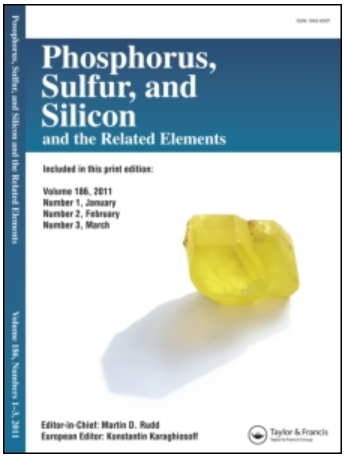

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MOLECULAR STRUCTURES OF NOVEL MACROCYCLES CONTAINING BIS(BICY CLOPHOSPHORANES)

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MOLECULAR STRUCTURES OF NOVEL MACROCYCLES CONTAINING BIS(BICYCLOPHOSPHORANES)

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Single crystal X-ray diffraction studies of the macrocyclic bis(bicyclophosphoranes), $[N(CH_2CMe_2O)_2PO_2]_2[(CH_2)_2O(CH_2)_2]$ $[(CH_2)_2S(CH_2)_2]$ (**1**) and $[N(CH_2CMe_2O)_2PO_2]_2[(CH_2)_2NPh(CH_2)_2][(CH_2)_2N\text{-}t\text{-}Bu(CH_2)_2]$ (**2**), revealed trigonal bipyramidal structures at the phosphorus atom. A comparison is made with the structures of related bicyclic phosphoranes containing similar ring systems that comprise both saturated (**1–4**) and unsaturated (**5-8**) members. A molecular mechanics treatment is performed which shows close agreement between the calculated and X-ray structures of **1** and **2**.

Keywords: phosphorus macrocycles; bicyclophosphoranes; trigonal bipyramids

INTRODUCTION

The literature on phosphorus-containing macrocycles is extensive and includes phosphorus bonded to a variety of atoms, *e.g.*, C, O, N, S, Si in large ring systems. Caminade and Majoral[2] have provided an excellent review covering most of the prominent macrocyclic types reported in the last two decades, the time period during which rapid development in this area has occurred. These phosphorus macrocycles are finding increasing use as metal complexing agents in forming catalyst systems or acting as transport agents, for example.

Previously, new macrocycles containing bis, tris, and tetrakis (bicyclophosphoranes) were reported by Houalla and coworkers[3–6] by means of a Todd[7] reaction

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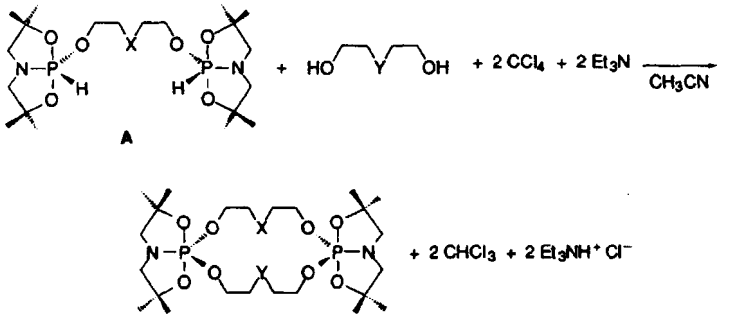
between bis(hydridobicyclophosphoranes) **A** and 1,5-pentanediols, HO-$(CH_2)_2$ -Y-$(CH_2)_2$-OH (Y = O, S, N-*t*-Bu, and N-Ph). An example of the reaction is illustrated in eq 1.



1 (X = 0, Y = S)
2 (X = N − Ph, Y = N−*t*−Bu)
A (X = Y = N−*t*−Bu) (1)
B (X = Y = N − Ph)

These macrocycles have been characterized by ^{31}P NMR and detailed ^{1}H NMR assignments.[5] Less symmetrical phosphorus macrocycles form[8] from **A** with diacrylic diesters by means of a Michael reaction or from precursor bicyclophosphoranes and polyethyleneglycols via a Todd reaction.[6]

In view of the increasing interest in phosphorus macrocycles and their structural comparisons, we report the X-ray studies and a molecular mechanics treatment of two members of the class that are depicted in eq 1, where X = O and Y = S (**1**) and where X = N-Ph and Y = N-*t*-Bu (**2**). These may be compared with the X-ray structures of the analogous bis(bicyclophosphoranes) **A** and **B** previously reported.[4]

EXPERIMENTAL

Samples of $[N(CH_2CMe_2O)_2PO_2]_2[(CH_2)_2O(CH_2)_2][(CH_2)_2S(CH_2)_2]$ (**1**) and $[N(CH_2CMe_2O)_2PO_2]_2[(CH_2)_2NPh(CH_2)_2][(CH_2)_2N$-*t*-$Bu(CH_2)_2]$ (**2**) were kindly supplied by Houalla and Wolf for the molecular structure studies.[9]

X-ray Studies. The X-ray crystallographic studies were done using an Enraf-Nonius CAD4 diffractometer and graphite monochromated MoKα radiation (λ = 0.71073Å). Details of the experimental procedures have been described previously.[10]

The colorless crystals were mounted in thin-walled glass capillaries which were sealed to protect the crystals from the atmosphere as a precaution. Data were collected using the $\theta - 2\theta$ scan mode with $3° \leq 2\theta_{MoK\bar{\alpha}} \leq 43°$ at $23 \pm 2°C$. No corrections were made for absorption. All of the data were included in the refinement. The structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least-squares. Refinements were based on F^2 and computations were performed on a 486/66 computer using SHELXS–86 for solution[11] and SHELXL–93 for refinement.[12] All the non-hydrogen atoms were refined anisotropically. For compound **2,** the disordered atoms were refined isotropically. Hydrogen atoms were included in the refinement as isotropic scatterers riding in either ideal positions or with torsional refinement (in the case of methyl hydrogen atoms) on the bonded carbon atoms. The final agreement factors are based on the reflections with $I \geq 2\sigma_I$.

Both compounds were disordered. Compound **1** is centrosymmetric with the chains bridging each of the two phosphorus atoms being disordered. Refinement was done with half occupancy for each to account for the two different (one sulfur containing and other oxygen containing) bridging chain units. For compound **2**, the disorder involves the 14 non-hydrogen atom unit which contains phosphorus P2 (see Figure 2). In this case refinement led to a 70:30% occupancy ratio. Crystallographic data are summarized in Table I.

TABLE I Crystallographic Data for Compounds **1** and **2**

Compound	1	2
formula	$C_{24}H_{48}N_2O_9P_2S.H_2O$	$C_{34}H_{62}N_4O_8P_2$
formula weight	620.66	716.82
crystal system	monoclinic	triclinic
space group	$P2_1/n$ (No.14)	$\bar{P}1$ (No.2)
crystal size, mm	0.07 × 0.12 × 1.60	0.20 × 0.20 × 0.75
a (Å)	6.291(4)	10.257(6)
b (Å)	15.291(3)	12.127(2)
c (Å)	17.019(2)	17.225(2)
α (°)	90	100.00(1)
β (°)	93.94(3)	90.95(3)
γ (°)	90	94.81(3)
V ($Å^3$)	1633(1)	2101(1)
Z	2	2
D_{calc} (g/cm^3)	1.262	1.133
$\mu_{MoK\alpha}$ (cm^{-1})	2.48	1.51
Total Reflns	1874	4787
Reflns with $I > 2\sigma_I$	1091	2420
R[a]	0.0717	0.0797
R_w[b]	0.1658	0.1720

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|Fo|$ [b] $R_w(F_o^2) = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4)^{1/2}$

RESULTS AND DISCUSSION

Atomic coordinates are given in Tables II and III for **1** and **2**, respectively, while bond parameters are given in Tables IV to VII. The atom labelling schemes for **1** and **2** are given in the ORTEX[13] plots of Figures 1 and 2. The thermal ellipsoids are shown at the 40% probability level and all hydrogens are omitted for clarity.

