

$O = P(i\text{-PrNCH}_2\text{CH}_2)_3\text{NCH}_3^+$: Novel Effect of Quaternization on the Structural Metrics of the Bicyclic Cage

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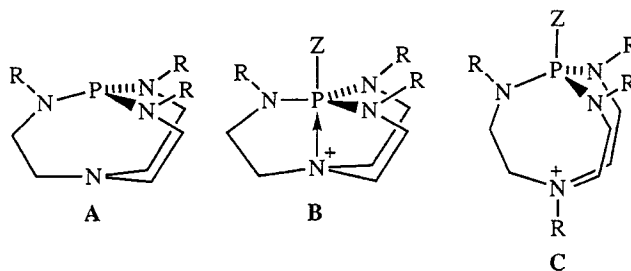
Received 10 August 1998; revised 20 October 1998

ABSTRACT: The title cation features the longest distance between the bridgehead atoms (3.56 Å) so far recorded for phosphatrane cages despite a nontetrahedral $CN_{\text{bridgehead}}C$ angle ($\sim 114^\circ$). The $70.8^\circ N_{\text{bridgehead}}CCN$ torsion angles in the bridging moieties produce a substantial twist along the C_3 axis of the cage that does not easily allow racemization of the cage. The resulting rigidity of the twisted cage gives rise to AB patterns for the methylene protons of this cation and its analogues. © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10:255–258, 1999

INTRODUCTION

Cage structures of type A (proazaphosphatranes) have been the subject of intense study in our laboratories in recent years because of their unusual phosphorus basicity, their remarkable catalytic activity in a variety of synthetically useful reactions, and the architectural diversity they display in the presence of electron-pair acceptors. Compounds of type A possess $P-N_{\text{ax}}$ distances (3.29 Å, $R = i\text{-Pr}$ [1]; 3.36 Å, $R = \text{SiMe}_3$ [2]) that are 2% to approximately 0% shorter than the sum of the $P-N_{\text{ax}}$ van der Waals

radii (3.35 Å [3]) and axial nitrogens with virtually trigonal planar geometries attributable to steric rather than electronic reasons (see later). Proazaphosphatranes of type A fully transannulate to structures of type B (azaphosphatranes) with $P-N_{\text{ax}}$ bond lengths that are $40 \pm 2\%$ shorter than the sum of the $P-N$ van der Waals radii when $Z = \text{H}^+$ [2.0778(4) Å, $R = \text{H}$ [4]; 1.967(8) Å, $R = \text{Me}$ [5]; 1.964(2) Å, $R = i\text{-Pr}$ [1]] or Cl^+ [1.937(8) Å, $R = \text{Me}$ [6]]. Increasingly longer $P-N_{\text{ax}}$ distances are observed in B ($R = \text{Me}$) in the order $Z = \text{H}^+ < \text{MeSC}(\text{NPh})^+ < \text{HPhN}^+ < \text{MeS}(\text{S})\text{C}^+ \cong \text{Me}^+ < \text{S}_2\text{C} < 1/2\text{Cl}_2\text{Hg} \cong \text{O} < \text{S} < \text{cis-Br}(\text{OC})_4\text{Re}$ until at $Z = 1/2\text{trans-Cl}_2\text{Pt}$ a maximum of 3.33 Å is reached [7], which closely matches the van der Waals radii sum.



The exceedingly strong Lewis basicity of nonionic bases of type A [pK_a of B ($R = \text{Me}$) $\cong 41$ in CH_3CN] [8] has been utilized by our group to improve substantially the synthesis of pyrroles [9], oxazoles [9], porphyrins [9], α -C-acylaminoacids [9], a chiral fluorescing agent [10], alkenes via dehydrohalogena-

Dedicated to Bob Holmes on the occasion of his seventieth birthday.

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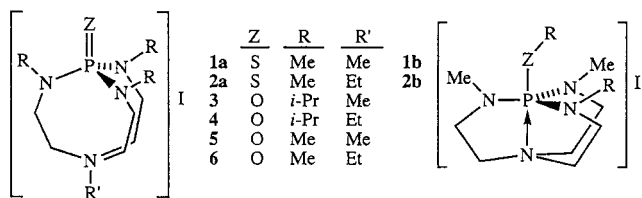
Contract Grant Sponsors: Petroleum Research Fund administered by the American Chemical Society

Contract Grant Sponsor: Ames Laboratory of the DOE

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tion reactions [11], and alkylated products of active methylene substrates [12]. It has been used by others for the improved synthesis of isoindoles from nitroaromatics [13] and as a thermal stabilizer for di-nitramide salts used as propellant oxidizers [14]. The flexibility of the transannular distance in **A** has been shown by us to play a crucial role in its ability when $R = \text{Me}$ to act as a superior catalyst for the protective silylation of alcohols [15], the synthesis of isocyanurates from isocyanates [15], the synthesis of α,β -unsaturated nitriles [17], and also as a very efficient promotor of alcohol acylation by anhydrides [18]. Others have discovered that **A** is a useful catalyst for anionic ring-opening polymerization of lactams to nylons [19]. The question of when bond formation occurs as the transannulation distance decreases has also been addressed [20].

