 (78)
H_{16}	−0.3152 (82)	0.2498 (43)	0.6545 (58)
H_{17}	−0.2247 (91)	0.3707 (47)	0.8200 (70)
H_{18}	−0.0766 (85)	0.3477 (47)	0.8876 (67)
H_{19}	−0.1187 (86)	0.4749 (46)	0.8127 (72)

individual actinides and lanthanides. The uses of such extractants in liquid-liquid extraction[10] and in liquid-liquid chromatography[10,11] have been recently reviewed. Because highly sterically hindered extractants of this type were shown to exhibit unusual metal ion extraction selectivity,[12,13] it seemed possible that a study of the structural characteristics of H[D*t*-BP] acid would help to elucidate many of these selective chemical properties.

Experimental Section

The preparation of H[D*t*-BP] has been described previously.[13] A sample which had been purified by several recrystallizations from *n*-heptane was used. Rather fragile, clear, parallelepiped-shaped x-ray size crystals were obtained by slow crystallization from benzene. A specimen with approximate dimensions 0.10 × 0.13 × 0.10 mm was selected and mounted on the end of a glass fiber with epoxy cement for x-ray examination.

Preliminary oscillation, Weissenberg, and precession photographs revealed $2/m$ Laue symmetry and systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$. These findings are consistent with the centrosymmetric monoclinic space group $P2_1/c$ [$C_{2h}{}^5$; No. 14]. The crystal was mounted on a eucentric goniometer head placed on a General Electric XRD-490 automated diffractometer controlled by an IBM 1130 computer.

The XRD-490 system is equipped with a CA-8S Coolidge standard-focus Mo x-ray tube operated at constant potential, 48 kV and 16 mA, automated shutters, 0.6-mm entrance and 1.0-mm exit collimators, a series of copper-foil attenuators (with a 2.77 attenuation factor for intensities greater than 10 000 counts/s), Ross 1 (Zr) filters, a pulse-height analyzer adjusted to pass 95% of the Mo Kα peak, and a scintillation counter operated at 750 V. The crystal was mounted along the b axis with the a^*c^* plane of the crystal parallel to the plane of the instrument. The takeoff angle was 2.0°.

The unit cell parameters were determined by least squares from the angular coordinates of 13 reflections selected to be in a 2θ range 16-30° and distributed over the hkl and $\bar{h}kl$ octants. The angular coordinates were manually determined using both "half-slit" and "half-height" techniques. The resulting cell parameters at 27 °C and their estimated standard deviations are $a = 8.973$ (6) Å, $b = 13.130$ (9) Å, $c = 10.539$ (7) Å, and $\beta = 117.95$ (3)°; the cell volume is 1096.9 Å^3. The observed density, ρ_{obsd}, is 1.089 g/cm^3 while ρ_{calcd} is 1.077 g/cm^3 for $Z = 4$. No crystallographic symmetry is imposed on the molecule.

Intensity data were measured with a coupled θ-2θ scan. The scan width of 1.6° was divided into steps of 0.05°, and each step was counted for 4 s. Background measurements of 20 s were taken at each end of the scan width. A total of 1064 reflections, 999 unique, in the range $1° \leq 2\theta \leq 40°$ for the hkl and $\bar{h}kl$ octants were collected. Two orthogonal check reflections were measured after every 50 reflections; the variation from the mean intensity was less than 5%.

The intensity data were assigned weights, ω, using the relation $\omega = 1/\sigma^2$ where σ is the standard deviation of the net count. The expression used to obtain $\sigma_{I_{\text{net}}}$ was

$$\sigma_{I_{\text{net}}} = \left[I_{\text{tot}} + \frac{t_c}{t_b} B_{\text{tot}} + 0.05 I_{\text{net}} \right]^{1/2}$$

where

$$I_{\text{net}} = I_{\text{tot}} - B_{\text{tot}}$$

and I_{tot} is the total count, B_{tot} is the total background equal to $t_c/t_b(B_1 + B_2)$, t_b = time counting background counts, t_c = time scanning the peak, and 0.05 is a fractional systematic error. All negative values of I_{net} were set to zero. Absorption corrections, based on measured crystal dimensions and an absorption coefficient equal to 2.13 cm^{-1}, and Lorentz and polarization factors were applied using the program DATALIB.[14] The transmission factors ranged from 0.89 to 0.85.

