In conclusion, the palladium-catalyzed carbonylation of azirines to fused β-lactams is a mild process of genuine novelty. β-Lactams are an important class of antibiotics, and there has been great interest in recent years in the synthesis of hetero (e.g., aza,[20] oxa[21]) as well as carbon (e.g., thienamycin)[22] analogues of penicillin. We are actively investigating the application of the above described reaction to the synthesis of appropriately functionalized aza analogues of penicillin.

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Cyclen Phosphonium and Homologous Cations. Dimerization in Strained PN_4^+ Systems

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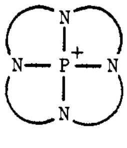
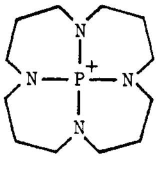
We wish to report the synthesis of the series of polycyclic tetrakis(substituted-amino)phosphonium ions (**1**) and the evidence that aminophosphonium ions can dimerize if the phosphorus is constrained from a tetrahedral geometry.[1]



1



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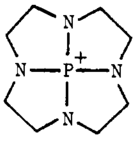
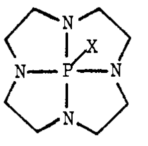


3

(Curved lines in **1** and **10** represent ethylene and/or trimethylene bridges.)

Models indicate that the four trimethylene bridges of **2** can easily accommodate a tetrahedral phosphonium center. However, the phosphorus in cyclen phosphonium ion (**3**) is constrained to a distorted tetrahedral geometry.[2]

We have found that cyclen phosphorane (**4**) is oxidized by carbon tetrachloride producing chloroform and a hygroscopic crystalline solid. The mass spectrum of this solid at high temperature exhibits the molecular ions of cyclen chlorophosphorane (**5**). The analogous reaction of **4** with trifluoromethyl iodide produces a crystalline iodide that analyzes correctly for **6**.

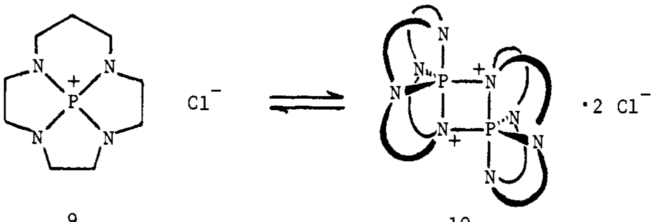


4, X = H
5, X = Cl
6, X = I
7, X = F

Other physical and spectroscopic properties of these solids are not consistent with covalent structures **5** and **6** but rather suggest ionic structures. Unlike the fluoro derivative **7**, which is known to be covalent,[2a] the chloro and iodo derivatives are insoluble in nonpolar solvents, nonvolatile, and high melting (>200 °C). The iodo compound in nitromethane has a conductance similar to that of tetrakis(dimethylamino)phosphonium iodide, $(Me_2N)_4P^+I^-$ (**8**).[3] However, the ^{31}P NMR spectra of these nitromethane solutions are very different: both **5** and **6** show unusually high-field singlets at −9.6 ppm, while **8** appears as a singlet at +43.3 ppm.[4]

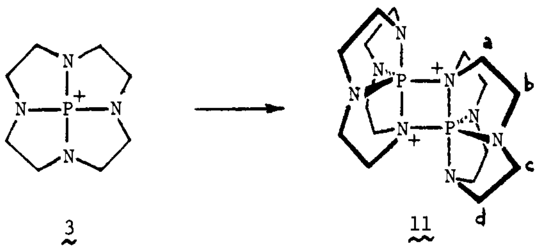
We originally assigned structure **3** to the common cation of the chloride and iodide salts. However, when we prepared the homologous series of cations represented by structure **1**,[5] we found that the chemical shift of the ion to which we had assigned structure **3** does not fit the trends in ^{31}P shifts for this series. Cation **2** shows a singlet at +15 ppm and the lower homologues of **2** exhibit singlets *at progressively lower* field. In dilute solution in $CDCl_3$ homocyclen phosphonium chloride (**9**) appears at +65 ppm.[6]

In addition to this low-field singlet (+65 ppm) more concentrated solutions of **9** also exhibit four higher field ^{31}P NMR signals from −23 to −30 ppm. We attribute these high-field signals to structures **10** which are formed by dimerization of **9**.[7]



9 **10**

Cyclen phosphonium ion (**3**) is expected to be more strained than **9** and the phosphonium center in **3** should show even greater tendency to dimerize.[1] On the basis of this comparison, it is reasonable that the singlet at −9.6 ppm originally assigned to cyclen phosphonium ion (**3**) actually arises from the dimeric cation (**11**). The ^{31}P shift of this cation is downfield from that for **10** by about the same difference in shift as that affected by a ring contraction in the monomeric cations (**1**).