Only where $Z = \text{O}$ or S have species of type **C** been found, though none have been subjected to structural analysis by X-ray means until now. Compounds **1a** and **2a** were reported earlier by us to form as a mixture with their regioisomers **1b** and **2b**, respectively, when the corresponding alkyl iodide was added to the parent proazaphosphatrane wherein $Z = \text{S}$ [21]. The upfield ^{31}P chemical shifts of **1b** and **2b** suggested that transannulation is present in these compounds. When analogous reactions were carried out for the corresponding unquaternized parents ($R = \text{Me}$ or $i\text{-Pr}$) wherein $Z = \text{O}$, only one regioisomer was obtained in each case, namely, **3–6** according to NMR spectroscopic analysis [6]. Here we report on the structural metrics for **3** that we were able to obtain recently by means of an X-ray diffraction study.

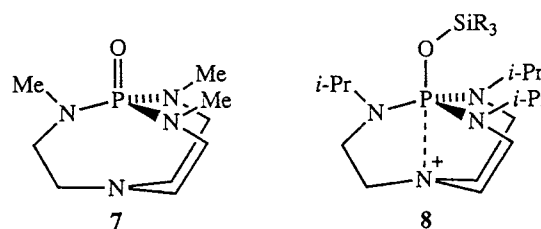


RESULTS AND DISCUSSION

Although quaternization of N_{ax} in forming **3** was expected to produce an elongation of the cage, it was not clear at the outset whether a bridgehead nitrogen in a bicyclic molecule of this type could assume at least a nearly tetrahedral geometry. Thus, the virtually planar geometry of N_{ax} in **A** is attributable to van der Waals repulsions among the hydrogens on the methylene groups adjacent to the N_{ax} [1,22], and such repulsions would presumably be intensified by downward pyramidalization of N_{ax} upon attack of an electrophile. Indeed, the $\text{CN}_{\text{ax}}\text{C}$ angle of **3** [avg

$113.9(10)^\circ$], whose structure is shown in Figure 1, is substantially greater than the tetrahedral angle. Although this result is consistent with augmentation of the aforementioned van der Waals repulsions, other more subtle strain-inducing geometry changes may also be occurring.

It is interesting to observe that the $\text{P}-N_{\text{ax}}$ distance in **3** (3.56 \AA) is 6% longer than the van der Waals sum and that this $\text{P}-N_{\text{ax}}$ distance constitutes a record axial elongation for phosphatrane cages. This elongation over the P, N van der Waals radii sum contrasts the 2.7% shortening of this distance [$3.564(7) \text{ \AA}$] over the Si, N van der Waals sum in the recently reported structure of $\{\text{trans}-(\text{PPh}_3)_2\text{Os}(\text{O})\text{Cl}[\text{Si}(\text{OCH}_2\text{CH}_2)_3\text{NMe}]\}\text{CF}_3\text{SO}_3$ [23]. However, the $\text{CN}_{\text{ax}}\text{C}$ angle in this complex (avg. 113.90 [23]) is essentially the same as in **3**, and this is probably so for the same reasons as it is in the $[\text{HC}(\text{CH}_2\text{CH}_2)_3\text{NH}]^+$ cation, wherein this angle has an average of 115.5° and the $\text{CC}_{\text{bridgehead}}\text{C}$ angle averages 113.9° [25].



Comparison of the structure determined for a parent analogue of **3**, namely, **7**, reveals that the NPN angle of **3** [avg. $106.2(5)^\circ$] is within experimental error of that of **7** [avg. $107.6(1)^\circ$ [24]], whereas the $\text{CN}_{\text{ax}}\text{C}$ angle decreases by *ca.* 6° upon quaternization of N_{ax} .

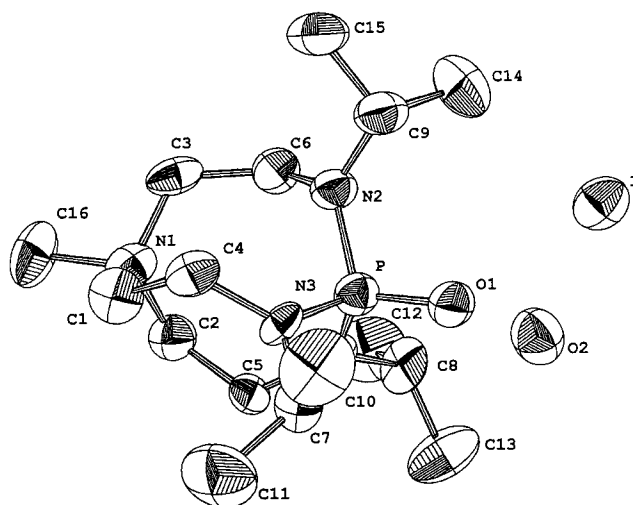


FIGURE 1 ORTEP view of **3**. Ellipsoids are drawn at the 50% probability level.

