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The Electronic Structure of the Tris(diaminophosphanyl)carbenium Ion. A Quantum Chemical Investigation

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In contrast to the triaminomethyl carbenium ion which adopts a planar structure, a diaminophosphanyl substituent attached at the electron-deficient carbenium center introduces anionic character. As a consequence the tris(diaminophosphanyl)carbenium ion possesses an unusual equilibrium structure with three different PC bond lengths. The bonding situation is rationalized in the framework of contributing donor−acceptor structures to the overall bonding. A similar bonding situation is obtained for the phosphanyl substituent attached to an electron-deficient center.

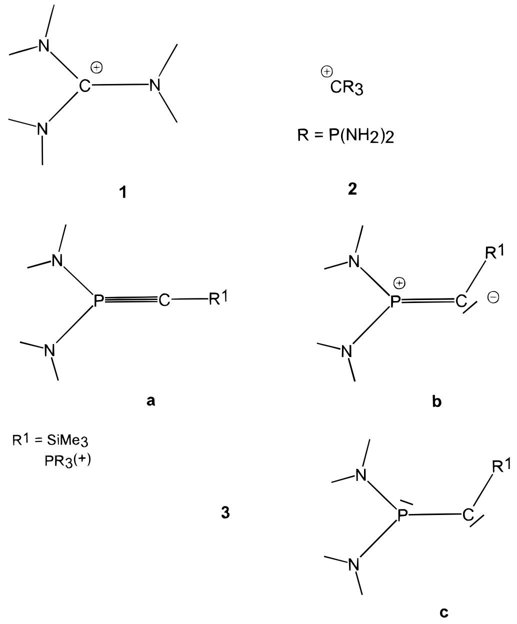
Introduction

The triaminomethyl cation, **1**, is one of the archetypal carbenium ions in organic chemistry.[1] It adopts a planar conformation (D_{3h} symmetry), and the NC bonds are shortened (1.323 Å) as compared with corresponding single bonds (1.47 Å).[2] This indicates a strong mesomeric interaction of the lone pairs at the nitrogens with the vacant p-orbital at the electron-deficient carbon atom (Chart 1).

In comparison with experimental as well as quantum chemical investigations on its valence isoelectronic congener, the triphosphanyl carbenium ion, **2**, is completely lacking. This fact prompted us to investigate the electronic structure of the latter species. We will evaluate the role of a phosphanyl- and a diaminophosphanyl substituent on the electronic structure of a carbenium ion.

The particular role of the diaminophosphanyl substituent has been explored in the pioneering work of Bertrand and coworkers on their studies on nitrenes.[3] Well-known is the recent characterization of a phosphaacetylene, **3** (R^1 = $SiMe_3$,[4] $PR_3^{(+)}$[5]). It possesses an unusual short PC bond, indicating the predominance of a phosphorus−carbon multiple-bond structure **3a** or **3b** over a carbenic structure, **3c**. This is in accord with the results of quantum chemical calculation.[5−7] They favor the canonical structure **3a** over **3b** with increasing π-acceptor ability of the substituent R^1 (SiH_3 versus H).[7] Although the phosphaacetylenes[5,6] **3** (R = $SiMe_3$, $PR_3^{(+)}$) are stable entities, diphosphinocarbenes have been reported[8] which are unstable toward further rearrangement.

Chart 1



In the present quantum chemical study we will show that **2** (R = $P(NH_2)_2$), which is formally described as a carbenium ion, bears anionic character at the central carbon atom. In other words, the substituents R shift a surplus of electron density to the central atom, inducing anionic character at the central carbon atom. Hence, the bonding situation is rather different in comparison with the triaminomethyl carbenium cation, **1**. The calculations indicate that the trend of the diaminophosphanyl substituent is pronounced to a lesser extent for the phosphanyl substituent at an electron-deficient carbon center.

An energy optimization[9] of **2** (R = $P(NH_2)_2$) at the MP2-(fc)/6-31g* level results in an unusual equilibrium geometry

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(1) Sundaralingam, M.; Chwang, A. K. in *Carbenium Ions*, Olah, G. A. and Schleyer, P.v. R.; Eds., Wiley: New York, 1976; Vol. 5, p 2427.

