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An Unusual Twist-Boat Conformation for a Six-Membered Ring Phosphorus Heterocycle

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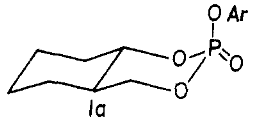
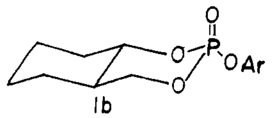
Abstract: Configurational and conformational analysis of isomeric 2-*p*-nitrophenoxy-2-oxo-1,3,2-dioxaphosphorinane (**1**) and isomeric 2-*p*-nitrophenoxy-2-oxo-1,3,2-oxazaphosphorinane (**2**) is presented. Based upon ^1H NMR coupling data and ^{31}P NMR spectra the axial and equatorial *p*-nitrophenoxy isomers of **1** are both in chair conformations as is the axial isomer of **2**. However, NMR data support the assignment of a twist-boat conformation for the equatorial isomer of **2**.

Introduction

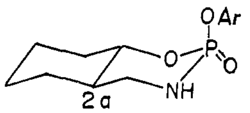
Recent work has established that an electronegative substituent on phosphorus in a 2-oxo-1,3,2-dioxaphosphorinane **1** prefers the axial orientation.[2-11] This result is consistent with molecular orbital calculations associated with the generalized anomeric or gauche effect.[12,13] Generally, the magnitude of this anomeric effect at phosphorus is small (less than several kcal/mol) and both axial and equatorial isomers of **1** are in the chair conformation. In the present paper NMR analysis of the conformation of both the axial and equatorial 2-*p*-nitrophenoxy esters of the 2-oxo-1,3,2-dioxaphosphoranes, **1**, confirms this conclusion. In contrast NMR analysis of the equatorial isomer of 2-oxo-1,3,2-oxazaphosphorinane **2b** shows it to be in an unusual twist-boat conformation.



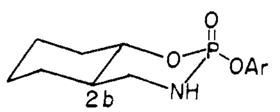
1a



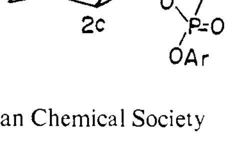
1b



2a



2b



2c

0002-7863/79/1501-4925$01.00/0

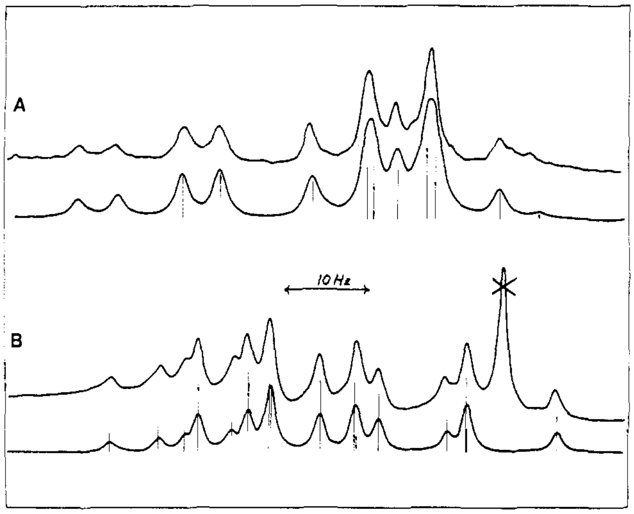


Figure 1. Actual (top) and computed (bottom) spectra for protons H-1 and H-2 of **2a** (A) and **2b** (B). Both stick figure transitions and simulated, line-broadened spectra are shown. Signal in (B) marked with (X) is an impurity.

Experimental Section

General Methods. ^1H and ^{31}P NMR spectra were recorded on a Bruker WP-80 spectrometer at 80 and 32.4 MHz, respectively, or ^1H NMR on a 60-MHz Varian T-60 spectrometer. Chemical shifts in parts per million for ^1H NMR spectra are referenced to Me_4Si and for ^{31}P spectra are referenced to 85% H_3PO_4. IR spectra were obtained on a Perkin-Elmer 521 or 700 spectrometer. Mass spectra were obtained on an AEI MS 30 spectrometer. Chemicals were generally of the highest purity. Baker analyzed 60–200 mesh silica gel was used for column chromatography after being activated at 130 °C overnight. Triethylamine and methylene chloride were distilled before use. Other solvents were dried over 4 Å molecular sieves (Grace Chemical Co.).

