Diphosphinonitrenium and -phosphenium Cations, Jahn-Teller Distorted Allyl Systems

Wolfgang W. Schoeller* and Thilo Busch

Fakultät für Chemie der Universität Bielefeld,
Postfach 8640, D-4800 Bielefeld 1, FRG

Ab initio calculations at SCF, MCSCF, and ACPF level were performed on a series of the phosphenium- and nitrenium-cation family. These show that they possess an allylic π-system with 4 electrons, which is distorted from planarity when the terminal groups of the allylic system are PR_2 (R = H) fragments. The distortion is such as to adopt C_2 symmetry, and is the consequence of Jahn-Teller distortion via mixing of the energy highest π_2 orbital with an energetically low lying σ^* orbital. The latter interaction is only operative if a symmetry breaking from C_{2v} to C_2 symmetry occurs. The importance of Jahn-Teller distortion on the biradical character in these systems is investigated by correlation calculations.

Phosphenium ions **1** were originally formulated as intermediate species[1,2], but can be stabilized by amino groups to give isolable compounds[3]. Both cyclic[4] and acyclic[5] stable phosphenium cations are known[6].

Here we report ab initio calculations on the electronic structures of the series **1—4**. It will be shown that the diphosphinonitrenium cation[7] (**4**) and the diphosphinophosphenium cation (**2**) reveal unusual bonding properties, in contrast to **1** and **3**.

All of the investigated structures were determined by ab initio calculations utilizing Huzinaga bases[8] of double-ζ quality. The bonding parameters resulting from geometry optimization[9,10] of **1—4** at SCF level are summarized in Scheme 1.

Scheme 1. Cations **1—4** with structural parameters; bond lengths are in Angstroems, bond angles in degrees
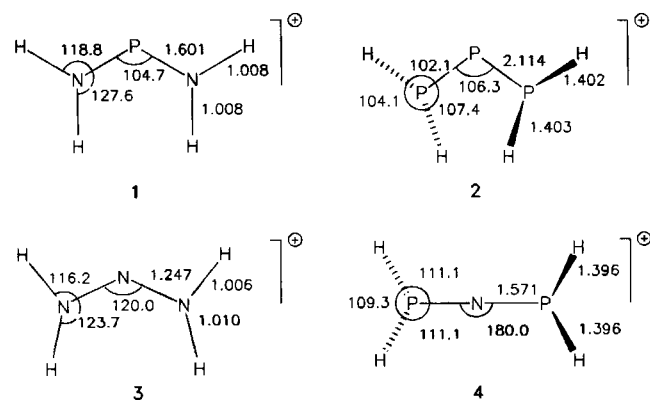
For structures **1** and **3** a planar delocalized allylic system with 4π electrons results. As expected, the valence angle at the central atom in **1** is smallest, since the phosphorus atom is surrounded by the (more) electronegative amino groups. The bond lengths are slightly longer than in corresponding double-bond systems[11a].

Unusual structures are obtained for **2** and **4**. Rather than adopting C_{2v} symmetry, the phosphino groups are twisted around the P—N bond axis, such as to adopt C_2 symmetry. In **4** the atoms P, N, P are also linear, and the resulting angle deformation potential (at the central atom) is extremely flat[11b]. The latter effect is similar to disilyl ethers[12a] and is the consequence of an electronegative central atom (N) surrounded by electropositive (P) ligands. Furthermore the electronegative central atom induces pyramidalization at the terminal PH_2 groups[12b]. The energy difference between planar (C_{2v}) and symmetry-distorted (C_2) geometries is considerable; e.g., according to correlation calculations at ACPF level[10a] for **2** a difference of 71 (68) kJ per mole for the singlet (triplet) states results. A qualitative explanation for symmetry lowering from C_{2v} to C_2 symmetry can be deduced from the MO scheme for planar **2** (**4**) [Figure 1].