Structure Determination and Refinement. Structure solution, refinement, and molecular drawings were performed with local versions adapted for the Xerox Sigma V computer of the Argonne National Laboratory Chemistry Division, of the programs ORXFLS3,[15a] Canterbury Fourier,[15b] ORFFE3,[16] and ORTEP.[17] Carbon, oxygen, and phosphorus scattering factors were taken from Cromer and Waber[18] and modified for the real and imaginary components of anomalous dispersion.[19] Hydrogen scattering factors were from volume 4 of the Crystallographic Tables.[20]

The coordinates of the phosphorus atom were determined from the Harker section of the Patterson function. Interpretation of the first Fourier calculation permitted placement of one oxygen unambiguously. The remaining nine non-hydrogen atoms were placed after a structure factor and Fourier calculation. The anisotropic full-matrix least-squares refinement of the heavy atoms resulted in a discrepancy index (R) of 0.119. Hydrogen atoms were located from successive difference Fourier maps, and an isotropic secondary extinction correction was applied ($G_{\text{final}} = 0.299$). The positional parameters of the hydrogen atoms were refined with a fixed thermal parameter of 5 Å^2. The R factor for all data converged to 0.091 for $F_o > \sigma(F_o)$. When reflections for which $F_o < 3\sigma(F_o)$ were omitted from the refinement, the R value was reduced to 0.059. The data set was very weak, 379 reflections had measured intensities less than 3σ, thus accounting for the large reduction of the R factor. The value of Σ_2, the standard error of an object of unit weight, was 1.58 indicating overall excellent refinement.

The final positional and isotropic thermal parameters for all atoms are listed in Table 1. Anisotropic thermal parameters for all non-hydrogen atoms are given in Table II. The observed and calculated structure factors are available as supplementary material.

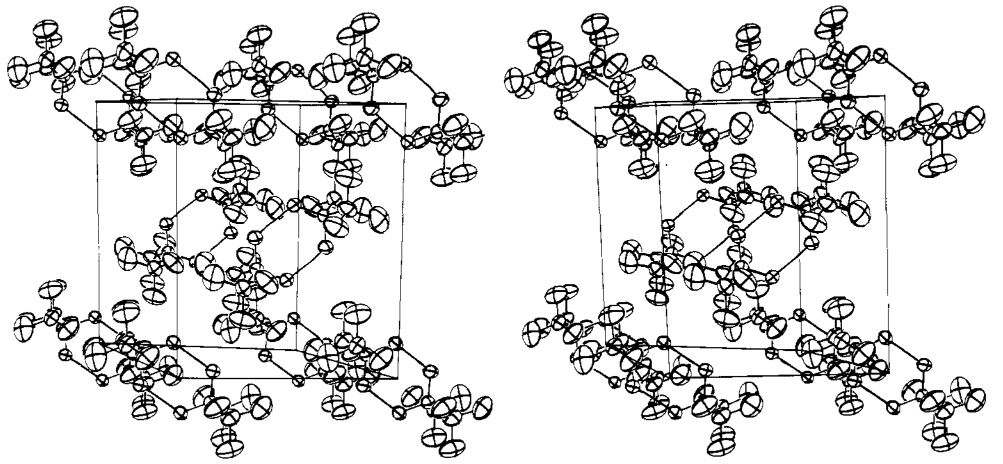


Figure 2. Stereoview showing packing of H[D*t*-BP] dimers within a unit cell.

