

The method utilized to construct the magnetic orbitals φ_μ likely deserves to be briefly discussed. This method consists of preventing any delocalization of a magnetic orbital toward the metal ion on which it is not centered. This situation is realized by contracting the atomic orbitals of this metal ion. So, the magnetic orbitals strictly describe the unpaired electrons *in the absence* of exchange interaction and the Heitler-London wave functions well correspond to 0th order functions in an approach where the exchange interaction is weak enough to be treated as a perturbation. We think that such a way to define the semilocalized magnetic orbitals could be extended to other problems in molecular magnetism, in particular when dissymmetrical polymetallic entities are involved.

Conclusion

We have emphasized elsewhere⁸ that the study of heterodinuclear systems has provided novel and important concepts in the area of molecular magnetism. This specific role of the heterodinuclear compounds is also true as far as the PND technique is concerned. Indeed, the spatial spin distribution is much more informative when the molecular entity is dissymmetrical. In particular, it allows testing of the validity of the wave functions used to describe the ground state. Moreover, owing to the non-compensation of the local spins, the technique is applicable for antiferromagnetically as well as ferromagnetically coupled compounds.

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In the case of Cu(salen)Ni(hfa)₂ in its doublet ground state, the spatial spin distribution closely follow what the Heitler-London wave functions associated with this state suggest. The ratio $p_{\text{Ni}}/p_{\text{Cu}}$ of the spin populations on the metals is found equal to -5.04. As for the spin population on the bridges, it is found to be almost negligible. This result in no way indicates that the interaction occurs through space. On the contrary, as expected, the phenolic oxygen atoms play the key role in transmitting the electronic effects; they receive a positive spin density from the nickel(II) and an almost equal (in absolute value) negative spin density from the copper(II).

The PND technique brings new insights on the mechanism of the exchange interaction that no other technique could provide. It deserves to be more often used, particularly in the field of the heteropolymetallic systems. Unfortunately, this technique is still difficult to implement. It requires not only a neutron source but also large and centrosymmetrical single crystals. Nevertheless, we intend to investigate other suitable systems in the near future.

Acknowledgment. We are most grateful to J. Hammann and E. Vincent, who helped us to measure the magnetization curve of Cu(salen)Ni(hfa)₂.

Registry No. Cu(salen)Ni(hfa)₂, 71073-29-5.

Supplementary Material Available: Tables SVIII-SX giving the atomic coordinates and the parameters used in the extended Hückel calculations (4 pages); table of structure factors (2 pages). Ordering information is given on any current masthead page.

Radical Cation(s) of (Hexamethyl-) Prismane: Ab Initio Calculations and Nuclear Spin Polarization Results

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Abstract: Ab initio molecular orbital calculations investigating the nature of the structure and energies of the radical cations of prismane are reported. The effects of polarization functions and electron correlation have been included in these calculations. We also report experimental studies using chemically induced dynamic nuclear polarization that establish the existence of such a radical cation derived from hexamethylprismane. Theoretical studies on the interaction complex between cyclopropenyl cation and cyclopropenyl radical are also reported.

The valence isomers of benzene¹⁻³ or at least relatively simple derivatives thereof⁴⁻¹² are readily available. Their thermal and light-induced rearrangements have been thoroughly explored;¹³ some of their thermochemical parameters have been evaluated;¹⁴ and their structural features have been probed by a variety of experimental techniques,¹⁵⁻²¹ including microwave spectroscopy as well as electron and X-ray diffraction analysis. In addition, ab initio molecular orbital (MO) calculations have been employed to elucidate a variety of features of these interesting molecules.^{14,22,23} On the other hand, the corresponding radical cations have received considerably less attention. We are interested in the radical cations of strained ring systems in general²⁴ and in those of the four valence isomers of benzene in particular.²⁵⁻²⁷ Just as the elucidation of the unique structure of benzene played an important role in the development of organic chemistry,²⁸ we

believe that insight into the structures of the radical cations derived from the (C₆H₆) valence isomers will contribute substantially to