***trans*-2-Hydroxymethyl-1-cyclohexanol** (**3**) was prepared from cyclohexene (Aldrich) and paraformaldehyde (Aldrich) according to procedure B of Blomquist and Wolinsky.[14]

2-*p*-Nitrophenoxy-2-oxo-5,6-tetramethylene-1,3,2-dioxaphosphorinane (2-*p*-Nitrophenoxy-1,3-dioxa-2-phospha-*trans*-decalin-2-one) (**1**). A solution of 2.50 g (19.2 mmol) of diol **3** and 5.7 mL of triethylamine in 25 mL of CH_2Cl_2 was added dropwise to a solution of 5.41 g (21.1 mmol) of *p*-nitrophenyl phosphorodichloridate (Aldrich) in 40 mL of CH_2Cl_2 at 0 °C under an argon atmosphere. The reaction mixture was stirred for an additional 1 h, washed four times with 100 mL of double distilled water, and dried over $CaCl_2$. The solution was filtered and the solvent rotoevaporated. The esters were separated on a silica gel column with ether as eluent. The axial isomer **1a** was eluted first followed directly by **1b**. **1a** was recrystallized from acetonitrile (mp 122–125 °C) and **1b** from carbon tetrachloride (mp 94 °C) with 50% yield for each.

IR ($CDCl_3$) **1a:** 2934 (m), 2854 (m), 1600 (s), 1525 (s), 1495 (m), 1354 (s), 1312 (s), 1239 (s), 1047 (s). **1b** ($CDCl_3$): 2943 (m), 2865 (m), 1600 (s), 1525 (s), 1495 (s), 1352 (s), 1290 (s), 1071 (s), 1038 (s), 978 (s), 958 (s) cm^{-1}. ^1H NMR ($CDCl_3$; also see Table I) **1a:** δ 1.20–2.18 (m, 9 H, ring CH), 4.12–4.45 (m, 3 H, H-1,2,4), 7.45 (dd, 2 H, aromatic, J = 9.1, 1.0 Hz), 8.25 (d, 2 H, aromatic, J = 9.1 Hz). **1b:** δ 1.18–2.17 (m, 9 H), 4.17–4.44 (m, 3 H), 7.39 (d, 2 H, J = 9.1 Hz), 8.25 (d, 2 H, J = 9.1 Hz).

MS (70 eV): molecular ion for **1a** and **1b** at *m/e* 313.

Anal. Calcd for $C_{13}H_{16}NO_6P$: C, 49.85; H, 5.15; N, 4.47; P, 9.89. Found for **1a:** C, 50.11; H, 5.28; N, 4.50; P, 9.93. Found for **1b:** C, 49.61; H, 4.93; N, 4.24; P, 10.08.

***trans*-2-Tosylmethyl-1-cyclohexanol** (**4**). A solution of 5.5 g (81 mmol) of *p*-toluenesulfonyl chloride in 25 mL of pyridine was added to a solution of 10.0 g (77 mmol) of diol **3** in 50 mL of pyridine. The mixture was stirred for an additional 2 h and then poured into water and extracted with ether. The extract was dried with $MgSO_4$, filtered, and rotoevaporated. Residual pyridine was removed by codistillation with toluene. The extract was a mixture of two compounds. The tosylate, **4**, was recrystallized from carbon tetrachloride by seeding. (Initial seed crystals were obtained by separating the compounds on a silica gel column.) After two recrystallizations, **4** was obtained in 30% yield (mp 69–72 °C).

IR ($CDCl_3$): 3580 (m), 2940 (s), 1785 (m), 1600 (m), 1450 (m), 1345 (s), 1195 (s), 1095 (m), 1040 (m) cm^{-1}. MS (70 eV): molecular ion at *m/e* 284. NMR ($CDCl_3$): δ 0.6–2.2 (m, 9 H), 2.3 (s, 3 H), 2.9 (s, 1 H), 3.0–3.5 (m, 1 H), 4.1 (d, 1 H), 7.3 (d, 2 H), 7.8 (d, 2 H).