Table II. Anisotropic Thermal Parameters[a] (× 10^4) of H[D*t*-BP] with Estimated Standard Deviations in Parentheses

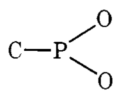
Atom[b]	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	208 (4)	49 (1)	107 (3)	−0 (2)	72 (3)	3 (2)
O_1	346 (15)	51 (4)	117 (7)	−17 (6)	98 (9)	−4 (4)
O_2	307 (13)	51 (3)	119 (7)	15 (5)	104 (8)	−1 (4)
C_1	238 (19)	76 (7)	174 (13)	38 (9)	92 (14)	36 (8)
C_2	239 (20)	78 (7)	135 (13)	−6 (9)	95 (14)	10 (7)
C_3	296 (24)	117 (11)	346 (29)	37 (15)	166 (25)	78 (14)
C_4	248 (27)	81 (10)	413 (29)	13 (11)	174 (23)	43 (12)
C_5	439 (37)	176 (14)	380 (27)	−73 (19)	303 (27)	−11 (18)
C_6	266 (23)	151 (11)	256 (19)	31 (14)	97 (20)	85 (14)
C_7	247 (27)	100 (11)	293 (22)	54 (12)	59 (19)	54 (11)
C_8	273 (25)	201 (14)	192 (17)	110 (17)	55 (17)	34 (13)

[a] The form of the anisotropic temperature factor is: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + hl\beta_{13} + 2kl\beta_{33})]$. [b] The heavy atoms are numbered as illustrated in Figure 1.

Description and Discussion of the Structure

The structure determination clearly shows H[D*t*-BP] to exist as a dimer in the crystal as can be seen in Figure 1. The two molecules of the dimer are related by a center of symmetry and are linked by strong O-H-O bonds 2.506 (18) Å in length. The eight-membered ring, **1**, resulting has site symmetry $\bar{1}$ and shows a chair conformation distortion from planarity.

The configuration of the rest of the dimer is determined by the near tetrahedral geometry of P and the staggered configurations adopted by the two *tert*-butyl groups with respect to the



moiety when viewed down the appropriate C-P bond. The hindering potential for rotation about the C-P bond is expected to be substantial in view of NMR measurements of the rotational barrier about this bond in several *tert*-butylphosphine derivatives.[21] The result is a staggered configuration in H[D*t*-BP] quite similar to those observed in the phosphine derivatives. The *tert*-butyl C atoms are thus completely ordered as are indeed all of the methyl protons and in such a way as to create an approximate mirror plane, containing the hydrogen bonded ring, which relates the two *tert*-butyl groups.

The unit cell and packing of the dimer units are shown in Figure 2. The two dimer units in the cell are related by the 2_1 axis. The packing is relatively open in agreement with the rather low density.

The nature of the hydrogen bonding in the H[D*t*-BP] dimer is of especial interest. The O-H-O bond is short enough to be in the range of possibly centered H bonds,[22] but, since the site symmetry is 1, the bonds are not required to be symmetric. Thus, there are several possibilities: (1) the proton is in an asymmetric location, (2) the proton is at the bond center, (3) the proton is disordered and may be statistically symmetric, and (4) the proton is disordered but asymmetrically distributed either as to location or population or both. The two P-O distances found in this study, 1.520 (6) and 1.521 (8) Å are virtually equivalent and are intermediate between expected values for P—O and P═O bond lengths. This finding tends to favor models 2 and 3. More direct information concerning the ring proton location given by a difference Fourier map placed it tentatively on the O- - -O bond line 0.85 Å from one oxygen atom. When refined through four cycles of full-matrix least squares, the proton position converged to 0.93 Å from the bonded oxygen atom. Although this would appear to verify model 1, the data were rather insensitive to the exact proton location. Thus, starting models with ordered symmetric and with disordered proton locations refined to give ordered asymmetric and disordered asymmetric proton distributions. Overall, an asymmetric model appears to be favored but no clear decision between ordered and disordered models could be reached.