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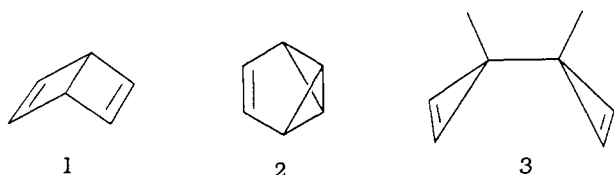
Table I. Structures, Energies, and Spin Densities of Prismane and Its Radical Cations

molecule	geom parameter, ^a Å				total energy, ^b hartrees		rel energy, ^c kcal/mol	carbon spin density	
	C ₁ -C ₄	C ₂ -C ₃	C ₁ -C ₂	C ₂ -C ₆	HF/6-31G*	MP2/6-31G*		C ₁ ^d	C ₂ ^e
prismane (<i>D</i> _{3h})	1.560	1.560	1.526	1.526	-230.501 74	231.268 61			
radical cation (<i>C</i> _{2v})									
² B ₁	1.571	1.481	1.510	1.731	-230.247 95	-230.992 44	0	-0.097	0.298
² A ₂	1.463	1.531	1.631	1.464	-230.242 67	-230.991 17	0.8	0.377	0.059
² B ₂	1.534	1.744	1.528	1.454	-230.169 98	-230.918 47	45.4	0.116	0.195
² A ₁	2.002	1.554	1.489	1.544	-230.183 48	-230.914 72	48.7	0.460	0.023

^aNot all parameters are listed. The geometries were, however, completely optimized with the 6-31G basis set. ^bWith HF/6-31G optimized geometries. ^cWith MP2/6-31G* level of theory. ^dTwo equivalent carbons have this spin density. ^eFour equivalent carbons have this spin density.

understanding the nature of radical cations.

Only one of the potential radical cation structure types, that derived from the parent benzene system, has so far been observed and characterized unambiguously by laser-induced fluorescence spectroscopy.²² Attempts to observe the molecular ions derived from hexamethyl Dewar benzene (1) either by steady-state



spectroscopy in frozen glasses²⁹ or by time-resolved (nanosecond) spectroscopy in fluid solution³⁰ have failed to provide evidence for any intermediate but the hexamethylbenzene radical cation. A second structure type has been inferred as an intermediate in the pulse radiolysis of cyclopropenylum cations.^{31,32} In the absence of any specific information the authors believed a sandwich structure to be the most likely. Several additional species have been brought to light by the application of chemically induced dynamic nuclear polarization (CIDNP) techniques. For example, we have established the existence of discrete radical cations derived from hexamethyl Dewar benzene (1),²⁵ benzvalene (2),²⁶ and

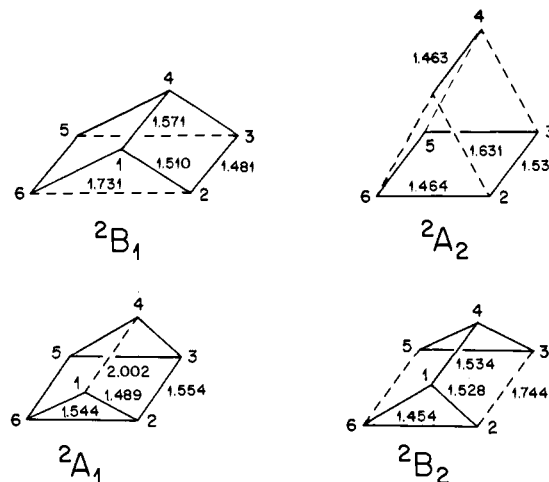
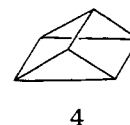


Figure 1. Geometrical features of four low-lying electronic states of the prismane radical cation.