The $CN_{ax}C$ angle decrease from **7** to **3** causes a concomitant enlargement of the $N_{eq}CC$ angle by *ca.* 3° , while the CCN_{ax} angle remains constant within experimental error [i.e., $3x(esd)$]. The decrease of *ca.* 3° seen in the internal $PN_{eq}C$ angle from **7** to **3** may be associated with the presence of the more bulky *i*-Pr group on N_{eq} in the latter. A major consequence of the $CN_{ax}C$ angle decrease in **3** is the induction of a twist of the cage (avg. $N_{ax}CCN_{eq}$ torsion angle = 70.8°) that is larger than that in **7** (avg. 58.2°). The inflexibility, with respect to a racemizing twisting motion along the C_3 axis, that results from these torsional angles of the bridges of **3–6**, gives rise to the appearance of AB patterns for the bridging-methylene protons in the 1H NMR spectra of these compounds [6]. These rigid structures are quite robust, and in the case of **3**, the AB pattern persists up to $80^\circ C$. Moreover, in the 1H NMR spectrum of **3**, two sets of $CH(CH_3)_2$ protons are observed. We also observed that $O=P(i\text{-Pr}NCH_2CH_2)_3N$, the unquaternized parent of **3** is a good catalyst for the protective silylation of alcohols [26]. By contrast, its quaternized analogue **3** displays no detectable catalytic properties in such reactions. Because the positive charge in **3** is localized at the opposite end of the cage from the active silylation site, which is the phosphoryl oxygen, we tentatively conclude that the catalytic activity of the unquaternized parent is at least in part associated with a flexibility of the cage that permits some degree of transannulation in the silylated intermediate **8**.

EXPERIMENTAL

Compound **3**, prepared according to our method reported earlier [6], was recrystallized from a CH_3CN solution at room temperature by allowing ether vapor to diffuse into it. After 48 hours, crystals suitable for X-ray diffraction were obtained.

A crystal of approximate dimensions $0.2 \times 0.2 \times 0.2$ mm was arbitrarily oriented on a glass fiber. Data were collected on a Siemens P4 computer-controlled diffractometer with $MoK\alpha$ radiation (0.71073 \AA). Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using 38 setting angles. The data were collected at room temperature using a variable omega scan. Three representative reflections were measured for every 100 reflections collected to check the stability of the crystal. No significant decay was observed. Due to the rapid loss of intensities as 2θ was increased, reflections were collected only to $2\theta = 45^\circ$. Lorentz polarization corrections were applied to the data, but no absorption correction was applied be-

TABLE 1 Crystallographic Data for **3**

| | |
|--|------------------------|
| Formula | $C_{16}H_{38}IN_4O_2P$ |
| F.W. | 476.37 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| <i>a</i> (Å) | 9.243(4) |
| <i>b</i> (Å) | 15.230(4) |
| <i>c</i> (Å) | 16.332(8) |
| β ($^\circ$) | 93.93(4) |
| Z | 4 |
| <i>F</i> (000) | 984 |
| $D_{\text{calcd.}}$ (g/cm^{-3}) | 1.380 |
| μ ($MoK\alpha$) (cm^{-1}) | 14.81 |
| Scan mode | ω |
| θ -range ($^\circ$) | 3–22.5 |
| Octants of reciprocal space explored | $+h, +/- k, +/- l$ |
| Measured reflections | 4838 |
| Unique refl. with $I > 3\sigma(I)$ | 941 |
| Final <i>R</i> and <i>R_w</i> indices ^a | 0.387, 0.1589 |
| No. of variables | 217 |
| GOF ^b | 0.840 |

$$^a R = [\sum(F_o - |F_c|)/\sum F_o], R_w = [\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2}.$$

$$^b \text{GOF} = [\sum w(F_o - |F_c|)^2/(N_{\text{observations}} - N_{\text{variables}})]^{1/2}.$$

cause of the small value of μ . The structure was solved by a combination of heavy atom methods and direct methods and was refined using SHELXL-93. All nonhydrogen atoms were refined anisotropically.

Scattering factors were taken from Cromer and Waber [27]. All calculations were performed on a PC with a Pentium processor. Details of the data collection and refinement of this structure are reported in Table 1. Atomic coordinates, displacement parameters, bond lengths, and angles for the structure have been deposited at the Cambridge Crystallographic Data Centre.

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