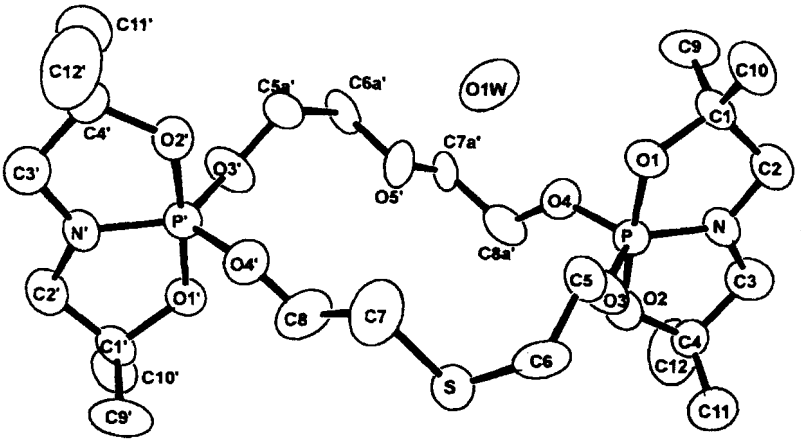


FIGURE 1 ORTEX plot of $[N(CH_2CMe_2O)_2PO_2]_2[(CH_2)_2O(CH_2)^2][(CH_2)_2S(CH_2)_2]$, **1** with hydrogen atoms omitted for clarity

TABLE II Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **1**

	x	*y*	*z*	*U(eq)*
P	497(3)	1981(2)	6388(1)	48(1)
O(1)	2374(9)	1397(4)	6912(3)	57(2)
O(2)	-1348(9)	2605(4)	5912(3)	64(2)
O(3)	1925(9)	1954(5)	5641(3)	68(2)
O(4)	-1087(10)	1182(4)	6355(4)	68(2)
O(5)	2204(27)	508(11)	4415(9)	54(4)
S	1742(14)	1311(5)	3971(4)	77(2)
N	716(11)	2722(4)	7083(4)	56(2)
C(1)	2764(13)	1634(6)	7725(5)	54(2)
C(2)	2223(15)	2592(6)	7746(5)	67(3)
C(3)	-503(19)	3514(7)	6991(6)	86(3)
C(4)	-1512(14)	3487(6)	6163(5)	56(2)
C(9)	1397(17)	1096(7)	8224(6)	88(3)
C(10)	5099(15)	1453(7)	7943(5)	80(3)
C(11)	-330(22)	4054(7)	5637(6)	110(4)
C(12)	-3841(17)	3716(8)	6119(8)	122(5)
C(5)	3566(28)	1561(12)	5475(10)	56(5)
C(5a)	1299(26)	1932(12)	4845(9)	56(5)
C(6)	3857(34)	1684(15)	4605(13)	63(6)
C(6a)	2593(41)	1398(18)	4352(14)	55(8)
C(7)	2039(75)	164(28)	4035(29)	137(18)
C(7a)	3509(37)	-22(17)	4036(14)	56(6)
C(8)	859(42)	-359(17)	3620(16)	101(8)
C(8a)	2859(30)	-971(14)	4119(10)	66(6)
O(1W)	2120(22)	-440(9)	6442(9)	93(5)

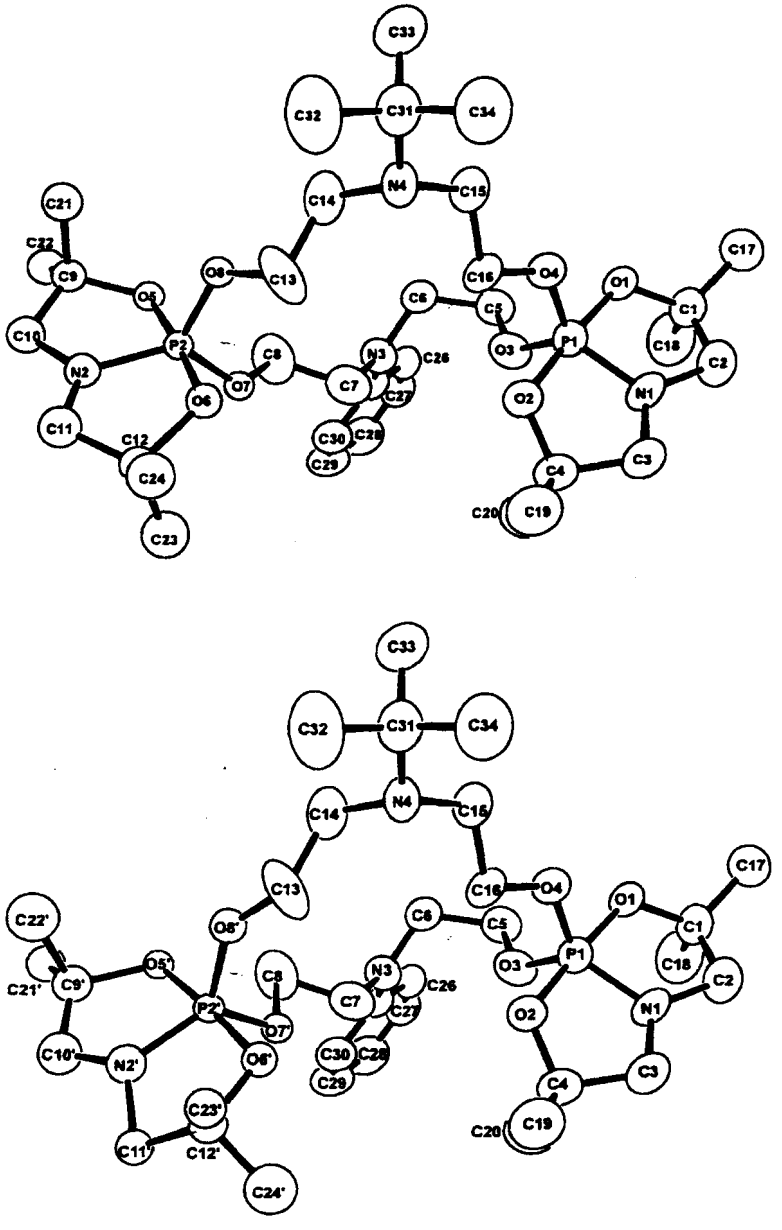


FIGURE 2 ORTEX plot of $[N(CH_2CMe_2O)_2PO_2]_2[(CH_2)_2NPh(CH_2)_2][(CH_2)_2N\text{-}t\text{-}Bu(CH_2)_2]$, **2**, (a) showing the form of the molecule in which the disordered fragment (P2, N2, 05-08, C9-C12, C21-C24) is in 70% occupancy. Hydrogen atoms are omitted for clarity, and (b) showing the form of the molecule in which the disordered fragment is in 30% occupancy

Basic Structures. Each of the bicyclotetraoxyphosphorane components of the macrocycles **1** and **2** have trigonal bipyramidal geometries. In accord with previous pentacoordinate phosphorus structures, the axial P-O bonds are longer than the equatorial P-O bonds. For the centrosymmetric structure of **1**, the axial P-O distances average 1.678(6) ± 0.008Å and the equatorial distances average 1.591(7) ± 0.016Å. For the more disordered macrocycle **2**, the average $P\text{-}O_{ax}$ distance is 1.675(12) ± 0.023Å while the average $P\text{-}O_{eq}$ distance is 1.611(13) ± 0.020Å. The equatorial P-N distance for **1** of 1.637(7)Å compares with an average of 1.681(16) ± 0.013Å for **2**. Due to the disorder in these macrocycles, the difference in the P-N distances between **1** and **2** loses much of its significance.

