Synthesis, Structural Characterization, and Conformational Bias in Solution of a Sterically Congested Pyrophosphite:[1] Experimental and Computational Evidence for Restricted Rotation about an sp^3-sp^3 P−O Single Bond

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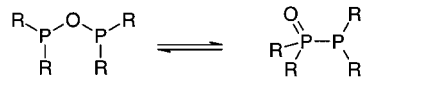
The synthesis and structural characterization of the sterically congested pyrophosphite 6-[(2,4,8,10-tetrakis(1,1-dimethylethyl)-dibenzo[*d,f*][1,3,2]dioxaphosphepin-6-yl)oxy]-2,4,8,10-tetrakis(1,1-dimethylethyl)-dibenzo[*d,f*][1,3,2]-dioxaphosphepin, **3**, is described. In solution at room temperature, a single species was observed that was consistent with a pyrophosphite structure without any evidence for the tautomeric diphosphine monoxide. Below the coalescence temperature (T_C), 0 °C, three atropisomers were observed with relative absolute configurations of (*R*,R*,R**), (*R*,S*,R**), and (*R*,R*,S**). Ring inversion of the seven-membered rings below the T_C is slow on the NMR time scale, which leads to observable diastereoisomerism because of the presence of two independent stereoaxes (sp^2-sp^2 C−C single bond connecting the two aryl rings). Additionally, a rotation about an exocyclic P−O single bond connecting the two seven-membered rings, which constitutes a third stereoaxis, is slowed on the NMR time scale. In the X-ray crystal structure of **3**, the solid-state conformation was found to be the same as the major conformation in solution below the T_C, namely, the (*R*,R*,S**) atropisomer. The results of a conformational search, performed with a specifically parametrized AMBER* force field, were in agreement with the ^{31}P NMR assignment of the major (*R*,R*,S**) atropisomer, which was found to be an energy minimum. Additionally, we could independently assign the relative configuration of the minor isomers based on the calculated results.

Introduction

Pyrophosphites are an interesting class of compounds that are the phosphorus analogues of the commonly found carboxylic acid anhydrides in organic chemistry. Pyrophosphites are useful reagents for peptide synthesis[2] and, quite recently, were found to be useful bridging ligands for the synthesis of polynuclear metal complexes.[3,4] The ability of three-coordinate P(III) to rehybridize to four-coordinate P(V) provides the basis for the observed anhydride to tetraalkoxydiphosphine monoxide tautomerism (eq 1).[5,6]



(1)

The position of the equilibrium is dependent upon both the electronic and steric properties of the substituents on phosphorus. Alkoxy substituents on phosphorus increase the stability of the pyrophosphite tautomer relative to the diphosphine monoxide, and tetralkoxydiphosphine monoxides are reported to isomerize to pyrophosphites rapidly.[6] Relatively little structural information is available for free uncomplexed pyrophosphites. We report herein the synthesis and structural characterization of a sterically congested pyrophosphite incorporating two substituted dibenzo-[*d,f*][1,3,2]dioxaphosphepin rings that appears to exist solely as the anhydride tautomer (Figure 1).

Furthermore, experimental and computational evidence is presented supporting the presence of a biased conformation in solution.

Experimental Section

All melting points were determined in open capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR (300.08 and 499.84 MHz, respectively) spectra were obtained on a Varian model Gemini-300 or Unity-500 spectrometer. ^{13}C NMR (125.70 MHz) spectra were obtained obtained on a Varian model Unity-500. ^{31}P NMR (202.33 and 121.47 MHz, respectively) spectra were obtained on a Varian model Unity-500 or Gemini-300 spectrometer. All ^{31}P chemical shift values are reported in parts per million relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. Significant ^{1}H NMR spectral data are tabulated in the following order: multiplicity (m, multiplet; s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dq, doublet of quartets; dt, doublet of triplets; ddq, doublet of doublets of quartets), atom assignments, coupling constant in hertz, and number of protons. IR spectra were obtained on a Bruker model Vector 22. Merck silica gel 60 (200−400 mesh) was used for column chromatography. Merck precoated (0.25 mm) silica gel F-254 plates were used for TLC. Reagents were purchased from commercial laboratory supply houses. Solvents were dried prior to use when necessary with appropriate drying agents.