3,3'-dimethylbicyclopentenyl (3).²⁷ The existence of radical cations derived from hexamethyl Dewar benzene is supported by the observation of ESR spectra in frozen matrices at 77 K.³³

In this paper we report the results of ab initio molecular orbital (MO) calculations on four low-lying radical cationic states of prismane (4, *D*_{3h}) and compare their structural characteristics with those of the corresponding states of radical cations derived from benzene and Dewar benzene. We also report CIDNP results



observed during the electron-transfer reactions of hexamethyl prismane with anthraquinone. Under these conditions the radical cation of hexamethyl-4 is generated, which regenerates some of the starting material by reverse electron transfer in geminate radical ion pairs. At the same time, however, it undergoes facile rearrangement to both hexamethyl Dewar benzene and hexamethylbenzene. The polarization observed for the former provides insight into the nature of the hexamethylprismane radical cation. The CIDNP results are discussed in light of appropriate radical cation structures and their potential interconversions.

Calculations

Ab initio molecular orbital calculations have been performed on prismane and several electronic states of the prismane (radical) cation, and the results are compared with our previous findings on analogous benzene²² and Dewar benzene systems.²⁵ All molecular geometries have been determined by complete geometry optimization within the given symmetry constraints at the Hartree-Fock (HF) level of theory by using the split valence 6-31G basis set.³⁴ Unrestricted HF theory (UHF) has been used for

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all open-shell radical cation systems. This level of theory has been shown previously to be reliable in the calculation of geometries for several hydrocarbon species.^{14,35} For example, our calculated bond lengths in prismane, $C_1-C_2 = 1.53 \text{ \AA}$ and $C_1-C_4 = 1.56 \text{ \AA}$, are in good agreement with the results obtained by Schulman and Disch using the larger 6-31G* basis set ($C_1-C_2 = 1.51 \text{ \AA}$ and $C_1-C_4 = 1.55 \text{ \AA}$).¹⁴

The highest occupied molecular orbital in prismane is e'' , which has significant bonding character in the cyclopropane-like bonds and has antibonding character in the transannular bonds. The next lower orbital is e' , which has bonding character principally in the three transannular bonds. Removal of an electron from the e'' orbital gives rise to a ${}^2E''$ state which on Jahn–Teller distortion yields a pair of states, 2A_2 and 2B_1 (in C_{2v} symmetry). These are expected to be the lowest electronic states for the prismane cation. Similarly, removal of an electron from the e' orbital yields two states, 2A_1 and 2B_2 , which are expected to be of higher energy.

Our detailed calculations are in accord with these expectations. The principal geometrical features are summarized in Table I and illustrated in Figure 1. They are best discussed in comparison with the geometry of prismane itself; we will refer to its two types of bonds as "cyclopropane" and "transannular" bonds, respectively. The 2B_1 state is lowest in energy; it corresponds to stretching of two cyclopropane bonds, C_2-C_6 and C_3-C_5 , from 1.53 to 1.73 \AA . Since the orbital from which the electron was removed is antibonding in the transannular bonds, there is also an accompanying shortening of the C_2-C_3 and C_5-C_6 bonds from 1.56 to 1.48 \AA . These changes are all very similar to the corresponding changes seen in the analogous bond lengths on going from quadricyclane to its radical cation, which we have reported previously.³⁵

The 2A_2 state lies very close in energy to the 2B_1 state; it corresponds to changes in the complementary cyclopropane bonds of the molecule. Now four equivalent bonds, C_1-C_2 , C_1-C_6 , C_3-C_4 , and C_4-C_5 are stretched from 1.53 to 1.63 \AA . Here, the change in bond length is smaller because more bonds are involved. The transannular bond C_1-C_4 now is shortened from 1.56 \AA in the neutral system to 1.46 \AA in the cation.

As mentioned earlier, the 2A_1 and 2B_2 states correspond to removing an electron from the transannular bonds. Thus, on going to the 2A_1 state, C_1-C_4 stretches from 1.56 to 2.00 \AA , and in the 2B_2 state, the C_2-C_3 and C_5-C_6 bonds stretch from 1.56 to 1.74 \AA .

