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Conjugation Involving Nitrogen Lone-Pair Electrons: Can It Lead to Stable Multiply Charged Cations?

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Introduction

Phosphenium cations are isoelectronic to singlet carbenes and silylenes.[1] Recently, their chemistry has received much attention in the literature due to the synthesis of their stable forms[2−6] as well as transition-metal complexes.[7−13] Interestingly, in almost all the reported phosphenium cationic species, the phosphorus atom is characterized by its bonding to two planar amino groups.[2,4,9] Typical P−N distances in these phosphenium cations are in the range of 1.62−1.66 Å, being much shorter than a typical P−N single bond.[14,15] This fact as well as the results of experimental and theoretical studies[2,16] led to the conclusion that conjugation involving the nitrogen lone pairs and the vacant phosphorus 3p orbital exists in these species, which would give the systems extra stability. Since the lone-pair electrons are involved in the conjugation, it is appropriate to call this conjugation *lone-pair π-conjugation*. In fact, numerous examples can be found in the literature where this type of conjugation is quite visible. A simple example is a chloromethyl cation, H_2CCl^+, and a classic one is neutral borazine.[17] In this paper, the lone-pair π-conjugation is further explored from the structure and stability of some phosphenium and nitrenium cations and related boron-containing neutral systems. In Figure 1, the geometries of the systems optimized at the B3LYP/6-31G(d)[18] level of density functional theory (DFT) using the Gaussian94 set of programs[19] are shown. Both experimental and theoretical studies regarding **1**, **3**, **6**, and **9** of these systems have

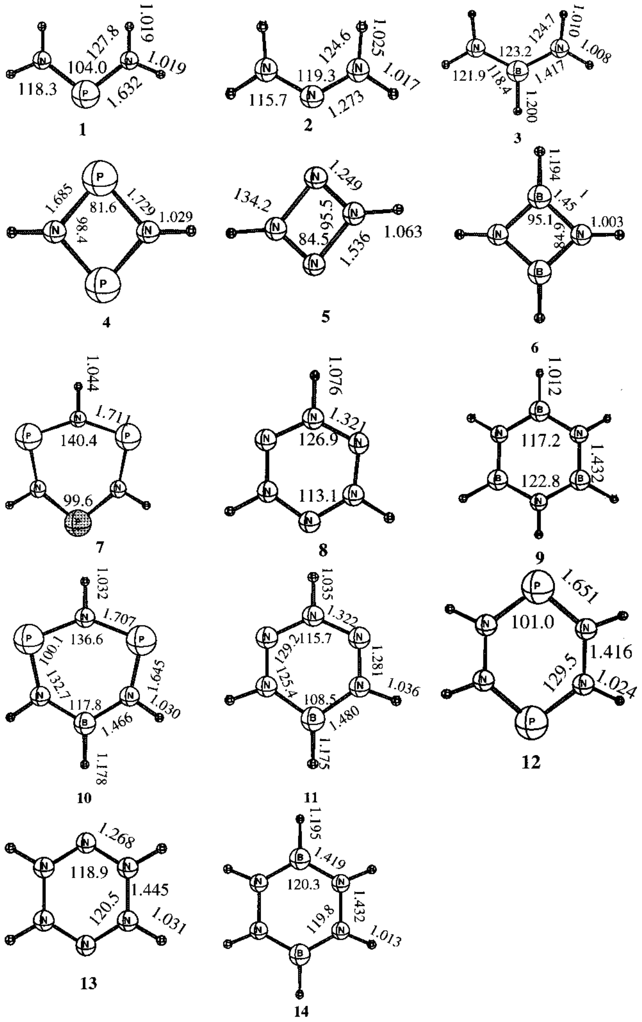

Figure 1. Planar geometries (Å, deg) of phosphenium and nitrenium cations and related neutral boron-containing systems.

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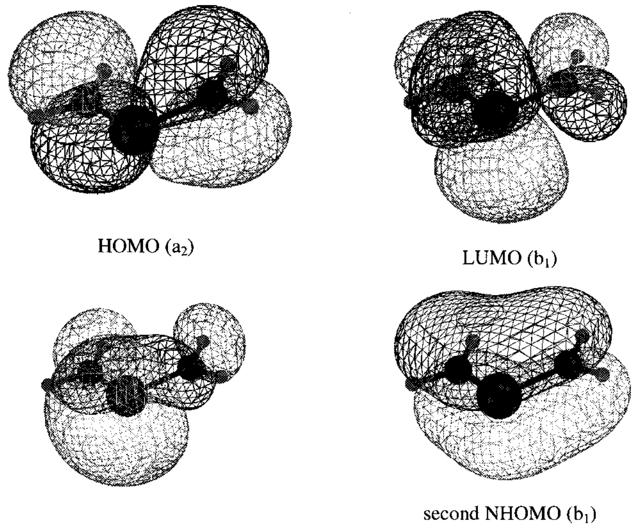

Figure 2. Selected Kohn−Sham orbitals of phosphenium cation **1**. HOMO and LUMO are the highest and lowest molecular orbitals, respectively, whereas NHOMO and second NHOMO are the next and second next HOMOs. While NHOMO is the phosphorus in-plane lone-pair orbital, the other orbitals are π orbitals perpendicular to the molecular plane. The second NHOMO, HOMO, and LUMO are the bonding, nonbonding, and antibonding orbitals, respectively, representing the nitrogen lone-pair π-conjugation.

appeared in the literature.[17,20] Borazine **9**, commonly known as “inorganic benzene”, is the most extensively studied among all of them.[20] Cowley et al.[4a] had tried the synthesis of multiply charged cationic compounds **4** and **7**, but could not succeed. Other molecules have not appeared in the literatures to our knowledge.