2 consists of an allylic π system ($\pi_1 - \pi_3$) and an energetically low lying σ^* orbital. The close proximity of π_2 and σ^* is the consequence of different extension in space of the 3s and 3p orbitals at the phosphorus atom. This fact as well
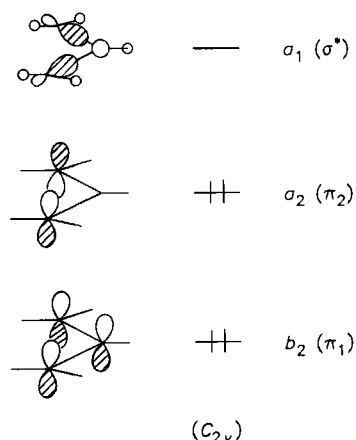

Figure 1. Molecular (frontier) orbitals of **2**

as its structural consequence can be predicted qualitatively with our recently developed model for *orbital non-hybridization*[13]. Consequently the formation of an energetically low lying σ^* orbital becomes facilitated. Interaction between π_2 and σ^* results in the singlet state as the consequence of Jahn-Teller distortion from higher to lower symmetry ($C_{2v} \rightarrow C_2$). Within C_{2v} symmetry it corresponds to an a_2 vibration[14] according to equation (1).

$$\Gamma_{\pi_2} \otimes \Gamma_{\sigma}^* = a_2 \otimes a_1 = a_2 \tag{1}$$

The change in symmetry for **2** and **4** is accompanied by pyramidalization at the terminal phosphorus atoms. Instead of a planar system the frontier orbitals are now combinations of lone pairs at the phosphorus atoms, either symmetric (n_a) or antisymmetric (n_b) with respect to the C_2 axis.

Scheme 2
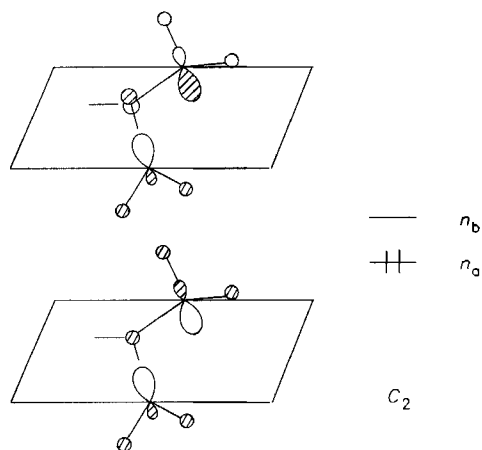
This gives rise to the important Slater determinants (2) to (4).

$$^1\psi_I = | \ldots n_a\bar{n}_a | \tag{2}$$

$$^1\psi_{II} = | \ldots n_b\bar{n}_b | \tag{3}$$

$$^3\psi_{III} = | \ldots n_a\bar{n}_b | + | \ldots \bar{n}_a n_b | \tag{4}$$

$^1\psi_I$ refers to the singlet wavefunction and results from optimization at SCF level.

In order to quantify the model we performed CI calculations with the averaged coupled pair functional method (ACPF)/10b/ with a 2×2 MCSCF/10a/ [consisting of a linear combination of equations (2) and (3)] or a RHF-triplet wavefunction as reference. For all cases the geometries resulting from optimization at HF level of the closed shell singlet state were used. The results of the investigations are collected in Table 1.

The magnitude of the biradical character in **1 – 4** emerges from the coefficients for ψ_I and ψ_{II}, in the 2×2 MCSCF calculation and the energy differences between singlet and triplet states. Thus, $^1\psi_{II}$ contributes most significantly only to the wavefunction of **4**. Multireference CI calculations with the ACPF method assigns a singlet ground state for all cations **1 – 4**, but yield the smallest energy difference be-

Table 1. ACPF energy differences (in kJ per mole) between singlet and triplet, and CI coefficients for the 2X2 MCSCF (singlet reference) wavefunction

Structure	ΔE (S – T)[a]	C_1	C_2
1	−450.9	0.993	−0.116
2	−185.5	0.989	−0.153
3	−444.9	0.987	−0.159
4	−136.6	0.937	−0.349

[a] Vertical energy differences between singlet (^1A) and triplet (^3B) [C_2 symmetry].

tween singlet and triplet for **4**. Consequently the latter possesses the strongest biradical character.

To summarize, the quantum chemical calculations for the isovalence electronic cation family **1 – 4** reveal unusual bonding properties for **2** and **4**, i.e. Jahn-Teller distorted geometries. The verification of this prediction remains a challenge for experimental synthetic chemists.

