# The First Nonclassical Distonic Ion

**Fabio C. Gozzo,[†] Luiz Alberto B. Moraes,[†] Marcos N. Eberlin,*,[†] and Kenneth K. Laali[‡]**

*Contribution from the Institute of Chemistry, State University of Campinas-UNICAMP, CP 6154,
13083-970 Campinas, SP Brazil, and Department of Chemistry, Kent State University, Kent, Ohio 44242*

*Received October 19, 1999*

**Abstract:** The gaseous and ionized prototype carbonyl ylide, the distonic ion $^{+}CH_2-O-CH_2^{\bullet}$, is found to transfer ionized methylene to 1-adamantylphosphaacetylene (1-Ad−C≡P), a kinetically stabilized phosphaalkyne, thus forming the 1-adamantylphosphaacetylenium P-methylide ion, 1-Ad−$C^{+}$=P−$CH_2^{\bullet}$, a novel phosphorus, and the first *nonclassical* distonic ion. The ion abstracts $CH_3S^{\bullet}$ from $CH_3SSCH_3$ and both $Br^{\bullet}$ and $C_3H_5^{\bullet}$ from allyl bromide, and this characteristic reactivity demonstrates its distonic character. MO calculations at the Becke3LYP/6-311G(d,p) and MCSCF [CAS(3,3)] levels confirm that 1-Ad−$C^{+}$=P−$CH_2^{\bullet}$ bears spatially separated charge and odd spin sites. They also reveal for the ion a phosphaallylic radical structure that stabilizes the radical site, and a $\sigma$-bridged structure with three-center two-electron bonds that stabilizes the charge site. This unique electronic structure characterizes 1-Ad−$C^{+}$=P−$CH_2^{\bullet}$ as the first *nonclassical* distonic ion.

## Introduction

Molecules exhibiting multiple bonding to phosphorus and its heavier congeners were, for a long time, considered to be nonexistent. Unsuccessful attempts to synthesize compounds with P=C and P≡C functionalities were rationalized by the double-bond rule[1] which, for thermodynamic arguments such as poor $p\pi-p\pi$ overlap and large interatomic distances, excluded P=C and P≡C organophosphorus molecules. But in recent years, a variety of phosphaalkenes ($RR^1C=PR^2$) and phosphaalkynes (R−C≡P) have been synthesized, and these compounds have made a rapid transition from elusive species to well-known and well-respected members of the family of low-coordination organophosphorus compounds with widespread synthetic use as versatile building blocks and synthons in organic, inorganic, and organometallic chemistry.[2]

Distonic ions,[3,4] chemically fascinating species with spatially or electronically isolated odd spin and charge sites, have also made a fast and recent transition from elusive species to well-recognized members of the family of gaseous and condensed-phase ions. Distonic ions also have been found to display a rich chemistry, both in solution and in the gas phase.[5]

The parent carbonyl ylide $H_2C=O^{+}-CH_2^{-}$ is so far unknown,[6] but in the gas phase, its ionized and distonic form $^{+}CH_2-O-CH_2^{\bullet}$ is stable and easily accessible; for instance, gaseous ionized ethylene oxide isomerizes rapidly by CC ring-opening to form the more stable $^{+}CH_2-O-CH_2^{\bullet}$ ion.[7] The intrinsic reactivity of $^{+}CH_2-O-CH_2^{\bullet}$ has been extensively investigated in the gas phase[8] and, as expected from its potential 1,3-coordination ability, $^{+}CH_2-O-CH_2^{\bullet}$ undergoes [3 + 2] 1,3-cycloaddition with ketones,[8j] α-diketones, and acyl chlorides.[8k] Net $CH^{+}$ and $CH_2^{+\bullet}$ transfers are, however, the most common reactions of $^{+}CH_2-O-CH_2^{\bullet}$; with nitriles, the $R-C\equiv N^{+}-CH_2^{\bullet}$ distonic ions are often formed to great extent. Since phosphaalkynes (R−C≡P) are formally phosphorus analogues of nitriles (R−C≡N), we anticipated that they could form novel

---

[†] State University of Campinas-UNICAMP.

[‡] Kent State University.

(1) For a discussion on the double-bond rule see: Schmidt, M. W.; Truong, P. N.; Gordon, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5217.

(2) (a) Weber, L. In *Advances in Organometallic Chemistry*; Academic Press: New York, 1997. (b) Appel, R.; Knoll, F. *Adv. Inorg. Chem.* **1989**, *33*, 259. (c) Regitz, M. *Chem. Rev.* **1990**, *90*, 191. (d) Nixon, J. F. *Chem. Rev.* **1998**, *88*, 1327. (e) For more recent reviews see also: *Carbocyclic and Heterocyclic Cage Compounds and Their Building Blocks: Synthesis, Structure, Mechanism and Theory*; Laali, K. K., Ed.; JAI Press Inc.: Stamford, CT, 1999.