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(2) (a) Anderson, G. W.; Blodinger, J.; Welcher, A. D. *J. Am. Chem. Soc.* **1952**, *74*, 5309. (b) Crofts, P. C.; Markes, J. H. H.; Rydon, H. N. *J. Chem. Soc.* **1958**, 4250.
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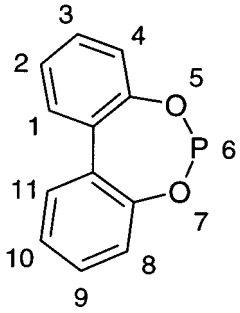


Figure 1. The Chemical Abstracts numbering system for the dibenzo-[*d*,*f*][1,3,2]dioxaphosphepin ring system.

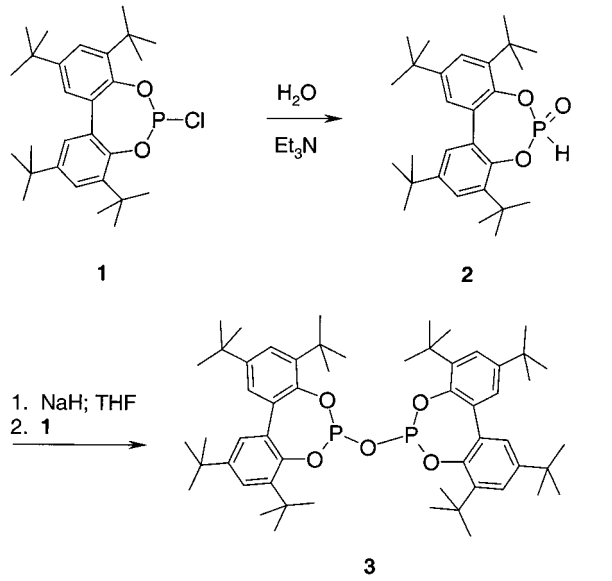
Reactions were carried out in flame-dried apparatus under a dry inert atmosphere of either nitrogen or argon. Elemental analyses were performed by the Analytical Research Department, Ciba Specialty Chemicals. Calculations were performed using MacroModel version 7.0 and Spartan version 5.1 on an SGI Octane or DEC Alphaserver 4000 workstation.

2,4,8,10-Tetrakis(1,1-dimethylethyl)-6-oxo-6*H*-dibenzo[*d*,*f*][1,3,2]-dioxaphosphepin (2). To a solution of 6.32 g (13 mmol) of **1**[7] in 150 mL of toluene at ambient temperature was added dropwise a solution of 0.24 mL (13 mmol) of water in 3.0 mL (22 mmol) of triethylamine. After the addition was complete, the reaction mixture was stirred at room temperature for 15 min. The volatiles were removed in vacuo, and the residue was triturated twice with acetonitrile (2 × 50 mL) to give 5.20 g (86%) of a white solid, mp 225−227 °C. ^{1}H NMR (C_6D_6): δ 1.19 (s, 18 H), 1.22 (s, 18 H), 6.93 (d, $^1J_{HP}$ = 724 Hz, 1 H), 7.52 (d, 2 H), 7.32 (d, 2 H). ^{1}H NMR ($CDCl_3$): δ 1.37 (s, 18 H), 1.52 (s, 18 H), 7.25 (d, 2 H), 7.30 (d, $^1J_{HP}$ = 726 Hz, 1 H), 7.51 (d, 2 H). ^{31}P{^{1}H} NMR (C_6D_6): δ 10.3. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 10.1. IR (ATR): ν 2457 cm^{-1} (P−H), 1286 cm^{-1} (P═O). Anal. Calcd for $C_{28}H_{41}O_3P$: C, 73.7; H, 9.1. Found: C, 73.7; H, 8.9.