The 16 atom cyclic arrangement formed by sulfur and oxygen containing chains linking the equatorial oxygen atoms of the two phosphorane units in **1** and the similar 16 atom cyclic arrangement in **2** with N-Ph and N-*t*-Bu groups in place of the oxygen and sulfur atoms of the chains show little conformational difference. For **2**, the tricoordinated nitrogen atom N3 has a planar arrangement. The sum of the angles is 359.7(7)°. Nitrogen atom N4 attached to the *t*-butyl group is considerably more pyramidal with the sum of the angles at 341.7(7)°. The same behavior has been observed for nitrogen atoms included in the 16-membered rings of the related macrocycles **A** and **B**.[4] The sum of the angles is 332.2(4)° for **A** which has the N-*t*-Bu group and 360.0(3)° for **B** which has the N-Ph group. For both **2** and **B**, the planarity at the nitrogen centers is most likely associated with electron delocalization caused by the presence of the attached phenyl group.

TABLE III Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **2**

	x	*y*	*z*	*U(eq)*
P(1)	2724(2)	5619(2)	8999(1)	55(1)
O(1)	2704(5)	5962(4)	9984(3)	58(2)
O(2)	2879(5)	5257(4)	8029(3)	61(2)
O(3)	1374(5)	6128(5)	8832(3)	72(2)
O(4)	2443(5)	4341(4)	9111(3)	63(2)
N(1)	4149(6)	6388(6)	9033(4)	63(2)
C(1)	3624(9)	6858(7)	10351(5)	64(2)
C(2)	4771(9)	6833(8)	9793(5)	79(3)
C(3)	4857(9)	6361(8)	8315(5)	74(3)
C(4)	3824(9)	5926(7)	7661(5)	63(2)
C(17)	4045(11)	6624(9)	11138(5)	101(4)
C(18)	3002(11)	7961(8)	10415(7)	108(4)
C(19)	4363(10)	5187(9)	6969(5)	95(3)
C(20)	3170(11)	6873(9)	7407(6)	102(4)
P(2)	−1672(4)	2495(3)	6158(2)	64(1)
O(5)	−3173(9)	2532(7)	6533(5)	76(3)

TABLE III Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 2 (continued)

	x	*y*	*z*	*U(eq)*
O(6)	–228(10)	2406(8)	5724(6)	85(3)
O(7)	–1337(10)	3834(8)	6446(5)	70(3)
O(8)	–1255(10)	1854(8)	6834(6)	72(3)
N(2)	–2402(13)	1839(11)	5293(7)	88(4)
C(9)	–4162(15)	1689(13)	6111(9)	91(5)
C(10)	–3790(19)	1538(19)	5285(11)	102(6)
C(11)	–1587(19)	1561(16)	4636(11)	116(6)
C(12)	–293(18)	2182(14)	4823(9)	93(5)
C(21)	–4061(17)	606(15)	6469(10)	114(6)
C(22)	–5517(18)	2129(15)	6258(11)	121(6)
C(23)	872(22)	1474(18)	4636(12)	130(7)
C(24)	–153(27)	3414(23)	4629(16)	156(11)
P(2')	–877(10)	2943(8)	5946(5)	68(2)
O(5')	–2524(22)	2877(17)	6131(12)	70(6)
O(6')	668(22)	3069(18)	5727(12)	84(6)
O(7')	–593(23)	4182(18)	6433(12)	75(6)
O(8')	–717(27)	2042(21)	6548(16)	94(8)
N(2')	–1205(37)	2584(29)	4963(19)	106(10)
C(9')	–3285(52)	2290(43)	5376(27)	118(15)
C(10')	–2532(52)	2431(41)	4704(29)	139(16)
C(11')	–253(40)	2948(38)	4379(25)	85(13)
C(12')	934(39)	2771(33)	4863(21)	92(11)
C(21')	–4726(42)	2668(35)	5559(24)	118(14)
C(22')	–3452(67)	952(59)	5494(40)	190(27)
C(23')	1649(40)	1840(33)	4767(22)	92(12)
C(24')	1978(59)	3632(49)	4811(33)	180(22)
N(3)	–1217(7)	6117(6)	8188(4)	59(2)
N(4)	1392(6)	1440(6)	8178(4)	59(2)
C(5)	321(8)	6328(8)	9363(5)	67(3)
C(6)	–938(8)	5766(7)	8934(5)	61(2)
C(7)	–757(9)	5439(8)	7481(5)	75(3)
C(8)	–1802(11)	4525(8)	7103(5)	93(3)
C(13)	204(11)	1740(9)	7002(6)	94(4)
C(14)	98(9)	1527(8)	7843(5)	73(3)
C(15)	1748(9)	2387(7)	8810(5)	65(2)
C(16)	2100(8)	3432(6)	8473(5)	60(2)
C(25)	–1790(8)	7099(7)	8167(5)	56(2)
C(26)	–2086(8)	7830(7)	8855(5)	61(2)
C(27)	–2680(10)	8785(8)	8827(7)	79(3)
C(28)	–2998(10)	9094(8)	8134(8)	87(3)
C(29)	–2743(10)	8392(9)	7439(7)	87(3)
C(30)	–2140(9)	7405(8)	7449(6)	71(3)
C(31)	1624(10)	313(8)	8348(6)	77(3)
C(32)	1270(13)	–571(8)	7613(7)	130(5)
C(33)	855(12)	34(9)	9050(7)	121(5)
C(34)	3084(11)	307(9)	8542(7)	108(4)

TABLE IV Bond lengths (Å) for **1**

P-O(4)	1.575(7)	N-C(2)	1.436(10)
P-O(3)	1.607(6)	N-C(3)	1.437(11)
P-N	1.637(7)	C(1)-C(9)	1.496(12)
P-O(2)	1.670(6)	C(1)-C(2)	1.504(12)
P-O(1)	1.686(6)	C(1)-C(10)	1.516(12)
O(1)-C(1)	1.434(9)	C(3)-C(4)	1.506(12)
O(2)-C(4)	1.421(10)	C(4)-C(11)	1.482(13)
O(3)-C(5)	1.24(2)	C(4)-C(12)	1.503(13)
O(3)-C(5a)	1.39(2)	C(5)-C(6)	1.52(2)
O(4)-C(8a)#1	1.37(2)	C(5a)-C(6a)	1.46(3)
O(5)-C(7a)	1.35(3)	C(7)-C(8)	1.27(4)
O(5)-C(6a)	1.39(3)	C(7a)-C(8a)	1.52(3)
S-C(6)	1.75(3)	C(8)-O(4)#1	1.27(2)
S-C(7)	1.77(4)		