(3) (a) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805. (b) Radom, L.; Bouma, W. J.; Nobes, R. H. *Pure Appl. Chem.* **1984**, *56*, 1831. (c) Yates, B. F.; Bouma, W. J.; Radom, L. *Tetrahedron* **1986**, *42*, 6225.

(4) For reviews on distonic ions see: (a) Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123. (b) Bouchoux, G. *Mass Spectrom. Rev.* **1988**, *7*, 203. (c) Stirk, K. M.; Kiminkinen, M. L. K.; Kenttämaa, H. I. *Chem. Rev.* **1992**, *92*, 1649.

(5) For a review on the formation and reactivity of distonic ions in condensed phase see ref 4a. For examples on the rich gas-phase chemistry of distonic ions see ref 4; for more recent examples see: (a) Yu, S. J.; Holliman, C. L.; Rempel, D. L.; Gross, M. L. *J. Am. Chem. Soc.* **1993**, *115*, 9676. (b) Wesdemiotis, C.; Polce, M. J. *Rapid Commun. Mass Spectrom.* **1996**, *10*, 235. (c) Thoen, K. K.; Smith, R. L.; Nousiainen, J. J.; Nelson, E. D.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1996**, *118*, 8669. (d) Flammang, R.; Gerbaux, P.; Nguyen, M. T.; Salpin, J.-Y.; Bouchoux, G. *J. Phys. Chem. A* **1998**, *102*, 861. (e) Chou, P. K.; Thoen, K. K.; Kenttämaa, H. I. *J. Org. Chem.* **1998**, *63*, 4470. (f) Moraes, L. A. B.; Eberlin, M. N. *J. Am. Chem. Soc.* **1998**, *120*, 11136. (g) Thissen, R.; Mourgues, P.; Audier, H. E. *Eur. Mass Spectrom.* **1998**, *4*, 79. (h) Moraes, L. A. B.; Eberlin, M. N. *J. Am. Soc. Mass Spectrom.* **2000**, *11*, 697.

(6) Doyle, M. P. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon Press: New York, 1995; Vol. 12, Chapter 5.2.

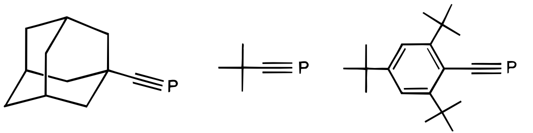
(7) (a) Corderman, R. R.; LeBreton, P. R.; Buttrill, S. E.; Williamson, A. D.; Beauchamp, J. L. *J. Chem. Phys.* **1976**, *65*, 4929. (b) van Velzen, P. N. T.; van der Hart, W. J. *Chem. Phys. Lett.* **1981**, *83*, 55. (c) Nobes, R. H.; Bouma, W. J.; MacLeod, J. K.; Radom, L. *Chem. Phys. Lett.* **1987**, *135*, 78 and references therein.

(8) (a) Blair, A. S.; Harrison, A. G. *Can J. Chem.* **1973**, *51*, 1645. (b) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1978**, 724. (c) Bouma, W. J.; MacLeod, J. K.; Radom, L. *Adv. Mass Spectrom.* **1979**, *8A*, 178. (d) Rusli, R. D.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 535. (e) de Koster, C. G.; van Houte, J. J.; van Thuijl, J. *Int. J. Mass Spectrom. Ion Proc.* **1995**, *141*, 1. (f) Yu, S. J.; Gross, M. L.; Fountain, K. R. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 117. (g) van Amsterdam, M. W.; Zappey, H.; Ingemann, S.; Nibbering, N. M. M. *Org. Mass Spectrom.* **1993**, *28*, 30. (h) Gozzo, F. C.; Eberlin, M. N. *J. Am. Soc. Mass Spectrom.* **1995**, *6*, 554. (i) Sorrilha, A. E. P. M.; Gozzo, F. C.; Pimpim, R. S.; Eberlin, M. N. *J. Am. Soc. Mass Spectrom.* **1996**, *7*, 1126. (j) Eberlin, M. N.; Sorrilha, A. E. P. M.; Gozzo, F. C.; Pimpim, R. S. *J. Am. Chem. Soc.* **1997**, *119*, 3550. (k) Gozzo, F. C.; Meurer, E.; Eberlin, M. N. Submitted for publication.