3 **11**

The ^{13}C NMR spectrum of cation **11** supports the symmetry of this cation. Four singlets are observed in the decoupled spectrum.[8] One of these four signals is broadened considerably more than the other three, as is expected for carbon a with two unresolved $^2J_{PC}$ couplings rather than one.

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(1) For analogous dimerizations in strained tris(substituted-amino)boranes, see: Richman, J. E.; Yang, N.-C.; Andersen, L. L. *J. Am. Chem. Soc.* **1980**, *102*, 5790.

(2) The X-ray structures of two pentavalent derivatives of **3**, dicyclenphosphorane and **7**, suggest that the geometry of PN_4^+ in **3** will be constrained to resemble that of SF_4. (a) Richman, J. E. *Tetrahedron Lett.* **1977**, *559*. (b) Richman, J. E.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 3955.

(3) The specific conductivities at 25 °C of 0.01 M solutions (based on monomeric structures) in nitromethene for **6** and **8** are 7.3 and 9.7 S/cm (× 10^5).

(4) Phosphorus and carbon chemical shifts are reported with positive values downfield from external 85% H_3PO_4 and Me_4Si.

(5) Oxidation of the homologues of **4** (Atkins, T. J.; Richman, J. E. *Tetrahedron Lett.* **1978**, 5149) with carbon tetrachloride in each case gives the phosphonium chloride salt with acceptable C, H, N analyses in good yield. Unpublished results (T. J. Atkins, DuPont) indicate that **2**-Cl can also be prepared by oxidation with *tert*-butyl hypochlorite.

(6) The phosphonium salt with a periphery of 15 atoms appears at +25.4 ppm, while the symmetrical and unsymmetrical salts with peripheries of 14 atoms appear at +31.4 and +43.2 ppm.

(7) The six isomers of **10** differ in location of the unique trimethylene bridges. Only four signals are expected for these six compounds because two of the isomers have chemically nonequivalent (broadened) phosphorus atoms.

(8) The four ^{13}C signals (in $CDCl_3$) are at −23.1, −26.4, −26.9, and −29.6 ppm.

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We believe that our data are uniquely consistent with the existence of the dimeric tetrakis(substituted-amino)phosphonium ions **10** and **11**. These dimeric cations are analogous to neutral dimeric tris(amino)boranes.[1] We attribute the dimerization in these phosphorus compounds to the same phenomenon as in the boron compounds—bond angle strain. The driving force for a distorted aminophosphonium ion to dimerize apparently is sufficient to overcome the repulsions of two cations forming a four-membered dicationic ring.

Chemiluminescence of Dioxetanone Investigated by Self-Consistent-Field Theory

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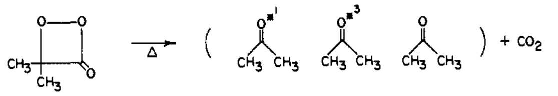
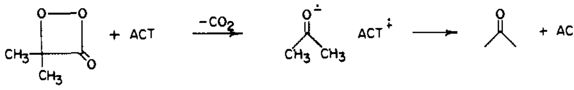
The unusual facility of the four-membered ring peroxides to generate electronically excited states by thermolysis has focused attention on their chemical behavior.[1] In recent reports we have described our findings on the chemical behavior of dimethyldioxetanone (**1**).[2-5] In particular we find that thermolysis of dioxetanone **1** in any one of a number of nonpolar solvents at 30 °C gives both excited singlet and triplet acetone in yields of 0.1% and 1.5% respectively (eq 1).[3] Also, we find that dioxetanone



(1)



(2)

1 is subject to catalytic decomposition by electron donors (activators, ACT) and excited-state generation by the path we have designated chemically initiated electron-exchange luminescence (CIEEL)[4,6] (eq 2).