Symmetry transformations used to generate equivalent atoms: #1 –x,–y,–z+1

TABLE V Bond angles (deg) for **1**

O(4)-P-O(3)	109.8(4)	O(1)-C(1)-C(2)	104.1(7)
O(4)-P-N	125.8(4)	C(9)-C(1)-C(2)	112.5(8)
O(3)-P-N	124.4(4)	O(1)-C(1)-C(10)	106.8(7)
O(4)-P-O(2)	90.5(4)	C(9)-C(1)-C(10)	110.3(8)
O(3)-P-O(2)	92.2(3)	C(2)-C(1)-C(10)	112.9(8)
N-P-O(2)	88.6(3)	N-C(2)-C(1)	104.8(7)
O(4)-P-O(1)	91.5(3)	N-C(3)-C(4)	105.4(8)
O(3)-P-O(1)	89.8(3)	O(2)-C(4)-C(11)	108.9(8)
N-P-O(1)	87.9(3)	O(2)-C(4)-C(12)	107.2(8)
O(2)-P-O(1)	176.5(3)	C(11)-C(4)-C(12)	111.2(10)
C(1)-O(1)-P	116.4(5)	O(2)-C(4)-C(3)	105.9(7)
C(4)-O(2)-P	117.3(5)	C(11)-C(4)-C(3)	110.6(9)
C(5)-O(3)-C(5a)	87.1(10)	C(12)-C(4)-C(3)	112.8(9)
C(5)-O(3)-P	135.2(10)	O(3)-C(5)-C(6)	108.7(14)
C(5a)-O(3)-P	129.6(8)	O(3)-C(5a)-C(6a)	116(2)
C(8a)#1-O(4)-P	133.7(11)	C(5)-C(6)-S	115.0(14)
C(7a)-O(5)-C(6a)	116(2)	O(5)-C(6a)-C(5a)	113(2)
C(6)-S-C(7)	102(2)	C(8)-C(7)-S	122(3)
C(2)-N-C(3)	121.4(7)	O(5)-C(7a)-C(8a)	111(2)
C(2)-N-P	119.3(6)	O(4)#1-C(8)-C(7)	123(3)
C(3)-N-P	119.2(6)	O(4)#1-C(8a)-C(7a)	113(2)
O(1)-C(1)-C(9)	110.0(7)		

Symmetry transformations used to generate equivalent atoms: #1 –x,–y,–z+1

TABLE VI Bond lengths (Å) for **2**

P(1)-O(4)	1.598(5)	P(2')-O(6')	1.64(2)
P(1)-O(3)	1.604(6)	P(2')-O(8')	1.65(3)
P(1)-N(1)	1.661(7)	P(2')-N(2')	1.69(3)
P(1)-O(2)	1.665(5)	P(2')-O(5')	1.72(2)
P(1)-O(1)	1.676(5)	O(5')-C(9')	1.53(5)
O(1)-C(1)	1.428(9)	O(6')-C(12')	1.51(4)
O(2)-C(4)	1.438(9)	O(7')-C(8)	1.73(2)
O(3)-C(5)	1.436(9)	O(8')-C(13)	1.33(3)
O(4)-C(16)	1.431(8)	N(2')-C(10')	1.41(5)
N(1)-C(3)	1.442(10)	N(2')-C(11')	1.51(5)
N(1)-C(2)	1.443(10)	C(9')-C(10')	1.43(6)
C(1)-C(17)	1.497(12)	C(9')-C(21')	1.60(6)
C(1)-C(18)	1.518(12)	C(9')-C(22')	1.67(8)
C(1)-C(2)	1.530(12)	C(11')-C(12')	1.51(5)
C(3)-C(4)	1.526(12)	C(12')-C(23')	1.38(5)
C(4)-C(20)	1.502(12)	C(12')-C(24')	1.45(6)
C(4)-C(19)	1.504(11)	N(3)-C(25)	1.377(10)
P(2)-O(8)	1.580(10)	N(3)-C(6)	1.454(10)
P(2)-O(7)	1.620(10)	N(3)-C(7)	1.455(10)
P(2)-O(6)	1.673(11)	N(4)-C(15)	1.457(9)
P(2)-O(5)	1.681(10)	N(4)-C(14)	1.458(10)
P(2)-N(2)	1.692(12)	N(4)-C(31)	1.483(11)
O(5)-C(9)	1.47(2)	C(5)-C(6)	1.524(11)
O(6)-C(12)	1.53(2)	C(7)-C(8)	1.526(13)
O(7)-C(8)	1.401(11)	C(13)-C(14)	1.518(13)
O(8)-C(13)	1.542(13)	C(15)-C(16)	1.503(11)
N(2)-C(11)	1.43(2)	C(25)-C(30)	1.402(11)
N(2)-C(10)	1.44(2)	C(25)-C(26)	1.404(11)
C(9)-C(10)	1.46(2)	C(26)-C(27)	1.361(12)
C(9)-C(22)	1.54(2)	C(27)-C(28)	1.354(13)
C(9)-C(21)	1.55(2)	C(28)-C(29)	1.385(13)
C(11)-C(12)	1.47(2)	C(29)-C(30)	1.395(12)
C(12)-C(23)	1.54(2)	C(31)-C(33)	1.525(14)
C(12)-C(24)	1.58(3)	C(31)-C(32)	1.527(12)
P(2')-O(7')	1.59(2)	C(31)-C(34)	1.531(13)