***trans*-2-Azidomethyl-1-cyclohexanol** (**5**). NaN_3 (4.0 g, 61 mmol) in 25 mL of H_2O was added to a solution of 10.0 g (35 mmol) of the tosylate **4** in 250 mL of methanol. The solution was stirred and refluxed for 20 h. The solution was cooled and poured into an equal volume of water and concentrated $CaCl_2$. This was extracted three times with ether. The ether was washed with 5% Na_2CO_3 solution, dried ($MgSO_4$), and concentrated. After distillation the azide **5** was obtained in 60% yield (bp 78–80 °C, 0.7 mmHg). IR ($CDCl_3$): 3460 (s), 3030 (m), 2950 (s), 2890 (s), 2140 (s), 1460 (s), 1295 (s), 1122 (m), 1070 (s), 1040 (s), 938 (m) cm^{-1}. NMR ($CDCl_3$): δ 0.9–2.1 (m, 9 H), 3.1–3.7 (m, 4 H).

***trans*-2-Aminomethyl-1-cyclohexanol** (**6**). The azide **5** (3.60 g, 23 mmol) in 60 mL of isopropyl alcohol was added to 2.05 g (54 mmol) of $NaBH_4$. The mixture was stirred and refluxed for 16 h. The isopropyl alcohol was removed on a rotary evaporator. The heavy solid was partitioned between water and ethyl acetate. The water extract was dried and evaporated. After distillation the amino alcohol was obtained in 26% yield (bp 89 °C, 1.1 mmHg). IR ($CDCl_3$): 3250–3400 (m), 3000 (s), 2950 (s), 2880 (s), 1590 (m), 1458 (s), 1393 (s), 1250 (m), 1139 (s), 1086 (s) 1020 (m), 952 (m), 860 (m) cm^{-1}. NMR ($CDCl_3$): δ 0.9–2.0 (m, 9 H), 2.6 (d, 2 H), 3.0–4.0 (m, 4 H).

2-*p*-Nitrophenoxy-2-oxo-5,6-tetramethylene-1,3,2-oxazaphosphorinane (2-*p*-Nitrophenoxy-1,3-oxaza-2-phospha-*trans*-decalin-2-one) (**2**). A solution of 2.23 g (17 mmol) of the amino alcohol **6** and 3.43 g (34 mmol) of triethylamine in 25 mL of CH_2Cl_2 was added dropwise to a solution of 4.86 g (19 mmol) of *p*-nitrophenyl phosphorodichloridate in 35 mL of CH_2Cl_2 under an argon atmosphere at 0 °C. The mixture was stirred for an additional 2 h, washed four times with water, dried, filtered, and concentrated. The isomers, which were produced in equal amounts, were separated on a silica gel column with chloroform in 60% yield overall (**2a**, mp 183–186 °C recrystallized from $CHCl_3/CCl_4$; **2b**, mp 124–126 °C recrystallized from CCl_4). IR ($CDCl_3$) cm^{-1} **2a:** 3405 (w), 3210 (w), 2930 (s), 2850 (m), 1595 (s), 1522 (s), 1490 (s), 1348 (s), 1272 (s), 1236 (s), 1110 (m), 1009 (s), 977 (m), 950 (m). **2b:** 3408 (w), 3210 (w), 2932 (s), 2854 (m), 1594 (s), 1522 (s), 1490 (s), 1348 (s), 1258 (s), 1237 (s), 1111 (m), 1023 (s), 966 (m), 953 (m) cm^{-1}. ^1H NMR (acetone-d_6; also see Table I) **2a:** δ 1.22–1.83 (m, 9 H), 2.84–3.34 (m, 2 H, H-1, H-2), 4.18 (m, 1 H, H-4), 4.91 (s, 1 H, NH), 7.54 (dd, 2 H, aromatic, J = 9.3 Hz), 8.29 (d, 2 H, aromatic, J = 9.3 Hz). **2b:** δ 1.22–1.83 (m, 9 H), 2.84–3.34 (m, 2 H), 4.21 (m, 1 H), 4.98 (d, 1 H, NH, J = 10.9 Hz), 7.49 (dd, 2 H, J = 9.3, 1.2 Hz), 8.27 (d, 2 H, 9.5 Hz). MS (70 eV): molecular ion for **2a** and **2b** at *m/e* 312. Anal. Calcd for $C_{13}H_{11}N_2O_5P$: C, 50.00; H, 5.49, N, 8.97; P, 9.92. Found for **2a:** C, 49.66; H, 5.45; N, 8.98; P, 9.86. Found for **2b:** C, 49.75; H, 5.42; N, 8.96; P, 9.70.