Bond angles, listed in Table IV, show the coordination about P to be somewhat distorted from tetrahedral with the O-P-O, C-P-C, and the average O-P-C bond angles equal to 114.3°, 115.4°, and 106.8°, respectively. The C-P-C angle in dimethylphosphinic acid is 107.3°,[5c] in comparison illustrating, perhaps, the greater repulsive effect of the *tert*-butyl groups.

Table III. Interatomic Distances in H[D*t*-BP] with Estimated Standard Deviations in Parentheses

Bond	Distance (Å)
(a) Heavy Atom Distances	
$P-O_1$	1.521 (8)
$-O_2$	1.520 (6)
$-C_1$	1.801 (14)
$-C_2$	1.815 (22)
C_1-C_3	1.500 (24)
$-C_4$	1.500 (18)
$-C_5$	1.532 (14)
C_2-C_6	1.541 (17)
$-C_7$	1.477 (13)
$-C_8$	1.518 (14)
(b) Methyl Hydrogen–Carbon Distances	
C_3-H_{11}	0.95 (6)
$-H_{12}$	0.86 (6)
$-H_{13}$	0.84 (6)
C_4-H_{14}	0.91 (6)
$-H_{15}$	0.85 (7)
$-H_{16}$	1.07 (6)
C_5-H_{17}	0.88 (6)
$-H_{18}$	1.06 (6)
$-H_{19}$	0.92 (6)
C_6-H_8	0.85 (6)
$-H_9$	1.09 (5)
$-H_{10}$	0.85 (6)
C_7-H_2	0.88 (6)
$-H_3$	0.92 (6)
$-H_4$	1.01 (6)
C_8-H_5	1.09 (6)
$-H_6$	0.97 (6)
$-H_7$	0.82 (6)
(c) Hydrogen-Bonded Distances	
H_1-O_1	0.93 (6)
H_1-O_2	1.62 (6)
(d) Dimeric Interaction	
$O_1\cdots O_{2'}$	2.506 (18)
(e) Close Hydrogen–Hydrogen Interactions	
$H_2\cdots H_{15}$	2.37 (10)
$H_5\cdots H_{18}$	2.08 (9)

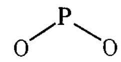
Table IV. Bond Angles in H[D*t*-BP] with Estimated Standard Deviations Given in Parentheses

Atoms	Angle (deg)	Atoms	Angle (deg)
(a) Angles Involving Non-Hydrogen Atoms			
O_1-P-O_2	114.3 (5)	$P-C_1-C_5$	113.1 (10)
C_1-P-C_2	115.4 (4)	$P-C_1-C_3$	106.7 (7)
C_1-P-O_1	107.2 (16)	$P-C_1-C_4$	115.7 (16)
C_1-P-O_2	107.9 (8)	$C_6-C_2-C_7$	106.5 (16)
C_2-P-O_1	104.8 (16)	$C_6-C_2-C_8$	106.8 (12)
C_2-P-O_2	107.4 (8)	$C_7-C_2-C_8$	109.1 (11)
$C_3-C_1-C_4$	106.2 (15)	$P-C_2-C_6$	106.6 (6)
$C_3-C_1-C_5$	106.0 (11)	$P-C_2-C_7$	113.3 (17)
$C_4-C_1-C_5$	108.4 (10)	$P-C_2-C_8$	114.0 (9)
(b) Angles Involving Methyl Hydrogen Atoms			
$H_{11}-C_3-H_{12}$	119.7 (75)	$H_8-C_6-H_9$	92.5 (60)
$H_{11}-C_3H_{13}$	104.6 (69)	$H_8-C_6-H_{10}$	128.0 (69)
$H_{12}-C_3-H_{13}$	81.1 (70)	$H_9-C_6-H_{10}$	121.1 (57)
$C_1-C_3-H_{11}$	116.7 (41)	$C_2-C_6-H_8$	110.2 (54)
$C_1-C_3-H_{12}$	105.9 (55)	$C_2-C_6-H_9$	106.8 (39)
$C_1-C_3-H_{13}$	124.9 (55)	$C_2-C_6-H_{10}$	97.4 (36)
$H_{14}-C_4-H_{15}$	70.6 (52)	$H_2-C_7-H_3$	101.9 (64)
$H_{14}-C_4-H_{16}$	128.9 (60)	$H_2-C_7-H_4$	89.6 (59)
$H_{15}-C_4-H_{16}$	104.5 (69)	$H_3-C_7-H_4$	107.9 (63)
$C_1-C_4-H_{14}$	111.6 (52)	$C_2-C_7-H_2$	117.3 (50)
$C_1-C_4-H_{15}$	125.3 (55)	$C_2-C_7-H_3$	120.4 (47)
$C_1-C_4-H_{16}$	111.4 (36)	$C_2-C_7-H_4$	115.0 (40)
$H_{17}-C_5-H_{18}$	77.1 (54)	$H_5-C_8-H_6$	130.2 (52)
$H_{17}-C_5-H_{19}$	140.3 (70)	$H_5-C_8-H_7$	73.9 (57)
$H_{18}-C_5-H_{19}$	132.6 (68)	$H_6-C_8-H_7$	135.9 (72)
$C_1-C_5-H_{17}$	102.0 (47)	$C_2-C_8-H_5$	111.0 (35)
$C_1-C_5-H_{18}$	100.5 (37)	$C_2-C_8-H_6$	97.1 (38)
$C_1-C_5-H_{19}$	97.4 (46)	$C_2-C_8-H_7$	107.4 (53)