An evaluation of the vibrational frequencies of the 2B_1 state at the HF/6-31G level shows the presence of an imaginary b_2 frequency, indicating that a distortion to C_s symmetry (where the bonds C_2-C_6 and C_3-C_5 are stretched in an asymmetric manner) leads to energy lowering. However, this appears to be an artifact of the HF/6-31G level of theory. Larger basis sets as well as electron correlation effects favor the C_{2v} structure significantly relative to the optimized C_s minimum. This finding is similar to the results obtained previously for the radical cations of norbornadiene and quadricyclane.³⁵ Thus, we expect that the 2B_1 state is a true minimum at the correlated levels of theory and, in fact, to be the ground state of prismane cation.

As mentioned earlier, the 2A_2 and 2B_1 states are closely related Jahn–Teller states resulting from the degenerate ${}^2E''$ state. In accordance with this, the 2A_2 state was found not to be a minimum; it has an imaginary b_1 frequency that takes it to the 2B_1 state through intermediate C_s pathways. Thus, the 2A_2 state is a transition state for the pseudorotation process involving the three equivalent 2B_1 structures.

Similarly, the 2A_1 and 2B_2 states are a pair of states connected on the pseudorotation hypersurface. In addition, vibrational analysis of the 2A_1 state indicates a distortion to C_2 symmetry which appears to eventually reach the 2A_2 structure which, in turn,

(35) In particular, this level of theory reliably reproduces the relative energies of both the neutral (theoretical $\Delta E = 27 \text{ kcal/mol}$; experimental $\Delta E = 22\text{--}27 \text{ kcal/mol}$) and the ionic species (theoretical $\Delta E = 11 \text{ kcal/mol}$; experimental $\Delta E = 9 \text{ kcal/mol}$) in the related norbornadiene–quadricyclane system: Raghavachari, K.; Haddon, R. C.; Roth, H. D. *J. Am. Chem. Soc.* **1983**, *105*, 3110–3114.

Table II. Electronic States and High-Lying Molecular Orbitals for the Different Radical Cations

molecule	state sym ^a	high-lying MOs
prismane cation	2B_1	$(4b_2)^2(8a_1)^2(3a_2)^2(6b_1)^1$
	2A_2	$(8a_1)^2(4b_2)^2(6b_1)^2(3a_2)^1$
Dewar benzene cation	2B_2	$(5b_1)^2(3a_2)^2(8a_1)^2(5b_2)^1$
	2A_1	$(5b_1)^2(3a_2)^2(5b_2)^2(8a_1)^1$
benzene cation ^b	2B_1	$(7a_1)^2(3a_2)^2(5b_2)^2(6b_1)^1$
	2B_2	$(7a_1)^2(3a_2)^2(6b_1)^2(5b_2)^1$
interaction complex ion ^c	2A_1	$(3b_2)^2(3a_2)^2(7b_1)^2(8a_1)^1$

^a All have been represented in C_{2v} symmetry with the same orientation to make comparisons possible. ^b The ground state has D_{2h} symmetry. ^c Interaction complex between cyclopropenyl cation and cyclopropenyl radical (see text). The ground state has only C_2 symmetry.

is connected to the 2B_1 state as discussed earlier. These findings suggest that the 2B_1 state may be the only true minimum of the four states considered in this work.

Electron correlation effects were included by means of second-order Møller–Plesset perturbation theory^{36,37} using a polarized 6-31G* basis set.³⁸ These calculations reveal that the 2A_2 and 2B_1 states are very close in energy, lying within 1 kcal/mol. The 2A_1 and 2B_2 states lie about 45–50 kcal/mol higher in energy.

The ground 2B_1 state of the prismane cation lies 16 kcal/mol higher in energy than the ground 2B_2 state of the Dewar benzene cation. This is considerably less than the corresponding energy difference between the neutral systems, which is 37 kcal/mol at the MP2/6-31G* level of theory. The decrease in the energy difference on ionization is very similar to the analogous norbornadiene–quadricyclane system.³⁵ This trend is in keeping with the generally lower ionization potentials of the more highly strained isomers, reflecting the fact that bonding interactions with less than the full complement of electrons can be accommodated with lesser strain energies.