10.1021/ja993749m CCC: $19.00

phosphorus distonic ions of the R−C$^+$═P−CH$_2^•$ type via CH$_2^{+•}$ transfer from $^+$CH$_2$−O−CH$_2^•$.

Herein we report on the reactions of gaseous $^+$CH$_2$−O−CH$_2^•$ with three kinetically stabilized phosphaacetylenes, namely 1-adamantylphosphaacetylene (**1**), *tert*-butylphosphaacetylene (**2**), and the supermesityl phosphaacetylene (**3**). In reactions with **1**, the novel phosphorus distonic ion 1-Ad−C$^+$═P−CH$_2^•$ (**4**) was formed, and its distonic radical character was demonstrated via two structurally specific ion−molecule reactions.[9,10] The geometry and electronic distribution of the novel **4** was then evaluated by MO calculations at the Becke3LYP/6-311G(d,p) and MCSCF [CAS(3,3)] levels. Ion **4** is predicted to display a unique phosphaallylic radical electronic structure that stabilizes its radical site and a nonclassical σ-bridged structure with three-center two-electron bonds that stabilize its charge site. We therefore report on the gas-phase formation and characterization of the first *nonclassical* distonic ion.



**1** **2** **3**

## Methods

Double (MS$^2$) stage mass spectrometric experiments[11] were performed with an Extrel [Pittsburgh, PA] pentaquadrupole (QqQqQ) mass spectrometer described in detail elsewhere.[12] Reactions of the phosphaacetylenes with $^+$CH$_2$−O−CH$_2^•$ were performed via ethylene oxide chemical ionization (CI). For the MS$^2$ ion/molecule reactions, Q1 was used to mass select the ion of interest for further reactions with a neutral in q2. Ion translational energies were set to near 0 eV as calibrated by the *m*/*z* 39:41 ratio in neutral ethylene/ionized ethylene reactions.[13] Product ion mass spectra were acquired by scanning Q5, while operating Q3 in the broad band rf-only mode. Multiple collision conditions that caused typical beam attenuations of 50−70% were used in q2 to increase reaction yields and to promote collisional quenching of both the reactant and product ions.[11b]

For MS$^2$ collision-induced dissociation (CID), the Q1 mass-selected ion was subjected to collisions with argon in q2. A collision energy of 15 eV was used, as calculated by the voltage differences between the ion source and the collision quadrupoles. The indicated pressures in each differentially pumped region were typically $2 \times 10^{-6}$ (ion-source), $8 \times 10^{-6}$ (q2), and $8 \times 10^{-5}$ (q4) Torr, respectively.

Energies and optimized geometries of idealized conformations were obtained by DFT calculations[14] at the Becke3LYP/6-311G(d,p) level[15] using Gaussian98.[16] Single-point MCSCF [CAS(3,3)][17] calculations were also applied to the Becke3LYP/6-311G(d,p) optimized structure of **4**. Samples of **1**−**3** were available from other studies; details of their synthesis have been reported.[18]

## Results and Discussion

**MS and MS$^2$ Experiments. (a) Generation of 4.** Ethylene oxide isomerizes spontaneously and completely in the course of 70 eV electron ionization (EI) to form the distonic ion $^+$CH$_2$−O−CH$_2^•$;[7] hence ethylene oxide chemical ionization (CI) has been used extensively to perform reactions of $^+$CH$_2$−O−CH$_2^•$ with neutral reagents.[8e] Under ethylene oxide CI, the phosphaalkynes **1**−**3** form a set of products in variable abundances, mainly the protonated and ionized phosphaalkynes, their ionic fragments, and their ionic adducts with ethylene oxide. But the 1-adamantylphosphaacetylene **1** is unique since it forms an additional and medium intensity product ion of *m*/*z* 192 corresponding to the expected CH$_2^{+•}$ transfer reaction. It is likely, therefore, that the novel phosphorus distonic ion 1-Ad−C$^+$═P−CH$_2^•$ (**4**) was formed.