Table V. Short C–H···O Interactions

C–H···O	C···O Distance (Å)	H···O Distance (Å)
$C_6H_9O_1$	3.08 (5)	2.58 (7)
$C_5H_{19}O_1$	3.15 (3)	2.61 (7)
$C_8H_7O_1$	3.09 (4)	2.61 (7)
$C_3H_{13}O_1$	3.05 (4)	2.77 (7)
$C_6H_8O_2$	3.05 (1)	2.60 (7)
$C_3H_{12}O_2$	3.10 (3)	2.70 (7)
$C_4H_{14}O_2$	3.19 (3)	2.76 (8)
$C_7H_4O_2$	3.18 (3)	2.79 (7)

The two *tert*-butyl groups attached to P are in an eclipsed conformation when viewed down the C_1-C_2 vector. A staggered conformation, in contrast, would be expected to minimize *tert*-butyl group repulsions but would result in an eclipsed conformation of one *tert*-butyl group with respect to



which is presumably destabilizing. Another factor in the conformational relationship is the methyl group orientation with respect to O_1 and O_2. It is observed that one hydrogen atom in each of four CH_3 groups and two hydrogen atoms in the other two CH_3 groups achieve relatively close approaches to either O_1 or O_2. (This arrangement results in two rather close H-H contacts (Table III) which are repulsive, but the eight C-H···O contacts (see Table V) probably yield a net attractive force.) Although none of the H···O separations are appreciably shorter than the expected van der Waals separation (2.6 Å) the rather marked directional orientations of the CH_3 groups may be taken as evidence in favor of terming these weak hydrogen bonds. The C-H distances which average to 0.94 Å are normal for x-ray work. The weighted average C-C distance is 1.508 (6) Å which is shorter than a normal C-C single bond distance. Similar findings have been reported previously[23] for 2,5-di-*tert*-butylthiophene sulfone.

The conformation of the ring **1** is of some interest. Due to the $\bar{1}$ site symmetry, the four oxygen atoms are constrained to a plane, and any out of plane P atom displacement must distort the ring into a chair conformation. The observed P-atom displacements are 0.24 Å above and below the plane of the four oxygen atoms which leads to a torsion angle, the angle between the oxygen plane and the plane defined by O_1PO_2, of 16.8°. This distortion is small compared to those observed in cyclohexane-type rings but is much larger than that observed in a similar ring system reported for 2-aminoethanol phosphate.[9] Hydrogen atoms of the ring are not included in this discussion because their positions are not well established, but they are expected to be essentially coplanar with the oxygen atoms.