6-[(2,4,8,10-Tetrakis(1,1-dimethylethyl)dibenzo[*d*,*f*][1,3,2]dioxaphosphepin-6-yl)oxy]-2,4,8,10-tetrakis(1,1-dimethylethyl)dibenzo-[*d*,*f*][1,3,2]dioxaphosphepin (3). To a stirred suspension of 0.18 g (7.5 mmol) of sodium hydride in 50 mL of tetrahydrofuran was added dropwise a solution of 3.56 g (7.8 mmol) of **2** in 80 mL of tetrahydrofuran. The reaction mixture was heated to 60 °C, and it was held at that temperature for 9.5 h. The resultant solution was cooled to 0 °C, and then to the reaction mixture was added 3.67 g (7.7 mmol) of **1**. The reaction mixture was allowed to warm to ambient temperature, and then it was stirred at this temperature for 14 h. The solvent was removed in vacuo and the residue purified by chromatography (silica gel; 95:5 hexane:ethyl acetate eluent) followed by sequential recrystallization from acetonitrile and 2-butanone to give 5.00 g (74%) of a white solid, mp 269 °C. ^{31}P{^{1}H} NMR (202.37 MHz) (CD_2Cl_2): δ 131.2. ^{31}P{^{1}H} NMR (202.37 MHz) (CD_2Cl_2) (−80 °C): δ 125.4 (s), 128.9 (d, $^2J_{POP}$ = 37 Hz), 131.2 (d, $^2J_{POP}$ = 37 Hz), 139.4 (s). ^{1}H NMR (499.87 MHz) ($C_2D_2Cl_4$) (120 °C): δ 1.33 (s, 36 H), 1.36 (s, 36 H), 7.12 (s, 4 H), 7.35 (s, 4 H). ^{13}C{^{1}H} NMR (C_6D_6) (125.6998 MHz) (60 °C): δ 31.63 (s), 31.66 (s), 34.73 (s), 35.73 (s), 124.60 (s), 126.92 (s), 133.94 (d, J_{CP} = 3.9 Hz), 146.00 (d, J_{CP} = 3.4 Hz), 147.03 (s). High-resolution MS (EI): 894.5461 (calcd 894.5481). Anal. Calcd for $C_{56}H_{80}O_5P_2$: C, 75.1; H, 9.0. Found: C, 74.8; H, 9.1.

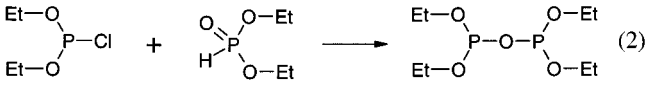
Suitable crystals for X-ray analysis (colorless prisms) were grown from an acetonitrile:toluene mixture. Crystal data: $C_{56}H_{80}O_5P_2$; formula weight (g·mol^{-1}) = 895.19; crystal size (mm) 0.52 × 0.48 × 0.31; crystal system is triclinic; cell parameters: a = 21.786(2) Å, b = 11.533(1) Å, c = 11.472(1) Å, α = 108.71(1)°, β = 78.51(1)°, γ = 87.85(1)°; V = 2659.4(8) Å^3; space group = $P1$; d_{calc} = 1.118 Mg·m^{-3}; F_{000} = 972; absorption correction = none; Z = 2. Data collection: scan range (2θ) = 6−46; temperature = 23 °C; Philips PW 1100 diffractometer; Mo Kα (λ = 1.54178 Å) radiation; highly oriented graphite crystal monochromator; scan mode θ/2θ; number of reflections collected 6584; Independent reflections 6206; observed reflections 4553 ($I > 2\sigma(I)$); h range −22 → 22; k range −11 → 11; l range 0 → 11. R indices: R = 0.061, R_w = 0.068. Solution: direct methods. Refinement method: full-matrix least-squares; Siemens SHELXS86 (VMS) system.

Scheme 1



Results and Discussion

Synthesis. Arbusov reported the synthesis of tetraethyl pyrophosphite by the reaction of sodium diethylphosphonate with diethyl phosphorochloridite (eq 2).[8] The seven-membered



cyclic phosphorochloridite **1** was prepared by the reaction of 3,3′,5,5′-tetra-*tert*-butyl-1,1′-biphenyl-2,2′-diol[7] with phosphorus(III) chloride as described in the literature.[9] The phosphonate **2** was prepared by hydrolysis of **1** with a stoichiometric quantity of water using triethylamine as a hydrogen chloride acceptor (Scheme 1). In the ^{1}H NMR spectrum of **2**, a doublet was observed at δ 6.93 ($^1J_{HP}$ = 723.8 Hz), which was assigned to the proton bonded to phosphorus. The magnitude of the observed $^1J_{HP}$ coupling constant is consistent with a phosphonate structure in which a proton is bonded to a pentavalent phosphorus atom.[10] The reaction of the sodium salt of **2**, prepared in situ by reaction with sodium hydride in tetrahydrofuran, with the phosphorochloridite **1** gave the pyrophosphite **3** (74% recrystallized).