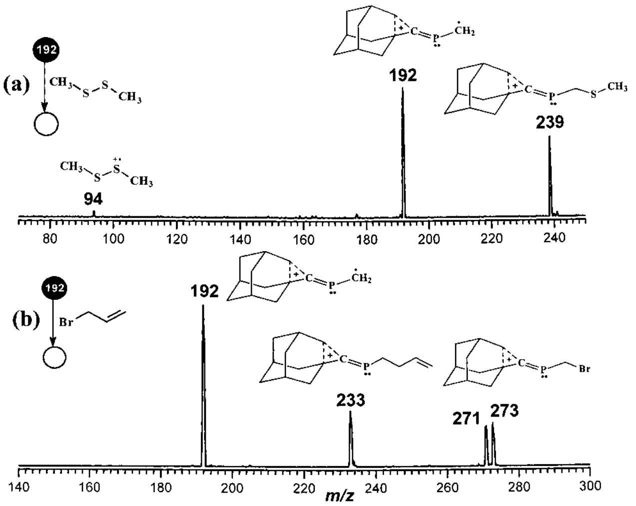


**Figure 1.** Double-stage (MS$^2$) product ion mass spectra for reactions of **4** with (a) dimethyl disulfide and (b) allyl bromide.

That the reaction forming the putative **4** involves neutral **1** and $^+$CH$_2$−O−CH$_2^•$, not ionized 1-Ad−C≡P (**1**$^{+•}$) and neutral ethylene oxide, was proved via an MS$^2$ experiment: **1**$^{+•}$, formed in the ion source by 70 eV EI, was mass-selected by Q1 and then reacted in q2 at near 0 eV energy with neutral ethylene oxide. No CH$_2^{+•}$ transfer product of *m*/*z* 192 was observed in the resulting product ion mass spectrum (not shown).

**(b) Free Radical Reactivity of 4.** Abstraction of CH$_3$S$^•$ (or CH$_3$Se$^•$) from CH$_3$SSCH$_3$ (or CH$_3$SeSeCH$_3$), the Kenttämaa reaction,[9] has been extensively used as an efficient, structurally diagnostic ion−molecule reaction for distonic radical cations: it characterizes ions displaying spatially[9] or electronically[5g] isolated radical sites. Iodine and bromine abstraction as well as C$_3$H$_5^•$ abstraction from the corresponding allyl halides have also been shown to serve as diagnostic reactions for distonic

---

(9) (a) Stirk, K. M.; Orlowski, J. C.; Leeck, D. T.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1992**, *114*, 8604. (b) Beasley, B. J.; Smith, R. L.; Kenttämaa, H. I. *J. Mass Spectrom.* **1995**, *30*, 384.

(10) Smith, R. L.; Thoen, K. K.; Stirk, K. M.; Kenttämaa, H. I. *Int. J. Mass Spectrom. Ion Processes* **1997**, *165*, 315.

(11) (a) Schwartz, J. C.; Wade, A. P.; Enke, C. G.; Cooks, R. G. *Anal. Chem.* **1990**, *62*, 1809. (b) Eberlin, M. N. *Mass Spectrom. Rev.* **1997**, *16*, 113.

(12) Juliano, V. F.; Gozzo, F. C.; Eberlin, M. N.; Kascheres, C.; Lago, C. L. *Anal. Chem.* **1996**, 68, 1328.

(13) Tiernan, T. O.; Futrell, J. H. *J. Phys. Chem.* **1968**, *72*, 3080.

(14) Gill, P. M. W.; Johnson, B. G.; Pople, J. A. *Chem. Phys. Lett.* **1992**, *197*, 499.

(15) (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(16) Gaussian 98, Revision A. 6., Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K. J. B.; Foresman, J.; Cioslowski, J. V.; Ortiz, B.; Stefanov, B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A., Gaussian, Inc.: Pittsburgh, PA, 1998.

(17) (a) Hegarty, D.; Robb, M. A. *Mol. Phys.* **1979**, *38*, 1795. (b) Eade, H. E.; Robb, M. A. *Chem. Phys. Lett.* **1981**, *83*, 362. (c) Yamamoto, N.; Vreven, T.; Robb, M. A.; Frisch, M. J.; Schlegel, H. B. *Chem. Phys. Lett.* **1996**, *250*, 373.

(18) (a) Rösh, W.; Allspach, T.; Bergstrasser, U.; Regitz, M. In *Synthetic Methods of Organometallic Chemistry*; Karsch, H. H., Ed.; Georg Thieme Verlag Stuttgart: New York, 1996; Vol. 3, pp 11−16. (b) Märkl, G.; Sejpka, H. *Tetrahedron Lett.* **1986**, *27*, 1771.

ions.[10] Therefore, to test the distonic character of the *m*/*z* 192 product ion, reactions with dimethyl disulfide and allyl bromide were performed.

As the resulting product ion mass spectrum shows (Figure 1a), **4** reacts scarcely with $CH_3SSCH_3$ by electron transfer (a reaction most characteristic of conventional radical cations)[9] to form $CH_3SSCH_3^{+\bullet}$ of *m*/*z* 94, but predominantly by $CH_3S^\bullet$ abstraction (eq 1) to form the product ion of *m*/*z* 239. In reactions with allyl bromide (Figure 1b), both the diagnostic bromine (*m*/*z* 271/273) and $C_3H_5^\bullet$ (*m*/*z* 233) abstraction products are formed (eqs 2 and 3). The distonic, charged radical character of the putative **4** is therefore evident.