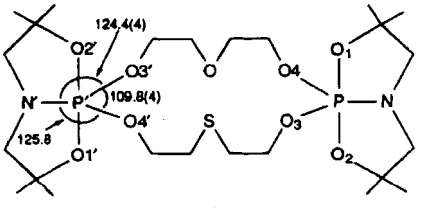
TABLE VII Bond angles (deg) for **2**

O(4)-P(1)-O(3)	109.9(3)	O(7')-P(2')-O(8')	108.6(12)
O(4)-P(1)-N(1)	128.8(4)	O(6')-P(2')-O(8')	95.9(14)
O(3)-P(1)-N(1)	121.3(4)	O(7')-P(2')-N(2')	127(2)
O(4)-P(1)-O(2)	92.6(3)	O(6')-P(2')-N(2')	87(2)
O(3)-P(1)-O(2)	89.0(3)	O(8')-P(2')-N(2')	125(2)
N(1)-P(1)-O(2)	88.3(3)	O(7')-P(2')-O(5')	93.8(12)
O(4)-P(1)-O(1)	86.9(3)	O(6')-P(2')-O(5')	175.9(12)
O(3)-P(1)-O(1)	95.9(3)	O(8')-P(2')-O(5')	88.2(13)
N(1)-P(1)-O(1)	88.2(3)	N(2')-P(2')-O(5')	91(2)
O(2)-P(1)-O(1)	175.0(3)	C(9')-O(5')-P(2')	109(2)
C(1)-O(1)-P(1)	116.8(5)	C(12')-O(6')-P(2')	115(2)
C(4)-O(2)-P(1)	117.3(5)	P(2')-O(7')-C(8)	112(2)
C(5)-O(3)-P(1)	127.4(5)	C(13)-O(8')-P(2')	139(2)
C(16)-O(4)-P(1)	123.5(5)	C(10')-N(2')-C(11')	115(4)
C(3)-N(1)-C(2)	121.4(7)	C(10')-N(2')-P(2')	118(3)
C(3)-N(1)-P(1)	118.3(6)	C(11')-N(2')-P(2')	121(3)
C(2)-N(1)-P(1)	118.6(6)	C(10')-C(9')-O(5')	110(4)
O(1)-C(1)-C(17)	108.8(7)	C(10')-C(9')-C(21')	127(4)
O(1)-C(1)-C(18)	109.1(7)	O(5')-C(9')-C(21')	101(3)
C(17)-C(1)-C(18)	112.4(8)	C(10')-C(9')-C(22')	112(4)
O(1)-C(1)-C(2)	104.7(6)	O(5')-C(9')-C(22')	103(4)
C(17)-C(1)-C(2)	110.9(8)	C(21')-C(9')-C(22')	102(4)
C(18)-C(1)-C(2)	110.7(8)	N(2')-C(10')-C(9')	107(4)
N(1)-C(2)-C(1)	102.9(7)	C(12')-C(11')-N(2')	93(3)
N(1)-C(3)-C(4)	104.3(7)	C(23')-C(12')-C(24')	99(4)
O(2)-C(4)-C(20)	108.9(7)	C(23')-C(12')-O(6')	107(3)
O(2)-C(4)-C(19)	108.7(7)	C(24')-C(12')-O(6')	99(3)
C(20)-C(4)-C(19)	111.3(8)	C(23')-C(12')-C(11')	128(4)
O(2)-C(4)-C(3)	103.7(7)	C(24')-C(12')-C(11')	110(4)
C(20)-C(4)-C(3)	111.3(8)	O(6')-C(12')-C(11')	110(3)
C(19)-C(4)-C(3)	112.6(8)	C(25)-N(3)-C(6)	120.8(7)
O(8)-P(2)-O(7)	109.2(5)	C(25)-N(3)-C(7)	122.1(7)
O(8)-P(2)-O(6)	93.3(5)	C(6)-N(3)-C(7)	116.8(7)
O(7)-P(2)-O(6)	90.5(5)	C(15)-N(4)-C(14)	110.5(7)
O(8)-P(2)-O(5)	88.7(5)	C(15)-N(4)-C(31)	116.1(7)
O(7)-P(2)-O(5)	92.1(5)	C(14)-N(4)-C(31)	115.1(7)
O(6)-P(2)-O(5)	176.0(5)	O(3)-C(5)-C(6)	107.7(7)
O(8)-P(2)-N(2)	123.4(6)	N(3)-C(6)-C(5)	114.8(7)
O(7)-P(2)-N(2)	127.3(6)	N(3)-C(7)-C(8)	111.8(7)
O(6)-P(2)-N(2)	88.4(6)	O(7)-C(8)-C(7)	111.9(9)
O(5)-P(2)-N(2)	87.5(6)	O(7)-C(8)-O(7')	28.8(7)
C(9)-O(5)-P(2)	114.7(8)	C(7)-C(8)-O(7')	83.2(10)
C(12)-O(6)-P(2)	115.4(9)	O(8')-C(13)-C(14)	128(2)
C(8)-O(7)-P(2)	128.3(8)	O(8')-C(13)-O(8)	30.9(12)
C(13)-O(8)-P(2)	120.2(8)	C(14)-C(13)-O(8)	98.3(8)
C(11)-N(2)-C(10)	124.6(14)	N(4)-C(14)-C(13)	110.3(8)
C(11)-N(2)-P(2)	117.8(12)	N(4)-C(15)-C(16)	110.2(7)
C(10)-N(2)-P(2)	117.5(11)	O(4)-C(16)-C(15)	108.5(6)
C(10)-C(9)-O(5)	105.1(13)	N(3)-C(25)-C(30)	121.1(8)

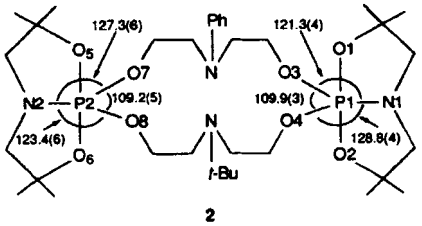
TABLE VII Bond angles (deg) for **2** (Continued)

C(10)-C(9)-C(22)	114(2)	N(3)-C(25)-C(26)	122.5(8)
O(5)-C(9)-C(22)	108.3(13)	C(30)-C(25)-C(26)	116.4(8)
C(10)-C(9)-C(21)	112(2)	C(27)-C(26)-C(25)	121.9(9)
O(5)-C(9)-C(21)	106.4(12)	C(28)-C(27)-C(26)	121.8(10)
C(22)-C(9)-C(21)	110.3(14)	C(27)-C(28)-C(29)	118.4(10)
N(2)-C(10)-C(9)	106.3(14)	C(28)-C(29)-C(30)	121.1(10)
N(2)-C(11)-C(12)	108(2)	C(29)-C(30)-C(25)	120.3(9)
C(11)-C(12)-O(6)	102.9(13)	N(4)-C(31)-C(33)	112.1(8)
C(11)-C(12)-C(23)	115(2)	N(4)-C(31)-C(32)	109.3(8)
O(6)-C(12)-C(23)	101.3(13)	C(33)-C(31)-C(32)	110.7(9)
C(11)-C(12)-C(24)	115(2)	N(4)-C(31)-C(34)	108.2(8)
O(6)-C(12)-C(24)	102.1(14)	C(33)-C(31)-C(34)	108.4(9)
C(23)-C(12)-C(24)	117(2)	C(32)-C(31)-C(34)	108.2(9)
O(7')-P(2')-O(6')	85.0(12)		

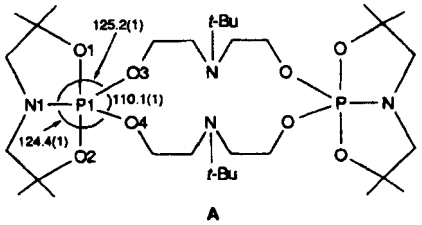
Structural Comparisons. Pertinent structural parameters for the related bicyclophosphoranes **3–8**[14–20] are listed in Table 8 for comparison with similar data for **1, 2, A,** and **B.**