In the ^{31}P{^{1}H} NMR spectrum (202.37 MHz) of **3** at the NMR probe temperature (CD_2Cl_2), a broadened singlet was observed at δ 131.2, which is in the region expected for a tricoordinate P(III) ester.[10] In the 500 MHz ^{1}H NMR spectrum of **3** at the NMR probe temperature ($C_2D_2Cl_4$), the observed

(7) (a) Müller, E.; Mayer, R.; Narr, B.; Rieker, A.; Scheffler, K. *Justus Liebigs Ann. Chem.* **1961**, *645*, 25. (b) Kushioka, K. *J. Org. Chem.* **1983**, *48*, 4948.

(8) (a) Arbusov, A. E.; Arbusow, B. A. *Chem. Ber.* **1932**, *65*, 195. (b) For the use of triethylamine as a base, see ref 2a. (c) Foss, V. L.; Veits, Yu. A.; Lukashev, N. V.; Lutsenko, I. F. *Phosphorus Sulfur Relat. Elem.* **1977**, *3*, 299.

(9) Pastor, S. D.; Shum, S. P.; Rodebaugh, R. K.; DeBellis, A. D.; Clarke, F. H. *Helv. Chim. Acta* **1993**, *76*, 900.

(10) (a) Emsley, J.; Hall, D. *The Chemistry of Phosphorus*; Harper & Row: New York, 1976; pp 85−91. (b) Tebby, J. C. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Weiheim, 1987; p 19. (c) Kleemann, S. G.; Fluck, E.; Tebby, J. C. In *Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; Tebby, J. C., Ed.; CRC Press: Boca Raton, 1991; pp 49−63.

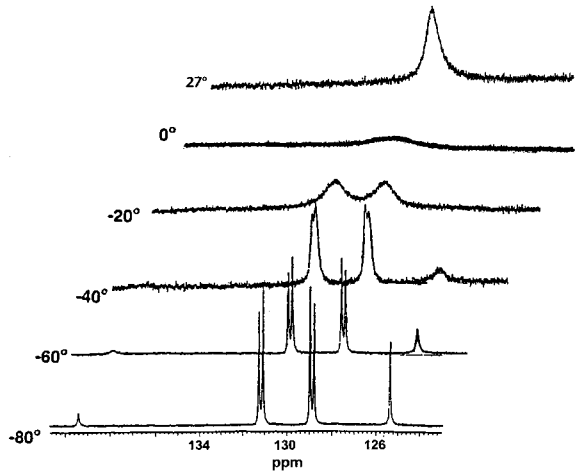


Figure 2. VT $^{31}P\{^{1}H\}$ NMR spectrum of **3**.

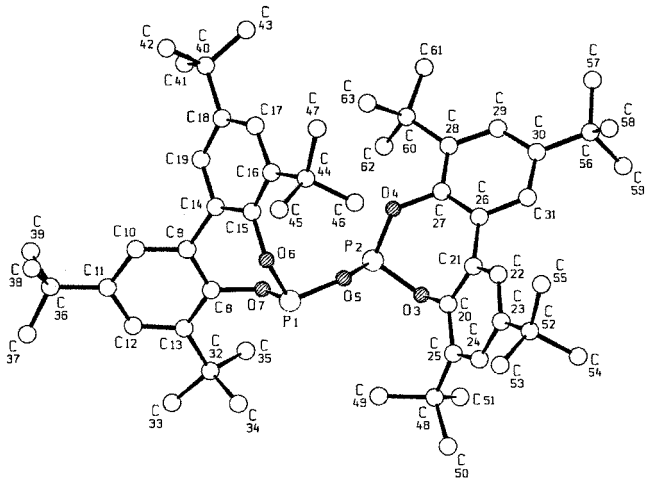


Figure 3. Molecular structure of **3** showing the crystallographic numbering scheme.