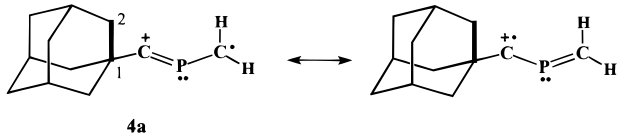
$$\underset{m/z\ 192}{\text{1-Ad}-C^+{=}P-CH_2^\bullet} + CH_3SSCH_3 \rightarrow \underset{m/z\ 239}{\text{1-Ad}-C^+{=}P-CH_2-SCH_3} + CH_3S^\bullet \quad (1)$$

$$\underset{m/z\ 192}{\text{1-Ad}-C^+{=}P-CH_2^\bullet} + CH_2{=}CH-CH_2-Br \rightarrow \underset{m/z\ 271/273}{\text{1-Ad}-C^+{=}P-CH_2-Br} + CH_2{=}CH-CH_2^\bullet \quad (2)$$

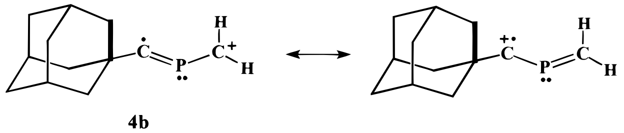
$$\underset{m/z\ 192}{\text{1-Ad}-C^+{=}P-CH_2^\bullet} + CH_2{=}CH-CH_2-Br \rightarrow \underset{m/z\ 233}{\text{1-Ad}-C^+{=}P-CH_2-CH_2-CH{=}CH_2} + Br^\bullet \quad (3)$$

**(c) Dissociation Behavior of 4.** The 15 eV collision-induced dissociation (CID) double-stage ($MS^2$) mass spectrum of **4** (not shown) indicates that the ion, under the relatively mild 15 eV energy collision conditions applied, is quite resistant to dissociation; it forms fragment ions of very low intensity, such as those of *m*/*z* 191 ($H^\bullet$ loss), 177 ($CH_3^\bullet$ loss), 164 ($C_2H_4$ loss), and 149 ($C_3H_7^\bullet$ loss).

**MO Calculations. (a) The Distonic, Phosphaallylic Radical Character of 4**. As depicted below, **4** can be represented by two electronic states: **4a** and **4b**. Both states should be stabilized by resonance since **4a** can be viewed as a phosphaallylic radical and **4b** as a phosphaallylic carbocation. For **4a**, therefore, the $CH_2$-orbital containing the lone electron is coplanar to those of the C=P double bond, and orthogonal to the empty C-orbital carrying the positive charge. For **4b**, the empty $CH_2$-orbital with the positive charge is coplanar to those of the C=P double bond, and orthogonal to the C-orbital carrying the lone electron.