In both the Dewar benzene–prismane and the norbornadiene–quadricyclane systems, the ground electronic states of the ions do not correlate (see Table II). Interconversions between the isomers (e.g., on going from prismane cation to Dewar benzene cation) are forbidden from both state-symmetry and orbital-symmetry considerations and are thus expected to have barriers. However, we have not attempted to evaluate the height of the barrier for either the $C_6H_6^+$ or the $C_7H_8^+$ isomers in this work. The symmetry of the singly occupied (SO) MOs of prismane and Dewar benzene cations is illustrated here:



We have also investigated the interaction complex formed between the cyclopropenyl cation, $C_3H_3^+$, and the cyclopropenyl radical, $C_3H_3^*$, to evaluate the relationship of this adduct to the four prismane cations considered in this work. The structure of this species was probed by placing the two reactants into two parallel planes at a distance of $>3 \text{ \AA}$. The energy of this array decreases as the two rings incline toward each other, forming a single long C–C bond. Initially, one element of symmetry was imposed, a plane bisecting the three-membered rings; this restriction was removed in subsequent refinements. The optimized structure was found to be symmetric between the two interacting units and has overall C_2 symmetry with the spin density essentially localized in a four-carbon plane. Vibrational analysis at the HF/6-31G level showed that it was a local minimum on the potential energy surface. The interaction distance between the closest pair of carbon atoms was 1.85 \AA and that between the next closest pair was 3.25 \AA . At the MP2/6-31G* level, this structure was 23 kcal/mol higher in energy than the 2B_1 ground state of

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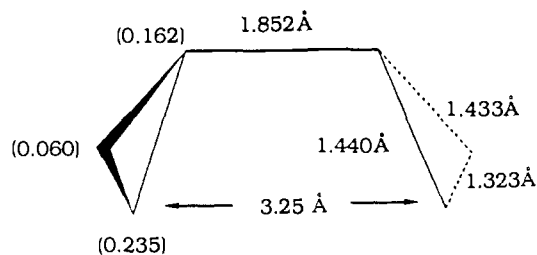


Figure 2. Optimized geometry and carbon spin densities of the adduct formed between cyclopropenyl cation, $C_3H_3^+$, and the cyclopropenyl radical, $C_3H_3^\cdot$.

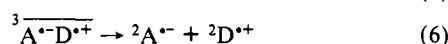
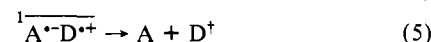
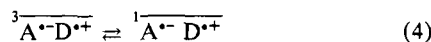
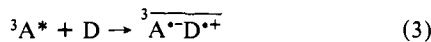
the prismane cation. The optimized geometry and carbon spin densities of the adduct are shown in Figure 2.

To consider the orbital correlations with the other prismane cation states, we have also calculated the geometry and energy of the interaction complex with imposed C_{2v} symmetry. The resulting constrained C_{2v} structure was found to have a slightly elongated long bond (1.97 vs 1.85 Å) and was 4 kcal/mol higher in energy than the C_2 minimum. The electronic state was 2A_1 , which does not correlate with the ground state of prismane cation. In addition there was also an orbital crossing, which might contribute further to a barrier for transformation into the prismane cation. Table II summarizes the nature of the occupied molecular orbitals and electronic states in the different cations.

Nuclear Spin Polarization Results

The radical cation of hexamethylprismane was generated in the probe of an NMR spectrometer by electron transfer to photoexcited quinones; in the case discussed here anthraquinone proved to be most suitable. This method has been utilized for the generation of numerous radical cations derived from strained-ring hydrocarbons (Scheme I).²⁴ Photoinduced electron transfer (eq

Scheme I



3) gives rise to radical ion pairs, initially of triplet spin multiplicity, whose lifetimes are dictated by the time required for intersystem crossing (eq 4) and recombination (eq 5). For the radical ion pairs discussed here, the fastest intersystem crossing mechanism available is hyperfine-induced singlet-triplet mixing. The competition of this process with diffusional separation (eq 6) leads to the induction of nuclear spin polarization and typically occurs on the nanosecond time scale.