signals for both the protons of the *tert*-butyl substituents and aromatic protons were broadened, and were seen to sharpen upon heating the sample. In the ^{1}H NMR spectrum ($C_2D_2Cl_4$) of **3** at 120 °C, four singlets were observed at δ 1.33, δ 1.36, δ 7.12, and δ 7.35 that were assigned to the protons of two pairs of four equivalent *tert*-butyl groups (upfield signals) and two pairs of four equivalent aromatic protons (downfield signals), respectively. These observations are consistent with rapid ring inversion of the dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings (a rotation about the single C−C bond connecting the two aryl groups) as well as rotation about any other potential stereoaxes on the NMR time scale (vide infra) at 120 °C. This must be the case because slow ring inversion on the NMR time scale of the dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings in **3** (the single C−C bond connecting the two aryl groups is a stereoaxis) would lead to the observation of four pairs of nonequivalent *tert*-butyl substituents as well as four pairs of nonequivalent aromatic protons.[11] Conformational averaging, because of rapid ring inversion and rotation of exocyclic bonds at 120 °C, leads to an overall C_{2v} symmetry for **3**.[12]

Solution and Solid-State Conformation. Previously, the barrier to ring inversion of substituted dibenzo[*d*,*f*][1,3,2]-dioxaphosphepins has been measured in our laboratory[9,11] and elsewhere,[13] and was found to vary between 10 kcal/mol (199 K) and 11.6 kcal/mol (258 K) depending upon the ring substitution. Quite interestingly, in the VT $^{31}P\{^{1}H\}$ NMR spectrum of **3** below 0 °C, the coalescence temperature, two singlets (δ 139.4 and δ 125.4) and two doublets [δ 128.9 (d, $^{2}J_{POP} = 37$ Hz) and δ 131.2 (d, $^{2}J_{POP} = 37$ Hz)] were observed, which were assigned to unequal populations of three diastereoisomers in a 4.4:16.8:78.9 ratio, respectively. The diastereomeric ratios were determined by integrating the peak areas of the appropriate resonances in the $^{31}P\{^{1}H\}$ NMR spectrum of **3** at −80 °C (Figure 2).

Caution must be exercised in the interpretation of the accuracy of isomer compositions determined by integrating peak areas of ^{31}P resonances, however, because the relaxation times of nonequivalent P atoms are often significantly different.[14] A homonuclear $\{^{31}P, ^{31}P\}$ 2D COSY spectrum was obtained at −80 °C in which the appropriate cross peaks were observed.

A reasonable explanation of these observations is that below the T_C, ring inversion of the seven-membered rings is slow on the NMR time scale, which leads to observable diastereoisomerism because of the presence of two independent stereoaxes (sp^2-sp^2 C−C single bond connecting the two aryl rings). Additionally, a rotation about an exocyclic P−O single bond connecting the two seven-membered rings, which constitutes a third stereoaxis, is slowed on the NMR time scale (vide infra). Below the T_C, three atropisomers would be expected to be observable with relative absolute configurations of (*R**,*R**,*R**), (*R**,*S**,*R**), and (*R**,*R**,*S**), which refers throughout this paper to the relative absolute configurations of the C(8)−C(9)−C(14)−C(15), the P(1)−O(5)−P(2)−O(3) stereoaxis, and the C(20)−C(21)−C(26)−C(27) stereoaxes (see Figure 3 or Figure 4 for the atom-numbering scheme).[15,16] In the (*R**,*R**,*R**) and (*R**,*S**,*R**) atropisomers of **3**, the phosphorus atoms are related by a C_2 axis and are therefore homotopic and equivalent in the $^{31}P\{^{1}H\}$ NMR spectrum. In the (*R**,*R**,*S**) atropisomer of **3**, the phosphorus atoms are not related by either a symmetry plane or an axis and are therefore heterotopic and nonequivalent in the $^{31}P\{^{1}H\}$ NMR spectrum.[17] A P−P $^{2}J_{POP}$ coupling of 37 Hz is observed. The free energy of activation, ΔG^*, for the process leading to the equivalence of the two phosphorus atoms in the (*R**,*R**,*S**) atropisomer of **3** was calculated from coalescence data to be 12.2 kcal/mol.[18,19] It is not clear whether the process leading to nonequivalence of these two phosphorus atoms involves the concerted slowing of all three stereoaxes or whether a stepwise process is operative.