**4a**



**4b**

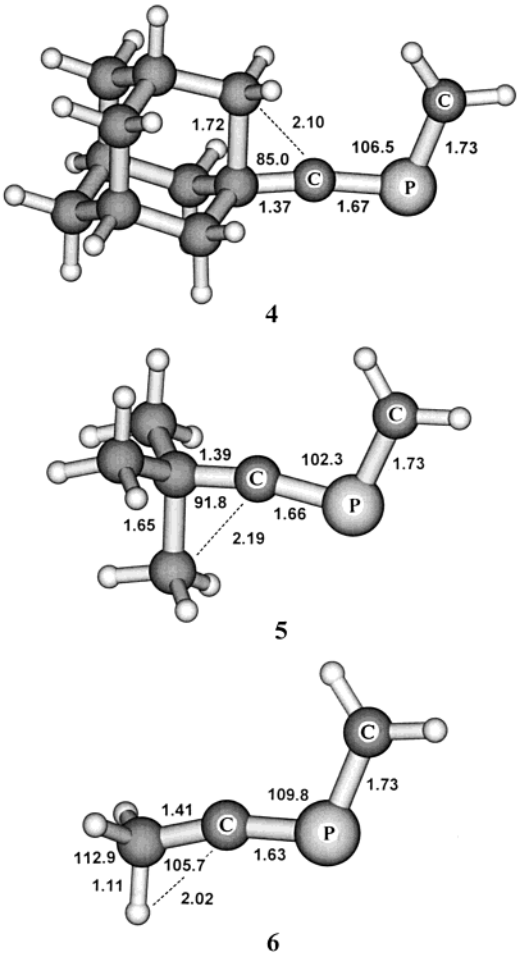


**Figure 2.** Becke3LYP/6-311G(d,p) fully optimized geometries of ions **4**, **5**, and **6**.

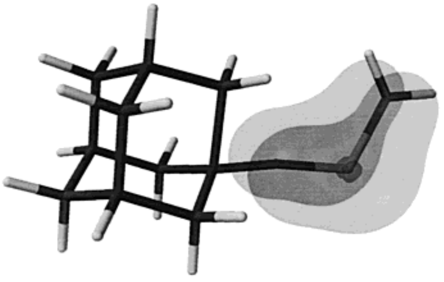
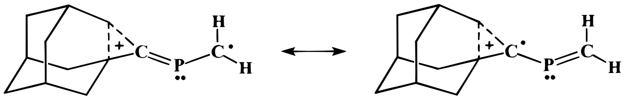


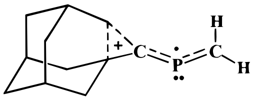
**Figure 3.** HOMO of ion **4** as predicted by MCSCF [CAS(3,3)] calculations.

Figure 2 shows the Becke3LYP/6-311G(d,p) optimized geometries with selected bond lengths and angles of **4**. For comparison, Figure 2 also shows the optimized geometries of $Bu^t-C^+{=}P-CH_2^\bullet$ (**5**) and $CH_3-C^+{=}P-CH_2^\bullet$ (**6**). Contrary to the N-analogue distonic ions $R-C{\equiv}N^+-CH_2^\bullet$, for which the calculations predict a linear structure (CNC bond angle of 180°), the phosphorus distonic ion **4** is predicted to display a CPC angle of 106.5°. This bond angle implies a lone pair on phosphorus. The predominance of the phosphaallylic radical electronic state **4a** and of a distonic electronic distribution is also evident: for $CPCH_2$ (charge, odd-spin density); C (−0.10, +0.57e); P (+0.62, −0.25e); $CH_2$ (−0.05, +0.67e). As expected mainly from inductive effects, the positive charge in **4** is concentrated on phosphorus; as expected for a phosphaallylic radical, the odd-spin density is delocalized over mainly the terminal methylene group and the allylic carbon. The MCSCF [CAS(3,3)] calculations predict a charge distribution more compatible with **4a** (and its nonclassical carbocation character, see below): $C2H_2$ (+0.06), C1 (+0.28), C (−0.02), P (+0.22), $CH_2$ (+0.12).

Becke3LYP/6-311G(d,p) calculations are, however, limited to a single electronic configuration; hence the ground and the excited electronic states are not probed simultaneously. MCSCF [CAS(3,3)][19] calculations consider, however, several electronic configurations and, when applied to **4**, they reveal that, for the electron configuration that makes the greatest contribution to the MCSCF wave function (coeficient of 0.96), the HOMO bearing the odd-spin electron is *orthogonal* to the CPC plane. Therefore, the most stable electronic state of **4** is characterized as the phosphaallylic radical state represented by **4a**.

**(b) The *Nonclassical* Carbocation[19] Character of 4.** Another very important finding that emerges from the optimized structure of **4** relates to some key bond lengths and angles: whereas all other CC bond lengths (1.55 Å) and CCC bond angles (109.5°) are near those expected for the saturated adamantyl group, the C1C2 bond (marked in bold in the structures of **4a** and **4b**) is substantially elongated (1.72 Å) and the C2C1C(P) angle is substantially narrowed (85.0°). An elongated CC bond and a reduced CCC angle for a saturated, relatively strain free carbon chain suggest charge stabilization in **4a** via delocalization of $\sigma$ electrons thus involving a *nonclassical* carbocation $\sigma$-bridged structure;[19] hence **4** is a distonic ion stabilized by both its phosphaallylic radical and nonclassical carbocation character.[20]





4

Nonclassical carbocations,[21] well-established and thoroughly studied $\sigma$-bridged species, have driven the expansion of bonding concepts beyond the classical two-center, two-electron bonds, and are stabilized via delocalization of $\sigma$ electrons to form three-center two-electron bonds. The nonclassical carbocation structure of **4** parallels those of several nonclassical carbocations, particularly that of the 2-adamantyl cation.[22] Nonclassical distonic ions are, however, without precedent.