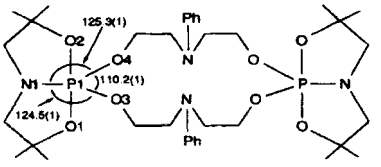
1



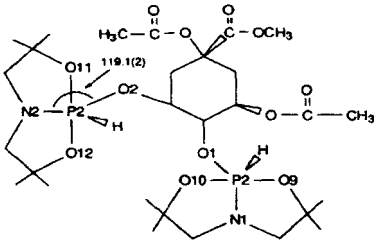
2



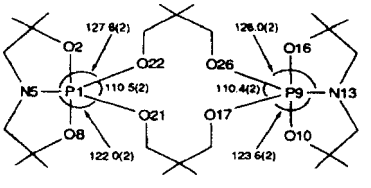
A



B



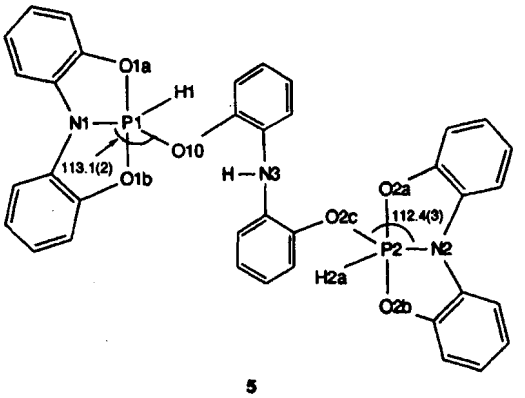
3



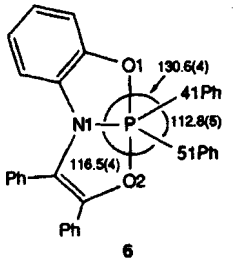
4

The bis(bicyclophosphoranes) **1–4**, **A** and **B** all possess the same type of saturated five-membered ring system. For these the P-N bond distance varies from 1.64–1.69Å. This compares with the higher range, 1.69–1.72Å present in the bicyclophosphoranes **5–8** that have unsaturated five-membered ring systems. The same relation holds true for the P-O axial bond distances which are found between 1.67–1.69Å for **1–4, A** and **B**, and in the range of 1.69–1.76Å for **5–8**. The latter comparison excludes the P-O axial distances for the disordered unit found in the X-ray analysis of **2** due to the greater uncertainty associated with them.

It is possible that the longer P-N_{eq} and P-O_{ax} distances for **5–8** are associated with the constraints imposed by ring unsaturation. However, analysis of the collective data indicates that this is not likely. Although ring unsaturation tends to induce planarity, both of the rings of the bicyclic component for **5–8** are not in one plane. For all of the bicyclic phosphoranes **1–8,** the sum of the angles at the equatorial nitrogen atom fall in the narrow range of 357.2° – 359.9° which expresses a high degree of planarity (Table VIII). However, the axial oxygen-phosphorus-axial oxygen angles for the unsaturated rings systems present in



5



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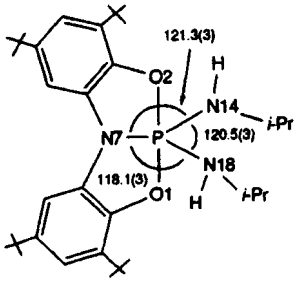
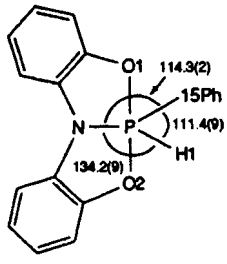


7

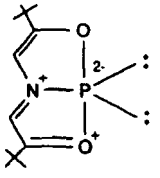


8

5–8 deviate more from linearity required to maintain planarity of the bicyclic system more so than that for the saturated bicyclic rings in **1–4, A** and **B.** The fomer show a range for the O_{ax}-P-O_{ax} angles of 166° – 176°, whereas for the latter, the axial angles are in a more narrow range, 172° – 177° (Table VIII). The lack of planarity indicated for the unsaturated derivatives is possible by having one of the ring components in a planar arrangement while the other attached ring is in an

envelope configuration caused by displacement of the phosphorus atom out-of-plane of the bicyclic system. This is precisely what occurs in **6**,[17,18] for example. As a result of this effect, displacements from ideal trigonal bipyramidal (TBP) symmetry occur. In **6**, the displacement follows the Berry[21] pseudorotational coordinate toward a square pyramid (SP) with the phenyl group labeled 51 acting as the pivotal ligand. In **8**,[20] the structural displacement is found to take place along the Berry coordinate to the extent of 43.9% from a TBP toward a SP. Here the phenyl group labeled 15 serves as the pivotal ligand. Another phosphorane listed in Table 8 that is indicated to undergo a similar pseudorotational displacement is **4** where the displacement is located at the P1 center. This is deduced from the value of the equatorial angles. All, *i.e.*, **4, 6,** and **8,** have the non-bicyclic equatorial angle (X_{eq}-P-X_{eq} in Table 8) in the range of 109° – 113° other than that for **7** which is 120.5(3)°. These reduced values for **4, 6,** and **8** compared to 120° for an ideal TBP are accompanied by an expansion in one of the other equatorial angles above 120°. In the other members, **1–3, A, B, 5,** and **7,** the other two equatorial angles are nearly equal. From the above analysis, it appears unlikely that ring unsaturation is causative in accounting for the longer P-N_{eq} and P-O_{ax} bond distances for **5–8.** A more likely occurrence is the electron donating ability of the common ring substituents present for the saturated systems of **1–4, A** and **B** which leads to a strengthening of the phosphorus-ligand bonds and an accompanying shortening effect. This contrasts with the electron delocalization that should be experienced by **5–8.** On a further note, the greater variability in the O_{ax}-P-O_{ax} angles for **5–8** compared to that for **1–4, A** and **B** is understandable in terms of the greater diversity in the compositions of the unsaturated rings in **5–8.**

It is interesting to compare the bond distances in Table 8 with that for the precursor phosphorane **9**,[22–24] termed ADPO,[25] which formally has two lone electron pairs. The P-O_{ax} bond distances for **9** are 1.835(2)Å and 1.792(2)Å which are over 0.1Å longer than those for **5–9.** The P-N_{eq} distance is 1.703(2)Å, again longer than most of the values in Table 8 for **5–8.** These longer



ADPO

9[22]

bond distances are consistent with expectations from VSEPR theory[26] where the lone pairs exert a major influence in lengthening nearby axial bonds of a TBP.

TABLE VIII Comparison of Bond Parameters for Bicyclophosphoranes

	bond lengths, Å				*bond angles, deg.*				
Compd [a]	*P-N_{eq}*		*P-O_{ax}*		*X_{eq}-P-X_{eq}*		*O_{ax}-P-O_{ax}*		*Σ ang., deg. ring N_{eq}*
1	P-N	1.637(7)	P-O2 P-O1	1.670(6) 1.686(6)	O3-P-O4	109.8(4)	O1-P-O2	176.5(3)	359.9
2 [b]	P2-N2	1.692(12)	P2-O5 P2-O6	1.681(10) 1.673(11)	07-P2-08	109.2(5)	05-P2-06	176.0(5)	359.9 (N2)
	P2′-N2′	1.69(3)	P2′-O5′ P2′-O6′	1.72(2) 1.64(2)	O7′-P2′-O8′	108.6(12)	O5′-P2′-O6′	175.9(12)	
	P1-N1	1.661(7)	P1-O1 P1-O2	1.676(5) 1.665(5)	O3-P1-O4	109.9(3)	O1-P1-O2	175.0(3)	358.3 (N1)
A [4]	P1-N1	1.650(3)	P1-O1 P1-O2	1.678(2) 1.682(2)	O3-P1-O4	110.1(1)	O1-P1-O2	175.7(1)	
B [4]	P1-N1	1.663(2)	P1-O1 P1-O2	1.672(2) 1.677(2)	O3-P1-O4	110.2(1)	O1-P1-O2	176.4(1)	
3 [14]	P2-N2	1.641(4)	P2-O11 P2-O12	1.683(3) 1.666(3)			O11-P2-O12	172.0(2)	357.2 (N2)
	P1-N1	1.652(4)	P1-O9 P1-O10	1.674(3) 1.682(3)			O9-P1-O10	174.9(2)	359.6 (N1)
4 [15]	P1-N5	1.665(3)	P1-O2 P1-O8	1.677(3) 1.672(3)	O21-P1-O22	110.5(2)	O2-P1-O8	175.2(2)	358.0 (N5)
	P9-N13	1.656(3)	P9-O16 P9-O10	1.678(3) 1.681(3)	O17-P9-O26	110.4(2)	O10-P9-O16	175.6(1)	359.8 (N13)
5 [16]	P1-N1	1.703(5)	P1-O1a P1-O1b	1.692(5) 1.692(5)			O1a-P1-O1b	168.1(3)	359.5 (N1)
	P2-N2	1.688(6)	P2-O2a P2-O2b	1.685(5) 1.699(5)			O2a-P2-O2b	169.5(3)	358.9 (N2)
6 [17,18]	P-N	1.703(6)	P-O1 P-O2	1.763(5) 1.700(5)	C41-P-C51	112.8(5)	O1-P-O2	171.6(3)	360.0
7 [19]	P-N7	1.713(6)	P-O1 P-O2	1.698(4) 1.714(4)	N14-P-N18	120.5(3)	O1-P-O2	175.8(3)	359.2 (N7)
8 [20]	P-N	1.715(3)	P-O1 P-O2	1.722(2) 1.714(2)	H1-P-C15	111.4(9)	O1-P-O2	165.9(1)	359.6