An X-ray crystal structure of **3** was obtained (Figure 3). The solid-state conformation of **3** was that of the major conformation observed in solution below T_C, namely, the (*R**,*R**,*S**) atropisomer. The dihedral angles of the stereoaxis in each dioxaphos-

(11) (a) Pastor, S. D.; Richardson, C. F.; NabiRahni, M. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *90*, 95. (b) Pastor, S. D.; Shum, S. P.; DeBellis, A. D.; Burke, L. P.; Rodebaugh, R. K.; Clarke, F. H.; Rihs, G. *Inorg. Chem.* **1996**, *35*, 949 and references therein.

(12) For a discussion of averaged symmetry, residual stereoisomers, and the NMR of conformationally mobile systems, see: Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; pp 54−58.

(13) Whiteker, G. T.; Harrison, A. M.; Abatjoglou, A. G. *J. Chem. Soc., Chem. Commun.* **1995**, 1805.

(14) Shortt, A. B.; Burham, L. J.; Mosher, H. S. *J. Org. Chem.* **1983**, *48*, 3125.

(15) Considering either one the exocyclic P(1)−O(5)−P(2)−O(3), P(1)−O(5)−P(2)−O(4), P(2)−O(5)−P(1)−O(6), or P(2)−O(5)−P(1)−O(7) dihedral angles leads to equivalent conclusions.

(16) In principle, the observed spectrum can also be explained by the presence of (*R**,*S**), (*R**,*R**), and (*R**,*R**,*S**) atropisomers. However, the (*R**,*R**,*R**), (*R**,*S**,*R**), and (*R**,*R**,*S**) atropisomers were found to be minima on the potential energy surface.

(17) For a discussion on topicity, see: Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; pp 465−508.

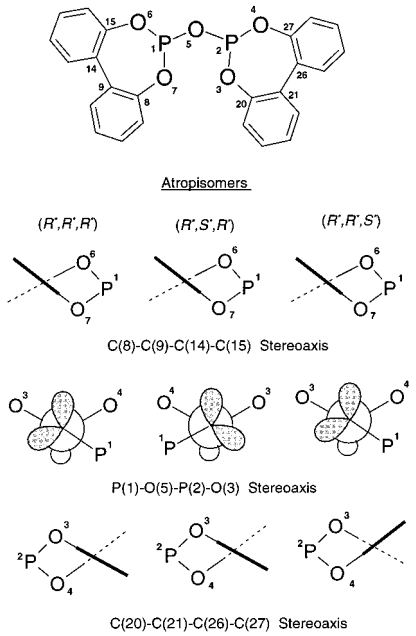


Figure 4. Stereoaxes of the atropisomers of **3** below the T_C (crystallographic atom numbering scheme).

phepin ring are −52.9° and 47.8° (the C(8)−C(9)−C(14)−C(15) and the C(20)−C(21)−C(26)−C(27) stereoaxes, respectively). The magnitude of these dihedral angles is in the range previously found for substituted dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings.[20,21] The P(1)−O(5)−P(2)−O(3) dihedral angle is −122.8°. The observation of a (*R**,*R**,*S**) atropisomer of **3** in the solid state is consistent with the suggestion that a (*R**,*R**,*S**) atropisomer is the predominant species in solution below T_C. However, caution should be exercised in the comparison of solution with solid-state conformations determined by X-ray structural analysis. Anet and Yavari warned that lattice energy, along with the resultant crystal-packing effects in the solid state, can render the solid-state conformation different from that observed in solution.[22]

One exocyclic O−P−O bond angle of each dibenzo[*d*,*f*]-[1,3,2]dioxaphosphepin ring of **3** was significantly smaller than the other exocyclic O−P−O bond angle. For example, the O(5)−P(1)−O(6) and O(5)−P(1)−O(7) bond angles were 104.4° and 95.8°, respectively. This difference has been observed before in substituted dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings.[20] The P−O−P bond angle was 139.3°. Given the posit that pyramidal geometry is achieved when the sum of the requisite bond angles about phosphorus is 270°, the two phosphorus atoms (296.9° and 298.2°) are midway between pyramidal and tetrahedral geometry. The six P−O bond lengths varied between 1.60 and 1.63 Å and are in the range previously found in substituted dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings.[20]