During the relatively short time required for intersystem crossing only radical cations with exceedingly low activation barriers can undergo reorganizations. On the other hand, reorganizations with higher barriers may occur, once radical cations have escaped from their semiquinone counterradicals, because of the considerably longer lifetimes of free ions. These considerations may be used for a qualitative classification of activation barriers. Thus, quadricyclane radical cations survive the period required for intersystem crossing (i.e., quadricyclane is regenerated by reverse electron transfer from geminate ion pairs), but they suffer rearrangement as free radical cations.³⁹ Similarly, the radical cations of benzvalene and its benzoannulated derivative, naphthalene, regenerate their precursor molecules by geminate recombination but suffer ring opening as free radical cations.²⁶

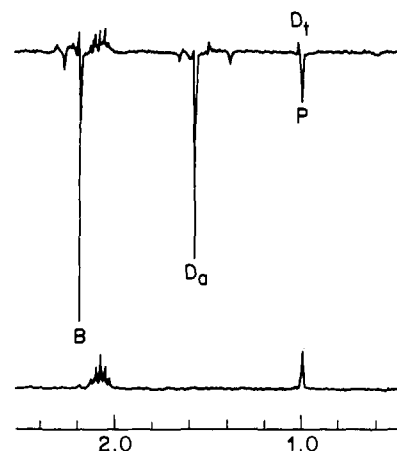


Figure 3. 1H NMR spectra (90 MHz) of acetone- d_6 solutions containing 0.02 M each of hexamethylprismane and anthraquinone in the dark (bottom) and during UV irradiation (top) [B = hexamethylbenzene; D = hexamethyl Dewar benzene, a = allylic methyl groups, t = tertiary methyl groups; P = hexamethylprismane].

The existence of activation barriers is further indicated by the temperature dependence of the observed rearrangements in the range $30^\circ C > T > -50^\circ C$.²⁶

The photoinduced electron-transfer reaction between hexamethylprismane and anthraquinone (Scheme I, A = anthraquinone, D = hexamethylprismane (HMP)) gives rise to three polarized products, regenerated starting material as well as the Dewar benzene and benzene derivatives as rearranged products. Regenerated hexamethylprismane appears in emission (Figure 3). Although relatively weak and without any information about the structure of the hexamethylprismane radical cation, this signal is nonetheless very important as it indicates that some prismane radical cations survive on the time scale required for intersystem crossing and recombination. The observed signal direction is consistent with geminate recombination of radical ion pairs generated from a triplet precursor.

The single resonance of hexamethylbenzene (HMB) and the allylic methyl signal of hexamethyl Dewar benzene (HMD) also appear in emission, indicating that these products are generated by geminate recombination as well. Accordingly, intersystem crossing and rearrangement must occur on comparable time scales, and the barriers separating the respective radical cations must be low, indeed lower than in the three systems discussed above.

Because HMD has two types of magnetically nonequivalent methyl groups, its polarization provides the key to the spin density distribution in either its immediate or its penultimate paramagnetic precursor. The allylic methyl signal (1.6 ppm) shows strong emission, whereas the signal representing the tertiary methyl groups (1.0 ppm) shows much weaker enhanced absorption (Figure 3). This indicates a radical cation in which spin and charge are located in four equivalent positions (or a subset thereof) and the remaining two centers are essentially without spin. This description fits either the 2B_1 state of the prismane radical cation or the 2B_2 state of the Dewar benzene radical cation, but cannot, in principle, differentiate between them.

Since the polarization pattern observed for HMD with HMP as electron donor is different from those observed previously with HMD as electron donor, a different radical ion intermediate must be invoked for the HMP reaction. This species can only be the HMP radical cation, whose intermediacy is also strongly suggested by the observation of polarized HMP. In summary, we consider the effects observed for HMP and HMD as firm evidence for the existence of the HMP radical cation on the nanosecond time scale.

Conclusion

The experimental results reported in this paper establish the existence of a new radical cation structure type derived from a highly strained valence isomer of benzene; the calculations support its existence and delineate its structure. The hexamethylprismane radical cation appears to be relatively unstable and most likely

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elusive to optical spectroscopic methods. The HMD radical cation, on the other hand, appears to be more stable and may be accessible by gentle oxidation of either HMP or HMD. Several approaches to HMD^{•+} will be pursued.