Tetramethyldioxetane (**2**) also generates electronically excited acetone upon thermolysis.[7] However, in contrast to dioxetanone **1**, it does not react readily with electron donors, and the yield of excited acetone from **2** is nearly 20 times greater than from **1** despite the fact that the dioxetanone rearrangement is more exothermic by ca. 20 kcal/mol.[8] Herein we report the results of theoretical calculations on the parent unsubstituted dioxetanone. These calculations offer considerable insight into the structure and reactivity of this molecule and provide a basis for understanding the different properties of peroxides **1** and **2**.

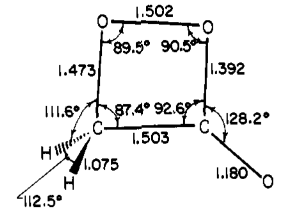


Figure 1. Optimized equilibrium structure of dioxetanone (bond distances are in ångstroms).

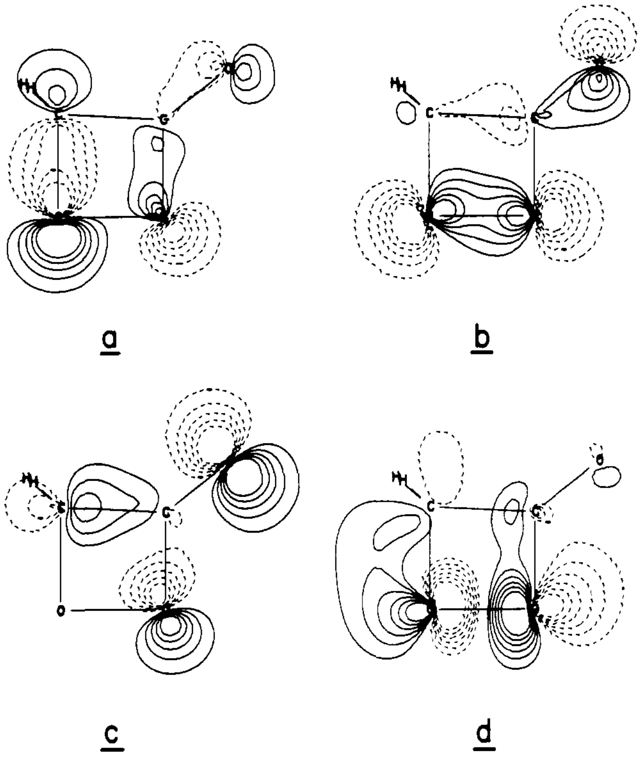


Figure 2. Molecular orbital contour plots[11] of the occupied or internal orbitals (a) 13a′, (b) 14a′, and (c) 15a′ and the virtual or external orbital (d) 16a′.

SCF calculations were performed on dioxetanone using a 4-31G basis set[9] of contracted Gaussian functions. The equilibrium structure, shown in Figure 1, was determined by using the gradient procedure of Pulay[10] and point-by-point searches. The energetics of stretching the oxygen–oxygen bond were investigated by fixing its length and then reoptimizing the two C–O–O ring angles, constraining the ring to be planar in these calculations. The effect of increasing the oxygen–oxygen bond length on the energy of the molecule and some orbital energies at these distorted structures are given in Table I. Plots of selected orbitals are given in Figure 2.[11] SCF energies of the $^2A'$ anion state, formed by adding an electron to the 16a′ orbital, were calculated at these optimized structures and are shown in Table I.

The equilibrium ground-state structure of dioxetanone that is predicted by these calculations has two noteworthy aspects. The oxygen–oxygen bond length is somewhat longer than that determined by X-ray crystallography for adamantylideneadamantane-1,2-dioxetane (**3**) by Wynberg and co-workers.[12] However, the most surprising feature of the predicted structure of dioxetanone is that the atoms of the four-membered ring are found to be essentially coplanar. This finding is in contrast to the structure of dioxetane **3** in which one oxygen atom of the

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