CAS Registry Numbers

1: 74900-33-7 / **2**: 87024-20-2 / **3**: 70102-55-5 / **4**: 126017-38-7

[1] E. Jungermann, J. J. McBride, Jr., R. Clutter, H. Mais, *J. Org. Chem.* **27** (1962) 606.
[2] Originally **1** was detected by mass spectroscopic investigations on phosphorus halides and diphosphenes; M. Halmann, *J. Chem. Soc.* **1962**, 3270; I. Granoth, *Top. Phosphorus Chem.* **8** (1976) 41.
[3] S. Fleming, M. K. Lupton, K. Jekot, *Inorg. Chem.* **11** (1972) 2534; B. E. Maryanoff, R. O. Hutchins, *J. Org. Chem.* **37** (1972) 3475.
[4] J. Luber, A. Schmidpeter, *Angew. Chem.* **88** (1976) 91; *Angew. Chem. Int. Ed. Engl.* **15** (1976) 111; J. H. Weinmaier, J. Luber, A. Schmidpeter, *Angew. Chem.* **91** (1979) 442; *Angew. Chem. Int. Ed. Engl.* **18** (1979) 412.
[5] R. W. Kopp, A. C. Bond, R. W. Parry, *Inorg. Chem.* **15** (1976) 3042; E. Niecke, R. Kröher, *Angew. Chem.* **88** (1976) 758; *Angew. Chem. Int. Ed. Engl.* **15** (1976) 692.
[6] For review see E. Fluck, *Top. Phosphorus Chem.* **10** (1980) 193; A. H. Cowley, R. A. Kemp, *Chem. Rev.* **85** (1985) 367.
[7] [7a] The nomenclature is chosen according to carbocation chemistry: G. A. Olah, *J. Am. Chem. Soc.* **94** (1972) 808. — [7b] First attempts for the synthesis of **4** were reported in the *dissertation thesis* of J. Böske (Universität Bielefeld, Bielefeld 1987).
[8] Huzinaga bases (S. Huzinaga, "Approximate atomic functions. II", Technical Report, The University of Alberta, Edmonton, Alberta, Canada 1971) of CGTO's according to:
P (11, 7, 1)/[5, 6 × 1/4, 3 × 1/1 d (ζ = 0.5)],
N (9, 5, 1)/[5, 4 × 1/3, 2 × 1/1 d (ζ = 0.95)],
H (4, 1)/[3, 1/1 p (ζ = 0.65)].
[9] The SCF calculations were performed with the Karlsruhe version [R. Ahlrichs, H. J. Böhm, C. Ehrhardt, P. Scharf, H. Schiffer, *J. Comp. Chem.* **6** (1985) 200] of Columbus program systems [R. M. Pitzer, *J. Chem. Phys.* **58** (1973) 3111]. Geometry optimizations were performed with an analytical determination of gradients utilizing a quasi-Newton method. All energy minima are defined by positive force constant matrices. The accuracy of energy determination is $\leq 10^{-8}$ au in energy.
[10] All correlation calculations were performed with the MOLPRO-89 program system of H.-J. Werner and P. J. Knowles. — [10a] H. J. Werner, W. Meyer, *J. Chem. Phys.* **73** (1980) 2342;

H.-J. Werner, P. J. Knowles, *J. Chem. Phys.* **82** (1985) 5053. —
[10b] R. J. Gdanitz, R. Ahlrichs, *Chem. Phys. Lett.* **143** (1988) 413.
[11] [11a] Calculated structures are r [Å]: (*trans*)-diphosphene 1.998; (*trans*)-iminophosphane 1.548; (*trans*)-diimine 1.211. — [11b] ⊀PNP [°], E_{rel} [kJ]: 180, 0.0; 150, 3.1; 120, 40.0.
[12] [12a] ⊀SiOSi of 140 — 180° in siloxanes; e.g., 149° in Me₃SiOSiMe₃ [M. J. Barrow, E. A. V. Ebsworth, M. M. Hardine, *Acta Crystallogr., Sect. B*, **35** (1979) 2093], 180° in Ph₃SiOSiPh₃ [C. Glidewell, D. C. Liles, *Acta Crystallogr., Sect B*, **34** (1978) 124]. —

[12b] C. C. Levin, *J. Am. Chem. Soc.* **97** (1975) 5649; A. Rauk, L. C. Allen, K. Mislow, *Angew. Chem.* **82** (1970) 453; *Angew. Chem., Int. Ed. Engl.* **9** (1970) 400.
[13] W. W. Schoeller, T. Dabisch, *Inorg. Chem.* **26** (1987) 1081; W. W. Schoeller, T. Dabisch, T. Busch, *Inorg. Chem.* **26** (1987) 4383.
[14] W. W. Schoeller, J. Niemann, *J. Am. Chem. Soc.* **108** (1986) 22; W. W. Schoeller, T. Busch, *J. Chem. Soc., Chem. Commun.* **1989**, 234.

[369/89]