Our calculations further indicate that the adduct formed by interaction of cyclopropenylum cation and cyclopropenyl radical may have a structure altogether different from that considered before. We plan to further pursue this problem. Finally, we note

that of the five radical cations of composition (CH)₆, the prismane species discussed here is the third one on which we have performed calculations. The interesting features of a fourth isomer, benzvalene, will be reported shortly.

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Novel Ditopic Receptors Based on the P₂N₂ Diphosphazane Ring: Synthesis and X-ray Structural Characterization of Cis and Trans Bis(crown ether) Annellated 1,3,2λ⁵,4λ⁵-Diazadiphosphetidine 2,4-Disulfide

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Abstract: The 1,3,2,4-diazadiphosphetidine ring is used for the construction of the bis(crown ether) derivative **1**, which occurs as cis and trans isomers. Refluxing triethylene glycol dianilino ether **3** with hexamethylphosphorous triamide (HMPT) in toluene followed by addition of sulfur gave **1** as a crystalline material in isolated yields ranging from 25% to 73%. The compounds have been characterized by a combination of ¹H, ¹³C, and ³¹P NMR and mass spectral data. The structural assignments of the two diastereoisomers are based on X-ray structural analysis. Crystal data at 291 K are as follows: *cis*-**1**·H₂O [Cu Kα (λ = 1.54178 Å)] *a* = 11.030 (9) Å, *b* = 11.169 (3) Å, *c* = 18.101 (13) Å, α = 85.68 (4)°, β = 87.06 (6)°, γ = 86.57 (4)°, *Z* = 2, triclinic, space group *P* $\bar{1}$, *R* = 0.087 for 5888 reflections with *I* ≥ 2.5σ(*I*); *trans*-**1**·2CH₂Cl₂ [Mo Kα (λ = 0.71069 Å)] *a* = 11.757 (3) Å, *b* = 11.140 (4) Å, *c* = 9.393 (1) Å, α = 65.51 (2)°, β = 101.12 (2)°, γ = 100.63 (3)°, *Z* = 1, triclinic, space group *P* $\bar{1}$, *R* = 0.054 for 3531 reflections with *I* ≥ 2.5σ(*I*). In the *cis* isomer, a water molecule is encapsulated in the cavity formed by the two macrocyclic moieties facing each other. The *trans* isomer, which crystallizes with two dichloromethane molecules, lies on a crystallographic center of symmetry. The macrocyclic intermediate precursor **4** is characterized together with the bis(crown) derivative **5**. The trivalent parent compounds are extremely sensitive to moisture. The macrocycle **8** containing a P(O)H fragment is a degradation product.

Numerous macrocyclic compounds have been designed and prepared for complexation of metal ions and neutral guests, and interest in macrocyclic polyhetero ligand systems continues unabated. The search for new macrocyclic hosts with higher specificities toward binding of ionic and neutral species is particularly attractive and exemplified by the recently reported preorganized structures of spherands,¹ cavitands,² calixarenes,³ and cryptophanes.⁴ Thus far, the majority of such systems contains the crown ether structure with oxygen, nitrogen, or sulfur atoms as binding subunits, although some phosphorus-containing ligands have also been reported and are being actively studied. Polyphosphamacrocycles have received considerable attention as potential ligands only in recent years, and interest in their synthesis and complexing properties is growing very rapidly.⁵ Besides the macrocyclic phosphanes, macrocyclic compounds containing phosphorus atoms directly bonded to oxygen, sulfur, or nitrogen atoms have been reported.^{6,7}

Our studies in this area are focused on the design of phosphorus macrocycles that involve aminophosphine groups with connectivities to crown ether like structure.⁷ This choice is considered attractive for the following reasons: (1) di- and triaminophosphine provide an efficient building block for the preparation of phosphorus macrocycles with a well-defined structure around the

phosphorus atoms; (2) aminophosphines and phosphoramides are potentially powerful ligands and can considerably enhance the

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