(2) Estimated by the Schomaker relationship, see: Huheey, J. E. *Inorganic Chemistry*; Harper International, New York, 1983.

(3) *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., and Scherer, O., Eds.; Thieme: Stuttgart, 1990. This reference contains a detailed summary of the research in low-coordinated phosphorus chemistry up to 1990. (b) See also: Markovskii, L. N.; Romanenko, V. D.; Ruban, A. V. *The Chemistry of Acyclic Twofold Coordinated Phosphorus Compounds*; Kiev, 1988 (in Russian).

(4) Igau, A.; Grützmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc*. **1988**, *110*, 6463.

(5) Soleihavoup, M.; Baceiredo, A.; Treutler, O.; Ahlrichs, R.; Nieger, M.; Bertrand, G. *J. Am. Chem. Soc.* **1992**, *114*, 10959.

(6) Treutler, O.; Ahlrichs, R.; Soleilhavoup, M. *J. Am. Chem. Soc*. **1993**, *115*, 8788.

(7) Dixon, D. A.; Dobbs, K. D.; Arduengo, A. J., III; Bertrand, G. *J. Am. Chem. Soc*. **1991**, *113*, 8782.

(8) Baceiredo, A.; Igau, A.; Bertrand, G.; Menu, M. J.; Dartiguenave, Y.; Bonnet, J. J. *J. Am. Chem. Soc*. **1986**, *108*, 7868.

S0020-1669(97)00152-3 CCC: $15.00

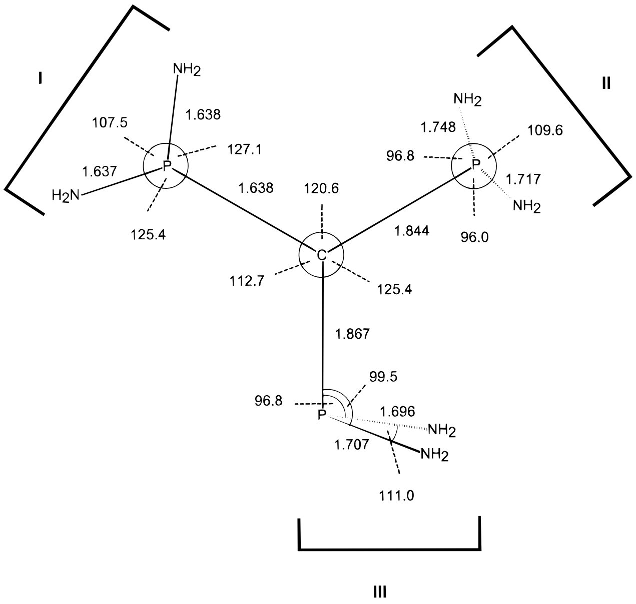

Figure 1. Equilibrium bonding parameters (bond lengths in Å, bond angles in degrees) of the triphosphanyl carbenium cation, at the MP2-(fc)/6-31g* level of optimization.

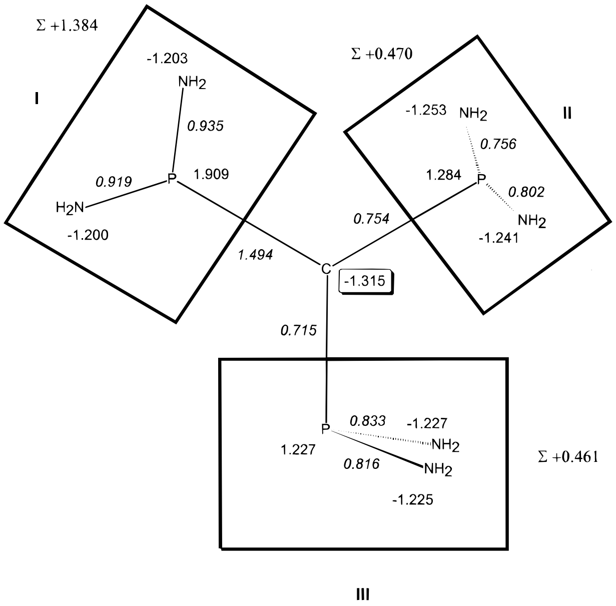

Figure 2. Natural charges of the triphosphanyl carbenium cation and Wiberg bond indices (in italics).