[a] References are shown as superscripts. [b] The bicyclo unit at P2 exhibits disorder. See Figure 2

Molecular Modeling of Macrocycles 1 and 2.[9] The molecular modeling of macrocycles **1** and **2** has been successfully performed using the Biosym Program Version 95[27] based on an ESFF force field assuming, as was clear from the X-ray structure, that the phosphorus atoms adopt a trigonal bipyramidal geometry. This version was modified to take into account the length of the apical P-O and equatorial P-O and P-N bonds as they result from the X-ray structures of the related macrocycles, **A** and **B**.[4]

Tables IX and X collect selected calculated and experimental structural parameters while Figures 3–5 depict the superimposition of calculated and experimental structures of the macrocycles, **1** and **2.**

TABLE IX Calculated and Experimental Values of Selected Structural Parameters of **1**

	Calcd., Å	*Exp., Å*		*Calcd., deg.*	*Exp., deg.*		*Calcd., deg.*	*Exp., deg.*
P-O1	1.67	1.686	O1-P-O2	174.27	176.5	O1′-P′-O2′	176.04	176.5
P-O2	1.66	1.670	O1-P-O3	92.67	89.8	O1′-P′-O3′	89.60	89.8
P-O3	1.60	1.607	O1-P-O4	89.11	91.5	O1′-P′-O4′	92.43	91.5
P-O4	1.59	1.575	O1-P-N	92.69	87.9	O1′-P′-N′	91.94	87.9
P-N	1.64	1.637	O2-P-O3	86.14	92.2	O2′-P′-O3′	89.36	92.2
P′-O1′	1.67		O2-P-O4	86.79	90.5	O2′-P′-O4′	84.71	90.5
P′-O2′	1.66		O2-P-N	92.76	88.6	O2′-P′-N′	91.90	88.6
P′-O3′	1.59		O3-P-O4	121.56	109.8	O3′-P′-O4′	118.69	109.8
P′-O4′	1.60		O3-P-N	120.16	124.4	O3′-P′-N′	119.53	124.4
P′-N′	1.64		O4-P-N	118.08	125.8	O4′-P′-N′	121.62	125.8
P-P′	7.54					E Kcal/mol	- 332.43	

TABLE X Calculated and Experimental (70% occupancy) Values of Selected Structural Parameters of **2**

	Calcd., Å	*Exp., Å*		*Calcd., deg.*	*Exp., deg.*		*Calcd., deg.*	*Exp., deg.*
P1-O1	1.67	1.676	O1-P1-O2	175.02	175.0	O5-P2-O6	174.79	176.0
P1-O2	1.66	1.665	O1-P1-O3	88-99	95.9	O5-P2-O7	90.8	92.1
P1-O3	1.59	1.604	O1-P1-O4	93.02	86.9	O5-P2-O8	88.9	88.7
P1-O4	1.60	1.598	O1-P1-N1	92.96	88.2	O5-P2-N2	93.20	87.5
P1-N1	1.64	1.661	O2-P1-O3	87.82	89.0	O6-P2-O7	87.21	90.5
P2-O5	1.67	1.681	O2-P1-O4	85.38	92.6	O6-P2-O8	88.05	93.3
P2-O6	1.67	1.673	O2-P1-N1	91.92	88.3	O6-P2-N2	91.97	88.4
P2-O7	1.60	1.620	O3-P1-O4	121.20	109.9	O7-P2-O8	122.65	109.2
P2-O8	1.59	1.580	O3-P1-N1	118.85	121.3	O7-P2-N2	118.44	127.3
P2-N2	1.65	1.692	O4-P1-N1	119.70	128.8	O8-P2-N2	118.82	123.4
P1-P2	7.29					E Kcal/mol	- 321.3	

Examination of Tables IX and X as well as Figures 3–5 indicates that there is good agreement between experimental and calculated bond lengths of the bicyclophosphorane components of **1** and **2.**

The experimental values of the equatorial angles included in the 16-membered rings O3-P–O4 (~110°) are far from the expected value, *i.e.,* 120°, while the calculated ones are very close to the latter. The pinching of the O3-P–O4 angles in **1** and **2** is compensated by an increase of the two other equatorial angles which reach up to ~125°. The same observation has been made with the macrocycles **A** and **B.**[4] Since calculations deal with isolated free molecules, one might consider that the pinching of the O3-P–O4 angles is due to the packing effect in the crystal.

The agreement between experimental and calculated parameters for **1** (Figure 3) is fairly good (RMS on 12 atoms = 0.42). Although the superposition of these two entities is not perfect, the shape of the calculated geometry and particularly the shape of the 16-membered ring, which is the site of complexation, is very close to the experimental one. The main divergence lies in the O-containing part of the 16-membered ring. Very likely this divergence is due to the presence in the crystal of a water molecule which forms a hydrogen bond with the oxygen atom (d $O_{water} - O_{macrocycle}$ = 3Å).

Figure 4 depicts the superposition of the calculated structure of **2** with the experimental molecule at 70% occupancy in the crystal while Figure 5 depicts the superposition of the same calculated structure relative to the molecule at 30% occupancy. There is somewhat better agreement between the experimental and calculated structures in the former instance (RMS on 12 atoms = 0.34) than in the latter (RMS on 12 atoms = 0.60).