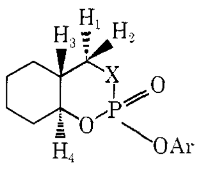
Conformational analysis for the phosphorinanes was based largely upon the coupling constant data of Table I. The spectral parameters were obtained by iterative fitting of the undecoupled and decoupled ^1H NMR spectra and the undecoupled ^{31}P NMR spectra using the Bruker Laocoon-type program NMRCAL. An example of the actual and computed spectrum for H-1 and H-2 of **2a** (Figure 1A) and **2b** (Figure 1B) is shown.

Results and Discussion

Dioxaphosphorinane 1 Conformation. The 1.1-ppm upfield ^{31}P chemical shift for **1a** relative to **1b** (Table I) strongly supports the assignment of the axial isomer to **1a** since in all previous studies on isomeric pairs of phosphorinanes the axial substituent has an upfield ^{31}P chemical shift.[2-4,6,10,15] The P=O stretching frequency for **1b** is 22 cm^{-1} lower than for **1a** (ν_{PO} 1312 cm^{-1}) consistent with our isomeric assignment and previous diagnostic use of P=O stretching frequencies.[6,10,11]

The coupling constants for **1a** are consistent with a normal chair conformation. A Karplus-type relationship has been established between the HCOP dihedral angle and the $^3J_{HCOP}$ coupling constant.[5,16] The small $^3J_{1P}$ and the large $^3J_{2P}$ indi-

Table I. Selected NMR Spectral Parameters[a] for **1a,b** and **2a,b**



compd		chemical shifts[b]			coupling constants[c]						
		δ_{H_1}	δ_{H_2}	$\delta_{^{31}P}$	J_{12}	J_{13}	J_{23}	J_{1P}	J_{2P}	J_{3P}	J_{4P}
1a[d]	X = O	4.22	4.35	−13.63	−10.8	11.4	4.4	1.0	24.6	0.0	~0
1b[d]		4.27	4.36	−12.55	−10.8	12.5	5.0	5.5	18.0	0.0	2.0
2a[e]	X = NH	3.02	3.22	−0.71	−12.4	10.7	4.4	2.0	27.9	0.0	~0
2b[e]		3.02	3.30	−0.77	−11.0	11.1	5.5	13.6	8.8	0.0	11.5

[a] Determined by ABCX analysis utilizing NMRCAL program (Bruker Instrument) on a Nicolet 1080 computer. NMR spectra taken on a Bruker WP-80 spectrometer at room temperature. [b] Proton chemical shifts in parts per million downfield from Me_4Si; ^{31}P chemical shifts in parts per million downfield from external 85% H_3PO_4. [c] Values in hertz, J_{12} assumed negative; all others given as absolute values. [d] In $CDCl_3$ (^1H NMR); in CH_3OH (^{31}P NMR). [e] In acetone-d_6 (^1H NMR); in CH_3OH (^{31}P NMR).

cate a gauche dihedral angle for H_1COP and trans dihedral angle for H_2COP.

Equatorial ester **1b** is likely in a slightly flattened chair conformation. The dihedral angle H_2COP is less than 180° because $^3J_{2P} = 18.0$ Hz. Unfortunately determination of accurate dihedral angles from these coupling constants is not possible since vicinal P-O-C-H coupling constants are modestly sensitive to factors other than the dihedral angle. However, using the relationship suggested by Kung et al.,[16b] we estimate a P-O-C-H_2 dihedral angle of ca. 150°. The smaller value for $^3J_{2P}$ in **1b** than in **1a** could also be interpreted in terms of a rapidly equilibrating mixture of undistorted chair and twist-boat conformations. However, the undecoupled ^{31}P NMR spectrum of **1b** is independent of temperature between 227 and 325 K and it therefore appears to exist in a single, slightly flattened chair conformation.