(Figure 1). No symmetry restrictions were imposed in the optimization of the singlet structure.

All PC bonds have different lengths (bond lengths are in Å, bond angles in degrees). One short (1.638 Å, phosphanyl unit I) and two long (1.844 and 1.867 Å, phosphanyl units II and III, respectively) PC bonds are obtained. Simultaneously these phosphanyl substituents (II and III) are strongly pyramidalized at the phosphorus atoms. The phosphanyl unit I has an angle sum around the phosphorus atom of 360° and the phosphanyl substituents II and III, 302.4 and 307.2°, respectively. The corresponding PN bonds are also elongated (1.696 to 1.748 Å) compared to the PN bonds (1.637, 1.638 Å) at the (trigonal) planar phosphanyl substituent I. The central carbon atom is almost planar (∑ bond angles = 358.7°).

Table 1. Various Structures of the Triphosphanyl Carbenium Ion

symmetry	CP (Å)	$E_{\mathrm{rel}}{}^{a}$ (kcal/mol)	ν^{b}(cm^{-1})
D_{3h}	1.734	0.0	i872; i872; i368
C_{3v}	1.785	−50.2	i100
C_3	1.785	−50.2	i124
C_1	1.783; 1.783; 1.760	−52.1	20

[a] MP2(fc)/6-31g* + zero-point vibrational energy correction (at the same level). [b] Energy lowest vibrations.

A better insight into the bonding situation is presented by the population analysis of the electron density (at the MP2/6-31g* level), based on the natural bond orbital analysis.[10]

The central carbon atom possesses a surplus of negative charge (−1.32 e) while all the surrounding phosphorus atoms are positively charged. However, there is a difference between the planar phosphanyl substituent (I) compared to the (at phosphorus) strongly pyramidalized substituents (II, III). Formally one can assign a charge to each $P(NH_2)_2$ substituent, here denoted as ∑. The phosphanyl unit I bears an overall strong positive charge (∑ +1.38 e) while II and III are much less positively charged (∑ +0.40, +0.47 e). It is also of interest to inspect the Wiberg bond indices (values in italics). The P(I)C bond is stronger (1.494) than a single bond while the bond indices P(II)C and P(III)C reveal bond strengths (0.715, 0.754) weaker than that of a single bond. In other words, the diaminophosphanyl units with a strongly pyramidalized phosphorus are more weakly bound to the central carbon atom than to the diaminophosphanyl unit with the planar phosphorus atom which exerts double-bond character toward the central carbon atom.

The diaminophosphanyl substituent is rather complicated in an electronic sense, as it contains three lone pairs for possible interaction with the central electron-deficient carbon center. Consequently many different conformations are possible. To put our considerations on a more clear-cut basis we also investigated various structures of the parent triphosphanyl carbenium ion. In this case each phosphanyl substituent bears only one lone pair for possible interaction with the electron-deficient carbon center. Various symmetry restrictions were probed, and the results are recorded in Table 1.

The D_{3h} symmetrical structure appears at an energy maximum. Second-order Jahn−Teller interaction[11] leads preferably to a distortional mode which allows pyramidalization at the central carbon atom (C_{3v}, C_3 symmetry). The most stable conformer, however, adopts C_1 symmetry. Hence the substituent R = PH_2 as compared with R = $P(NH_2)_2$ exerts a similar bonding situation on the resulting equilibrium structure of the carbenium ion.