Scheme 2

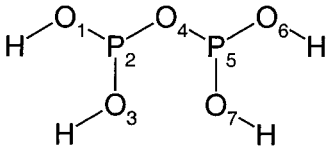


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Table 1. AMBER* Parameters Used in This Work[a]

angle	θ_0	k_θ
P2−O4−P5	130.0	26.0

torsion	V_1 (offset)	V_2 (offset)	V_3 (offset)	V_4 (offset)
O1−P2−O4−P5	2.3 (230)	−0.3 (460)	0.44 (510)	0.3 (920)
O1−P2−O4−P5	0.0 (0)	0.0 (0)	0.0 (0)	0.0 (0)
O1−P2−O4−P5	2.3 (230)	−0.3 (460)	0.44 (510)	0.3 (920)
O1−P2−O4−P5	0.0 (0)	0.0 (0)	0.0 (0)	0.0 (0)

[a] Parameters appear exactly as would be entered into the force field file.

Computational Results

Molecular Mechanics Parametrization. A specific parametrization of the AMBER* force field[23] (as implemented in the MacroModel program[24]) was undertaken to further study compound **3**. A strategy was employed in which both the torsional potential of the exocyclic P−O bonds and the bending potential of the P−O−P linkage were determined using ab initio molecular orbital calculations. The potentials were determined, for the model compound **4**, at the MP2/6-31G(d) level using the HF/6-31G(d) geometry and with relaxation of all degrees of freedom except the four O−P−O−H torsions (Scheme 2).

These angles were held fixed at 180° to avoid the formation of intramolecular hydrogen bonds. Additionally, in the determination of the exocyclic P−O torsional potential, only one P−O bond was rotated while the other was held fixed at 54°. Partial atomic charges were determined by a fit to the molecular electrostatic potential and were averaged over 11 molecular configurations spanning a 360° rotation of the exocyclic P−O bond. The parametrization procedure involved setting the partial atomic charges followed by a determination of the torsional and angle bending parameters to best fit the ab initio calculated energy profiles (Table 1 and Figure 5). Taking the ab initio result as a reference, the shape of the potential energy curve was not correctly reproduced by the original AMBER* parametrization. This fact is not surprising considering pyrophosphite structures were not used in the generation of the original AMBER* parameter set.

Conformational Search. To study the relative stability of the three atropisomers of **3**, two separate conformational searches were performed using the fully substituted pyrophosphite (including all the *tert*-butyl groups). One search included the constraint of an (*R**,*R**) conformation of the seven-

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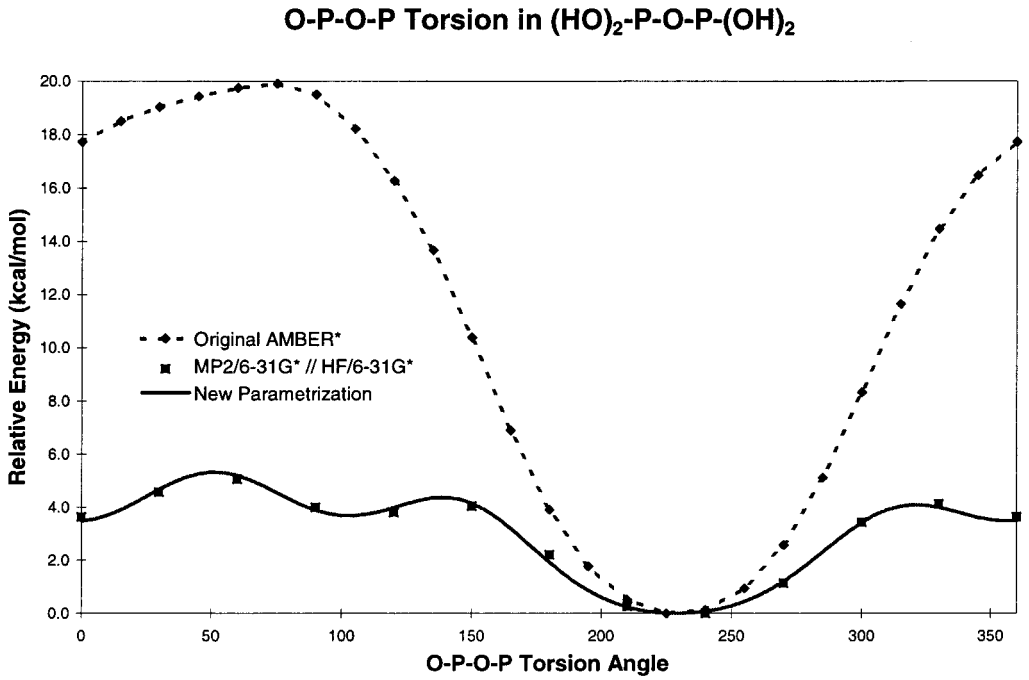