Oxazaphosphorinane 2 Conformation. Configurational and conformational analysis of **2a** and **2b** is made difficult since there is little ^{31}P chemical shift difference between the two isomeric phosphoramidates. The P=O stretching frequency for **2a** (1272 cm^{-1}) is higher than the stretching frequency for **2b** (1258 cm^{-1}) but the difference is ca. ½ that in **1a**/**1b**. The assignment of structure **2a** to the higher melting isomer is largely based upon the higher IR P=O stretch and its normal ^1H NMR spectrum ($^3J_{2P} = 27.9$ and $^3J_{1P} = 2.0$ Hz). The axial ester phosphoramidate is the anomerically favored isomer and there is no reason to believe that it should not exist in a normal chair conformation (as **1a**). Coupling constants for the lower melting isomer, however, are quite unusual with $^3J_{1P}$ (=13.6 Hz) being *larger* than $^3J_{2P}$ (=8.8 Hz). These values are inconsistent with a chair conformation but could be explained by a twist-boat conformation for the phosphorinane ring (although we cannot rule out an additional small contribution from a chair conformation). The large $^3J_{4P}$ (=11.5 Hz) and $^3J_{1P}$ coupling constants require nongauche dihedral angles H_4COP and H_1CNP and hence a nonchair conformation. Furthermore, the H_2CNP dihedral angle is no longer trans, but gauche-like. It is likely that **2b** is a rapidly equilibrating mixture of skew-boat structures, although no evidence supporting this equilibration could be obtained. Thus the ^1H NMR spectrum of **2b** was independent of temperature from 200 to 310 K.

By flipping from the chair conformation **2b** to the twist-boat conformation **2c**, the equatorial ester bond moves into a pseudoaxial position. The anomeric preference for this axial conformation is likely the basis for the unique twist-boat distortion in this ring system. The conformation represents a balance between the anomeric effect favoring the axial orientation in the twist-boat and the 1,3-steric and eclipsing interactions favoring the chair conformation.

The similarity between the ^{31}P chemical shifts and the smaller IR stretching frequency difference for **2a** and **2c** is now quite reasonable since *both* isomers have an axial ester bond. Anomalous ^{31}P chemical shift and ^1H NMR coupling constant data for similar isomeric phosphorinane structures have previously been reported,[10b] but have been left unexplained or interpreted in terms of a chair to chair equilibration,[17] although Mosbo[18] has recently suggested that some 1,3,2-dioxaphosphorinanes may exist in twist-boat conformations ca. 20% of the time. By utilizing the rigid *trans*-decalin ring system in **1** and **2** we can rule out the complicating chair to chair flip in the analysis of the unusual NMR data for the equatorial isomers.

After the submission of this manuscript, Bentrude, Newton, Hargis, and co-workers[19] reported that *cis*-2-oxo-2-dimethylamino-3-phenyl-5-*tert*-butyl-1,3,2-oxazaphosphorinane exists in a twist-boat conformation in the solid state and in solution. The normal chair conformation for this oxazaphosphorinane would place the *tert*-butyl group equatorial and the dimethylamino group axial. Apparently steric (see also ref 4b) or electronic effects favor the twist conformation with the dimethylamino group *equatorial*. Twist forms apparently are also found in the 1,3,2-dithiaphosphorinane ring system.[20]

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Host–Guest Complexation. 18. Effects on Cation Binding of Convergent Ligand Sites Appended to Macrocyclic Polyethers