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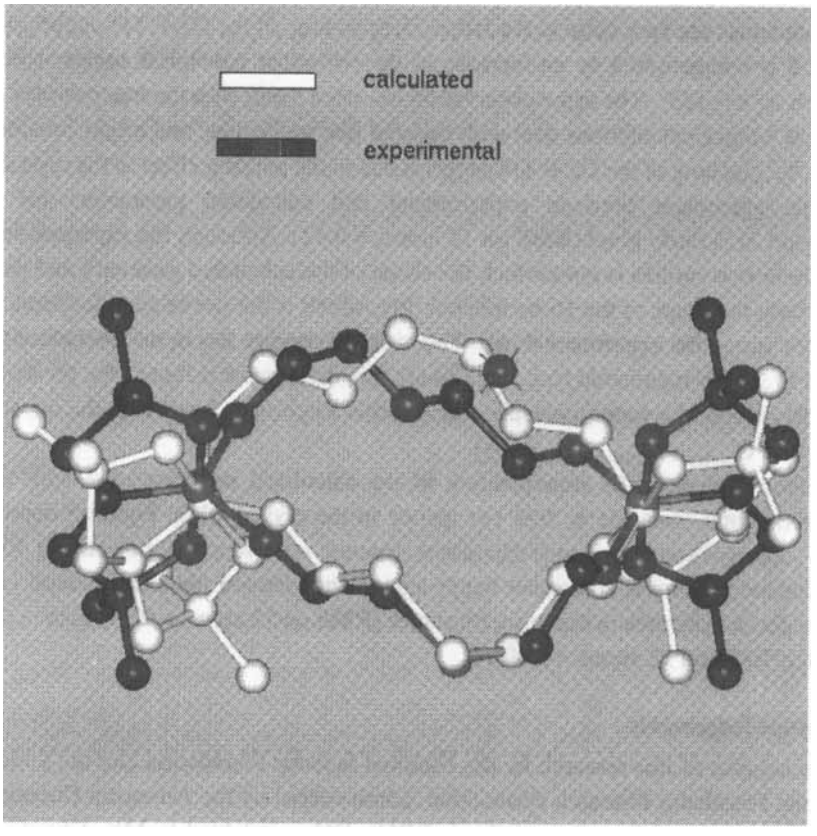

FIGURE 3 Superposition of experimental and calculated structures of **1**. The symbol O depicts the oxygen atom of the water molecule present in the crystal. Refer to color Plate 1 at the back of this volume

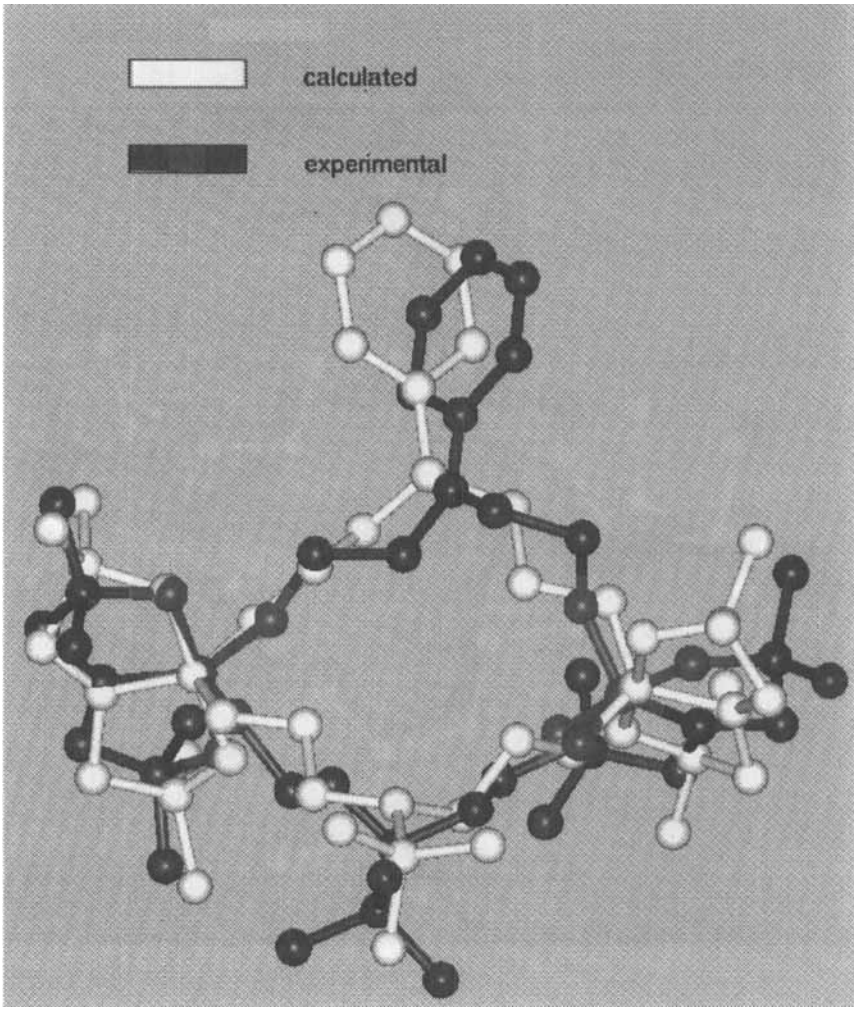

FIGURE 4 Superposition of experimental (70% occupancy) and calculated structures of **2**. Refer to color Plate 2 at the back of this volume

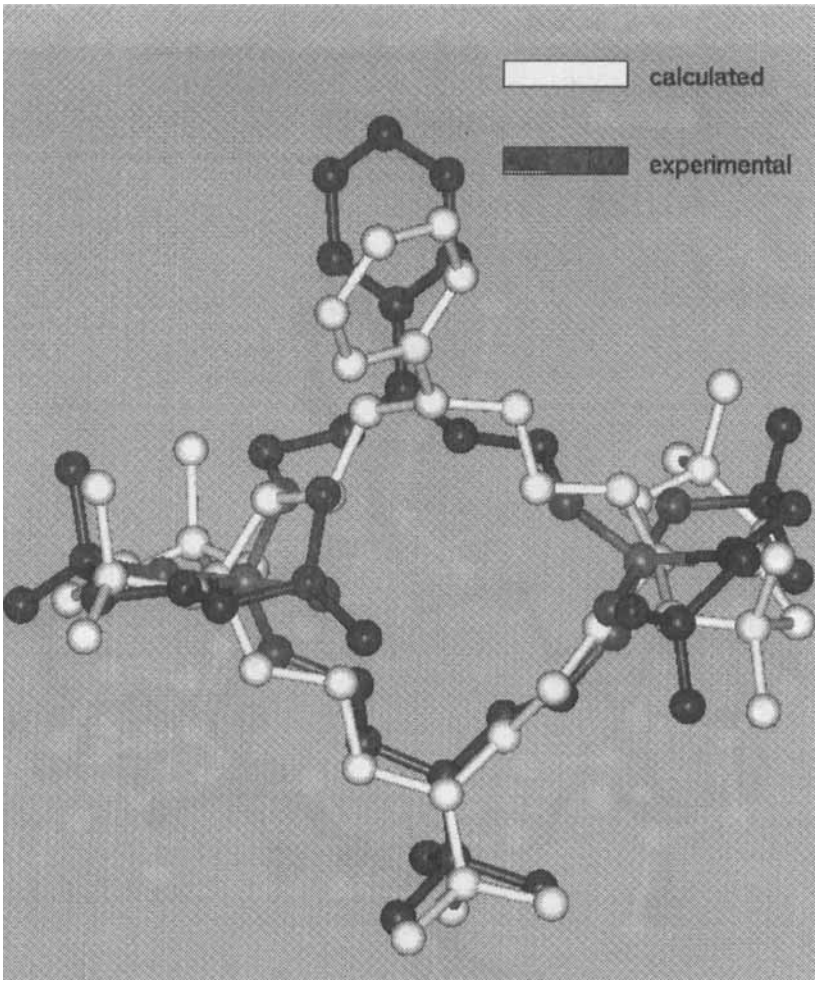

FIGURE 5 Superposition of experimental (30% occupancy) and calculated structures of **2**. Refer to color Plate 3 at the back of this volume

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