**(c) Reaction Enthalpies for Formation of R−C$^+$=P−CH$_2^•$ Ions**. To rationalize reactivity trends, the enthalpies for $CH_2^{+•}$ transfer from $^+CH_2{-}O{-}CH_2^•$ to R−C≡P, leading to $CH_3{-}C^+{=}P{-}CH_2^•$ (eq 5), $Bu^t{-}C^+{=}P{-}CH_2^•$ (eq 6), $1\text{-}Ad{-}C^+{=}P{-}CH_2^+$ (eq 7), and $C_6H_5{-}C^+{=}P{-}CH_2^•$ (eq 8), were estimated by Becke3LYP/6-311G(d,p) calculations (Table 1). To compare two model nitrogen and phosphorus distonic ions, the enthalpy for $CH_2^{+•}$ transfer from $^+CH_2{-}O{-}CH_2^•$ to acetonitrile forming $CH_3{-}C{\equiv}N^+{-}CH_2^•$ was also estimated (eq 4).

**Table 1.** Electronic Energies from Structure Optimization at the Becke3LYP/6-311G(d,p) Level

| species | energy (hartree) | species | energy (hartree) |
|---|---|---|---|
| $CH_3{-}C{\equiv}N$ | −132.79333 | $CH_3{-}C{\equiv}N^+{-}CH_2^•$ | −171.78077 |
| $CH_3{-}C{\equiv}P$ | −419.37166 | $CH_3{-}C^+{=}P{-}CH_2^•$ | −458.31472 |
| $Bu^t{-}C{\equiv}P$ | −537.34531 | $Bu^t{-}C^+{=}P{-}CH_2^•$ | −576.30299 |
| 1-Ad−C≡P | −769.66524 | $1\text{-}Ad{-}C^+{=}P{-}CH_2^•$ | −808.63583 |
| $C_6H_5{-}C{\equiv}P$ | −611.15642 | $C_6H_5{-}C^+{=}P{-}CH_2^•$ | −650.13808 |
| $CH_2O$ | −114.53634 | $^+CH_2{-}O{-}CH_2^•$ | −153.48816 |

For acetonitrile, $CH_2^{+•}$ transfer that forms $CH_3{-}C{\equiv}N^+{-}CH_2^•$ is considerably exothermic (−22.4 kcal/mol, eq 4), but that for the analogue phosphaalkyne forming $CH_3{-}C^+{=}P{-}CH_2^•$ is endothermic (+5.5 kcal/mol, eq 5), hence, thermodynamically unfavorable. The geometry and electronic distribution of $CH_3{-}C^+{=}P{-}CH_2^•$ (**6**) reveal a characteristic phosphaallylic radical character but just a tenuous nonclassical character likely insufficient to make formation of **6** thermodynamically favorable from **3**: one of the CH bonds in **6** is slightly elongated (1.11 Å) and the HCC(P) angle is slightly reduced to 105.7° (Figure 2). The enthalpies for reactions 4 and 5 are therefore useful in rationalizing the general ready reactivity of nitriles in $CH_2^{+•}$ transfer from $^+CH_2{-}O{-}CH_2^•$,[8] whereas phosphaalkynes appear to be, in general, less reactive or unreactive.

$$CH_3{-}C{\equiv}N + {}^+CH_2{-}O{-}CH_2^• \rightarrow CH_3{-}C{\equiv}N^+{-}CH_2^• + CH_2O \qquad \Delta H = -22.4\ \text{kcal/mol} \quad (4)$$

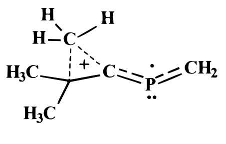
$$CH_3{-}C{\equiv}P + {}^+CH_2{-}O{-}CH_2^• \rightarrow CH_3{-}C^+{=}P{-}CH_2^• + CH_2O \qquad \Delta H = +5.5\ \text{kcal/mol} \quad (5)$$

$$Bu^t{-}C{\equiv}P + {}^+CH_2{-}O{-}CH_2^• \rightarrow Bu^t{-}C^+{=}P{-}CH_2^• + CH_2O \qquad \Delta H = -3.7\ \text{kcal/mol} \quad (6)$$

$$1\text{-}Ad{-}C{\equiv}P + {}^+CH_2{-}O{-}CH_2^• \rightarrow 1\text{-}Ad{-}C^+{=}P{-}CH_2^• + CH_2O \qquad \Delta H = -11.8\ \text{kcal/mol} \quad (7)$$

$$C_6H_5{-}C{\equiv}P + {}^+CH_2{-}O{-}CH_2^• \rightarrow C_6H_5{-}C^+{=}P{-}CH_2^• + CH_2O \qquad \Delta H = -18.7\ \text{kcal/mol} \quad (8)$$