For completeness we also calculated the corresponding bis(diaminophosphanyl) carbene in the lowest energy singlet state,[12] utilizing the same computational level (MP2(fc)/6-31g*). In accordance with previous considerations[6] an asymmetrical bent carbene structure is obtained: PC = 1.582, 1.776 Å; ∠PCP =

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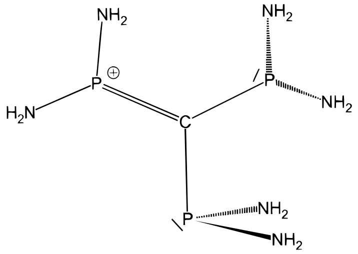
(9) All quantum chemical calculations were performed with the *Gaussian 94* set of program systems. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, R. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. W.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defree, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

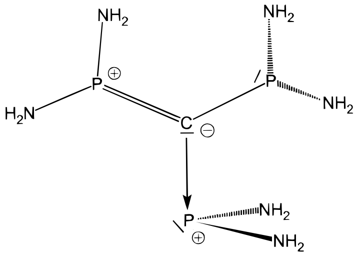
(10) Reed, A. F.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(11) (a) Pearson, R. G. *Symmetry Rules for Chemical Reactions*; Wiley: New York, 1976. (b) Schoeller, W. W.; Niemann, J. *J. Am. Chem. Soc.* **1986**, *108*, 22.

Chart 2



4a



4b

121.2°. At our given computational level we obtained a sharper ∠PCP bending angle as obtained previously.[6] As in **2** the phosphorus center with the short PC bond is almost in-plane with the PCP moiety while the phosphorus atom at the longer PC bond is strongly pyramidalized. Since the structure of the singlet state of the diphosphanyl carbene has already been discussed previously,[6] we will not comment further on it. In the essential bonding features (geometrical details, charge distributions) our findings agree with the previous results.[6]

Hence the addition of a third diaminophosphanyl substituent to the central carbon atom under the formation of a cationic structure causes an elongation of all PC bonds. In more detail, the structure may best be understood as a donor−acceptor adduct[13] of the diphosphanyl carbene with a diaminophosphenium cation, envisaged as shown in Chart 2.

The two canonical structures, **4a** and **4b**, participate in bonding. In **4a** the carbon atom is surrounded by three two-electron two-center bonds with the neighboring phosphanyl substituents. In more simple terms it forms three sp^2 hybrid orbitals. In addition, one phosphorus forms a double bond toward carbon. The canonical structure builds up one double bond and three single bonds surrounding the central carbon atom. However, it does not explain the creation of negative charge at the central carbon atom. This is a fact attributed to the canonical structure **4b**. One diphosphanyl carbene interacts weakly with a diaminophosphenium cationic unit. Negative charge is now assigned to the central carbon atom. The charge is further partly transmitted to the diaminophosphenium cation. Overall this results in an additional weak PC bond.

We note that this view of bonding in **4** with the participation of a limiting donor−acceptor bonded structure requires a strong singlet−triplet energy separation in the diaminophosphenium cation fragment. In particular in the case at hand, it is a singlet−singlet coupling of a diphosphanylcarbene with a diaminophosphenium cation, within the pioneering concept of Trinquier and Malrieu[14] on mutual fragment interactions. Quantum chemical calculations on a variety of different substituted $PX_2^{(+)}$ cations ($X = NH_2$, F, Cl, Br, I) reveal a sizable energy difference between lowest energy singlet and triplet states.[15] For the diaminophosphenium cation it is 65.5 kcal/mol.[15] On the basis of these considerations one expects that a triphosphanyl carbenium ion with anionic character at the central carbon atom is obtained for cases where the surrounding substituents R possess a strong singlet stability (as a corresponding cationic fragment).

One important question still remains, how stable is **2** toward fragmentation in a diphosphanyl carbene (singlet) and a diaminophosphenium unit? For this purpose we have analyzed the reaction 1.

$$C(P(NH_2)_2)_3^{(+)} \rightarrow C(P(NH_2)_2)_2 + P(NH_2)_2^{(+)} + \Delta E \quad (1)$$

At the given MP2(fc)/6-31g* level of optimization, ΔE is 69.4 kcal/mol. In other words, reaction 1 is strongly endothermic and **2** can be considered as a structure that is stable toward decomposition into a carbene and a phosphenium cation. On the basis of these quantum chemical calculations the existence of a triphosphanyl carbenium ion seems likely. However, its synthetic verification remains a challenge.

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(12) Although in phosphaacetylene the lowest energy singlet and triplet states are close in energy,[7] it is not clear which of both is the electronic ground state. For the discussion presented here, i.e., for comparison of the various structures, only the singlet state of the related bis(phosphanyl)carbene was explored.

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