Figure 5. Comparison of original AMBER* with new parametrization based upon ab initio [MP2/6-31G(d)//HF/6-31(d)] MO calculated parameters for the O−P−O−P torsion in $(HO)_2POP(OH)_2$.

membered rings while the second constrained the ring conformations to be (*R**,*S**). The searches were of the Monte Carlo type as implemented in the MacroModel program. Ten rotatable bonds were included, the eight C(sp2)−C(sp3) bonds connecting the *tert*-butyl groups to the aromatic rings and the two exocyclic P−O bonds. The Monte Carlo procedure was halted when the rate of finding new conformations approached zero. The Monte Carlo searching procedure found 169 conformations within a 1.5 kcal/mol window of the global energy minimum for the (*R**,*R**) search, and 235 conformations within a 2.1 kcal/mol window of the global minimum for the (*R**,*S**) search. Comparison of the relative energy of the global minima from both searches revealed that the (*R**,*S**) minimum is 0.6 kcal/mol more stable than the (*R**,*R**) minimum. This result agrees with the NMR result in that a conformation with *opposite* ring configurations is the most populated.

Direct comparison of the (*R**,*S**) minimum to the X-ray crystal structure revealed that the structures were not identical. The most important difference was in the value of the P(1)−O(5)−P(2)−O(3) dihedral angle, which was −122.8° in the X-ray crystal structure and −167.3° in the calculated structure. Most importantly, however, *the relative absolute configurations of the three stereoaxes were equivalent*. In addition, if just the global minima are taken as representative of each conformational manifold, we would predict a 80:20 ratio of (*R**,*S**) to (*R**,*R**) at −80 °C. This is to be compared to the 78.9:21.2 ratio obtained by NMR spectroscopy. Consideration of the Boltzmann factors for all conformations (from both searches), gives populations of 88:12 and 83:17 at −80 °C for 1.5 and 2.1 kcal/mol windows above the global (*R**,*S**) minimum, respectively. Furthermore, all of the conformations found in the (*R**,*R**) search possessed the same orientation of the P−O stereoaxis, which was *equivalent* to that of the global (*R**,*S**) minimum and the experimentally determined X-ray crystal structure. On the basis of these results, the singlets in the $^{31}P\{^1H\}$ NMR spectrum at δ 125.4 and δ 139.4 can be assigned to the (*R**,*R**,*R**) and (*R**,*S**,*R**) atropisomers of **3**, respectively.

Summary

The steric restraints imposed upon the pyrophosphite **3** by *tert*-butyl substitution of the dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings lead to a preferred conformation in solution. The steric congestion in this molecule is manifested in restricted rotation about a sp^3-sp^3 P−O single bond, which leads to three observable diastereoisomers in the $^{31}P\{^1H\}$ NMR spectrum below the T_C. The solid-state conformation of **3** was that of the major conformation observed in solution below T_C, namely, the (*R**,*R**,*S**) atropisomer. Previously, the suggestion was made that steric congestion within a molecule may be used to rationally design bidentate ligands with defined,[11b] and perhaps unique,[25,26] coordination spheres about a metal. Additionally, a specific parametrization of a pyrophosphite structure, within the AMBER* force field, was determined (via a fit to ab initio data at the MP2/6-31G(d) level) that can be used for additional calculations on the pyrophosphite structural motif.

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Supporting Information Available: Data from X-ray crystallographic analysis of **3** including crystal data, bond angles, bond lengths, and atomic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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