Ionized methylene transfer to $CH_3{-}C{\equiv}P$ is endothermic (eq 5), hence thermodynamically unfavorable, but for $Bu^t{-}C{\equiv}P$ (−3.7 kcal/mol, eq 6) and 1-Ad−C≡P (−11.8 kcal/mol, eq 7) this reaction becomes slightly or substantially exothermic. Favoring of $CH_2^{+•}$ transfer to 1-Ad−C≡P (**1**) is easily rationalized by the additional and substantial stabilization of $1\text{-}Ad{-}C^+{=}P{-}CH_2^•$ (**4**) owing to its pronounced phosphaallylic radical and $\sigma$-bridged nonclassical carbocation character. Similarly, the optimized structure also reveals for the distonic ion $Bu^t{-}C^+{=}P{-}CH_2^•$ (**5**, Figure 2) a considerably nonclassical character (see structure below): the C1C2 bond is elongated (1.65 Å) and the C2C1C(P) bond angle is reduced (91.8°). Reaction 6 is, however, just slightly exothermic (−3.7 kcal/mol) and it is likely that $Bu^t{-}C^+{=}P{-}CH_2^•$ (**5**) is not formed from $Bu^t{-}C{\equiv}P$ (**2**) since other more favorable competitive reactions dominate under ethylene oxide CI conditions.



5

---

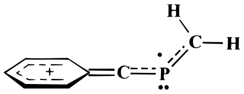
[19] A carbocation is nonclassical if it cannot be adequately described by a single Lewis structure, see: (a) Brown, H. C., with comments by Schleyer, P. v. R. *The Nonclasical Ion Problem*; Plenum: New York, 1977. (b) Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 3542.

[20] Several nonclassical ion geometries have been appropriately reproduced by Becke3LYP calculations; for instance, the Becke3LYP/6-31(G) geometries of the 1,2-dimethyl- and the 1,2,4,7-*anti*-tetramethyl-2-norbornyl cations closely resemble the X-ray structure of the latter, see: Schleyer, P. v. R.; Maerker, C. *Pure Appl. Chem.* **1995**, *67*, 755.

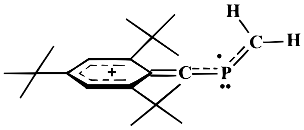
[21] (a) Olah, G. A. *Carbocations and Electrophilic Reactions*; Wiley: New York, 1974. (b) Barkhash, V. A. *Top. Curr. Chem.* **1984**, *116*, 265. (c) Olah, G. A.; Prakash, G. K. S.; Willians, R. E.; Field, L. D.; Wade, K. W. *Hypercarbon Chemistry*; Wiley: New York, 1987. (d) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1393. (e) Olah, G. A.; Laali, K. K.; Wang, Q.; Prakash, G. K. S. *Onium Ions*; Wiley: New York, 1998; Chapter 8.

[22] Nordlander, J. E.; Haky, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 1518.

Owing also to a pronounced phosphaallylic radical character of the model distonic ion $C_6H_5{-}C^+{=}P{-}CH_2^\bullet$ (**7**), see below, and the "classic" effect of charge delocalization across the phenyl ring, $CH_2^{+\bullet}$ transfer to phenylphosphaacetylene ($C_6H_5{-}C{\equiv}P$, eq 8) is thermodynamically favored by −18.7 kcal/mol. The analogue and kinetically stabilized supermesityl phosphaacetylene **3** fails, however, to form the corresponding "classic" distonic ion **8**. Probably $CH_2^{+\bullet}$ transfer to **3** is suppressed by the strong steric hindrance on the $C{\equiv}P$ group caused by the two bulky ortho *tert*-butyl substituents.



**7**



**8**

## Conclusions

The gaseous $^+CH_2{-}O{-}CH_2^\bullet$ distonic ion transfer ionized methylene to 1-adamantylphosphaacetylene, $1\text{-Ad}{-}C{\equiv}P$, to form $1\text{-Ad}{-}C^+{=}P{-}CH_2^\bullet$. This ion displays pronounced reactivity characteristic of a distonic ion, and is best represented by a phosphaallylic radical structure that stabilizes its radical site and a nonclassical $\sigma$-bridged three-center two-electron structure that stabilizes its charge site. This unique electronic structure and reactivity characterize the novel $1\text{-Ad}{-}C{\equiv}P^+{-}CH_2^\bullet$ as the first *nonclassical distonic ion*.

**Acknowledgment.** This work has been supported by the Research Support Foundation of the State of São Paulo (FAPESP) and the Brazilian National Research Council (CNPq). We thank a reviewer for helpful suggestions on the electronic structure of **4**.

JA993749M