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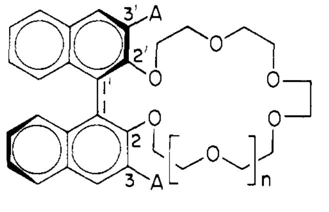
Abstract: Syntheses are reported for 16 new macrocyclic polyether ligand systems which contain potentially convergent side chains containing additional binding sites. The free energies of association of these systems in $CDCl_3$ at 25 °C with Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, $CH_3NH_3^+$, and t-$BuNH_3^+$ picrates were determined. The structures of these hosts are indicated by the following abbreviations: E is CH_2CH_2; D is 1,1′-dinaphthyl attached to two macroring oxygens at its 2,2′ positions and to two substituents at its 3,3′ positions; T is 1,1′-bitetralyl attached to two macroring oxygens at its 2,2′ positions and to two substituents in its 3,3′ positions; Ur is the cyclic urea unit, $N(CH_2)_3(CO)NCH_3$; Py is α-pyridyl; Bz is $C_6H_5CH_2$. The hosts prepared and examined were $(CH_3)_2D(OEOEO)_2E$ (**3**), $(OCH)_2D(OEOEO)_2E$ (**5**), $(CH_3O_2C)_2D(OEOEO)_2E$ (**6**), $(HO_2C)_2D(OEOEO)_2E$ (**7**), $(CH_3CO)_2D(OEOEO)_2E$ (**9**), $(UrCH_2)_2D(OEOEO)_2E$ (**11**), $[(EtO)_2OPCH_2]_2D(OEOEO)_2E$ (**12**), $[(EtO)_2OPCH_2]_2D(OEOEOE)_2O$ (**13**), $(PySCH_2)_2D(OEOEO)_2E$ (**14**), $(PyCH_2OCH_2)_2D(OEOEO)_2E$ (**15**), $[(EtO)_2OPCH_2]_2T(OEOE)_2O$ (**20**), *cis*-$(BzOCH_2)_2E(OEOEO)_2E$ (**22**), *trans*-$(BzOCH_2)_2E(OEOEO)_2E$ (**23**), *cis*-$(o$-$ClC_6H_4)_2E(OEOEO)_2E$ (**24**), *trans*-$(o$-$ClC_6H_4)_2E(OEOEO)_2E$ (**25**), and $E(OEOEOCH_2)_2E(OEOEO)_2E$ (**26**). Noncyclic model compounds were also prepared: $(CH_3)_2D(OEOEOCH_3)_2$ (**1**) and $[(EtO)_2OPCH_2]_2D(OCH_3)_2$ (**17**). The free energies of association ($-\Delta G°$) of these compounds with various picrate salts were compared with one another and with those of known hosts, $D(OEOEO)_2D$ (**2**), 2,3-naphtho-18-crown-6 (**21**), and dicyclohexyl-18-crown-6. The highest $-\Delta G°$ value (kcal/mol) observed involved $[(EtO)_2OPCH_2]_2D(OEOEO)_2E$ (**12**) and Na^+ (12.4), and the lowest, $(CH_3)_2D(OEOEOCH_3)_2$ (**1**) and t-$BuNH_3^+$ (3.38), as complexing partners. The $-\Delta G°_{av}$ of association (kcal/mol) with Li^+, Na^+, K^+, Rb^+, Cs^+, and NH_4^+ picrates allowed the hosts to be ranked as general ligand systems. Values of $-\Delta(\Delta G°)_{max}$ (the difference in free energies of the best and poorest bound of these six picrate salts) allowed the ligand systems to be graded with regard to ion selectivity. Values of $-\Delta(\Delta G)^{NH_4^+}_{t\text{-}BuNH_3^+}$ allowed the ligand systems to be judged with regard to their capacity for structural recognition of NH_4^+ vs. t-$BuNH_3^+$ ions. With respect to all three parameters, the $[(EtO)_2OPCH_2]_2D(OEOEO)_2E$ (**12**) system ranked the highest. The location, binding, and steric properties of the two P → O oxygens in this ligand system appear responsible for its superior properties.

Previous papers in this series dealt with the synthesis and complexing properties of neutral host compounds toward metal, ammonium, and alkylammonium picrate salts in $CHCl_3$.[2] Binding sites incorporated directly into the macroring systems include ethyleneoxy, m-xylyl,[2a] 2,6-substituted anisyl,[2d] 2,6-substituted phenylcarbomethoxy,[2b] 2,6-substituted phenylcarboxy,[2b] 2,6-substituted pyridine, 2,6-substituted pyridine oxide, ortho,ortho′-substituted arylphosphoryl, and N,N'-tetrasubstituted urea units.[2e] Two types of negatively charged macrocycles have been designed and prepared for complexation of cations. In one type, acetylacetonide units incorporated in the ring systems were examined.[3a] In a second study, carboxylate groups terminating side chains grafted to the macroring were designed and investigated.[3b]

This paper reports the design, syntheses, and complexing properties of 16 new macrocyclic polyethers in which additional convergent binding sites were appended to the macroring system. To provide for convergence of the extra binding sites, three strategies were employed. The first employed the rigid 1,1′-binaphthyl unit bonded to oxygens of the macroring system in its 2,2′ positions. The 3,3′ positions were substituted with side chains (A in formulas I and II). The planes of the two naphthalene rings in CPK molecular models are roughly perpendicular and tangential to the best plane of the macroring, as indicated in formulas I and II. In proper conformations, the termini of appropriate A side chains can locate on an axis that passes through the center of the macroring. Thus, additional binding sites may be strategically positioned on either side of the central binding cavity. In all systems reported here, the two side chains are identical, so the systems possess a C_2 axis. Al-



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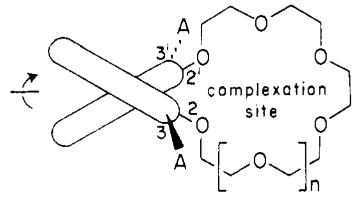

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