The structure of H[D*t*-BP] is dimeric, the first (X)(Y)-PO(OH) dimer to be reported. From previous structure determinations, it appears that most organic phosphorus compounds with O and O-H ligands adopt a spiral hydrogen-bonded configuration in the crystalline state presumably due to the better packing and higher density which it promotes. However, a spiral configuration is sterically forbidden when large, bulky groups such as *tert*-butyl are attached to P as in H[D*t*-BP]. Thus, the spiraling of hydrogen-bonded H[D*t*-BP] monomers about a 2_1 axis would result in intolerably close methyl group hydrogen atom contacts for the first and third molecules, the second and fourth and so on. Since there are no steric barriers to the formation of a second paired intermolecular hydrogen bond, the dimer configuration is strongly favored. Dimer formation should then be expected in other examples of highly hindered organophosphinic acids and organophosphoric acids. We are currently investigating the structures of several other organophosphorus compounds which are efficient extractants for heavy elements.

Supplementary Material Available: Listings of structure-factor amplitudes (2 pages). Ordering information is given on any current masthead page.

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Nucleophilic Substitution at Phosphorus in Tertiary Phosphines. Evidence against Pseudorotation in a Potential Intermediate

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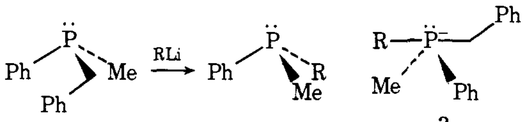
Received February 2, 1976

Abstract: The possibility of the formation of a hypervalent tetracoordinated phosphorus anion as an intermediate in nucleophilic substitution at phosphorus in tertiary phosphines was investigated. Treatment of (+)-(*S*)P-4-*tert*-butylphenylmethylphenylphosphine with *t*-BuLi resulted in displacement of phenyl and 4-*tert*-butylphenyl anions (in a ratio of 1.4:1, respectively) with complete inversion of configuration at phosphorus with both leaving groups. These data are used to show the absence of any pseudorotation in the potential intermediate (the hypervalent anion) and that the substitution may best be considered to be a classical SN2-type of process.

We recently reported that nucleophilic displacement at phosphorus ($S_N{}^P$) by alkyllithium reagents on (+)-(*R*)P-benzylmethylphenylphosphine (**1**) occurs with complete inversion of configuration at phosphorus (eq 1).[1] A possible mechanism for this reaction would involve nucleophilic attack on the phosphine phosphorus atom, which could lead to a valence-expanded anionic intermediate (e.g., **2**).[2] This potential intermediate has one more electron than a phosphoranyl radical, some of which are known to be stereochemically nonrigid[3] due to pseudorotational processes (ψ).[4] As the analysis below will show, the stereochemical results of the $S_N{}^P$ reaction on **1**, with only one good leaving group, indicated, but did not prove, that **2** was stereochemically rigid. The use of a phosphine with poorer leaving groups than the benzyl anion might bestow a longer lifetime upon species analogous to **2**, potentially allowing ψ to become observable. It was thus of interest to investigate whether or not a stereochemical result other than complete inversion of configuration at phosphorus for an $S_N{}^P$ reaction was possible under more biased conditions than with substrate **1**. Before describing the specific substrate chosen, it is important to consider the potential pseudorotations in species analogous to **2**.



1 2 (1)

A hypervalent, tetracoordinated phosphorus anion (e.g., **2**) may be considered to be analogous to the neutral pentacoordinated phosphoranes, with the lone pair of electons (1p) replacing one of the ligands. Consequently, the analysis of pseudorotational interconversions of phosphoranes, as elegantly described in detail by Mislow,[4b,5] will be applied to the potential interconversions of the hypothetical tetracoordinated phosphorus anion intermediates. If one uses the descriptors 1, 2, 3, 4 to represent a substituted phosphine 123P4 (**3**) where 4 represents the 1p, and 3^- the *only leaving group*, and, further, 5^- represents the nucleophile of an alkyllithium, then Scheme I represents the types of transformations to be con-