Results and Discussion

Geometries. The geometries of the acyclic planar two-lone-pair π-conjugated systems **1** and the analogous species **2** and **3** are minima in the B3LYP calculations. The structure of **3** is quite similar to that previously obtained by Skancke[17c] at the MP2/6-31G* level. The N−P−N bond angle in **1** shows a reduction by 16° from 120° for sp^2 hybridization. Invoking observations by Kutzelnigg[21] on the chemical bonding of higher main group elements, this small angle would appear to be quite natural; the less isovalent hybridizations involving phosphorus atomic orbitals would lead to almost pure p orbitals in contrast to the cases for the first-row nitrogen and boron atoms. The Kohn−Sham orbitals for **1** in Figure 2 clearly demonstrate that the lone-pair π-conjugation takes place, because the π orbitals are similar to those of allyl. Such conjugation is expected to make the P−N bonds in **1** and the N−N bonds in **2** shorter than the corresponding single bonds. At the present level of calculations, as a matter of fact, the P−N bond distance of **1** (1.632 Å) is 0.1 Å shorter than that of phosphazene (1.736 Å),[22] and the N−N bond distance of **2** (1.273 Å) is 0.16 Å shorter than that of hydrazine (1.437 Å).

Systems **4**, **5**, and **6** are particularly interesting due to their similarity to the most popular antiaromatic cyclobutadiene. The minimum-energy structures of **4** and **5** have the shape of a parallelogram. Their square structures are located as transition states. The energy difference between the square and parallelogram forms of **4** is negligibly small, whereas the square and parallelogram forms of **5** show a difference of 36.68 kcal/mol in total energy. Consistent with these results, much larger bond alternation takes place in **5** ($[N_4H_2]^{2+}$), which indicates that the four electrons from the two nitrogen lone pairs localize over the two shorter ring bonds. A very similar observation can be seen in the geometry of the neutral N_4 molecule obtained at the B3LYP/6-31G(d) level by Schleyer et al.[23] They have reported N−N bond distances in rectangular N_4 as 1.534 and 1.249 Å, which are almost the same as the N−N bond distances in $[N_4H_2]^{2+}$. However, the main difference between the two structures is in their N−N diagonal distances. Neutral N_4 has an N−N diagonal distance of 1.972 Å, whereas the major and minor diagonals of $[N_4H_2]^{2+}$ are equal to 2.071 and 1.886 Å, respectively. In the case of **6**, the planar assumption gave a square structure with two imaginary vibrational frequencies. The minimum-energy conformation of **6** has a puckered structure (18.3° puckering) with pyramidalization at the nitrogen atoms. This structure is 1.27 kcal/mol more stable than the planar structure. It can be argued that, since the boron atom is less electron withdrawing, the nitrogen lone-pair π-conjugation is weaker in **6**, and therefore the pyramidalized structure is favored.

Employing the nitrogen lone-pair π-conjugation, the theoretical construction of multiply charged cationic systems **7** and **8** is rather easy. The structure for **9** is in very good agreement with the experimental results.[24] For instance, the experimental B−N bond length is 1.436 Å, whereas the calculated length is 1.432 Å. Schleyer et al.[20d] performed the calculations on borazine as well as the related molecules at the B3LYP/6-311+G** level to obtain the B−N bond length of 1.431 Å, with which our value of 1.432 Å obtained using the smaller basis set is in good agreement. Unlike the four-electron systems, the planar structures of these three six-electron systems with all the N−X (X = B, N, P) bonds having equal lengths are energy minima (cf. Figure 1), fulfilling the geometrical criterion of aromaticity.[25] Compared to the N−P, N−N, and N−B bonds in **1**, **2**, and **3**, the corresponding bonds in **7**, **8**, and **9** are longer, whereas they are still shorter than typical single bonds. It can be argued that these three systems possess double bond character due to the lone-pair π-conjugation. In all these systems, the HN−X−NH (X = P, N, B) angles are smaller than 120° and the X−NH−X angles are larger than 120°. Compared with those in **1**, **2**, and **3**, the HN−X−NH angles in **7**, **8**, and **9** are 4.4−6.2° smaller. The HN−P−NH and P−NH−P angles in **7** are much smaller and larger, respectively, compared with the

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Table 1. Isodesmic Reactions and the Corresponding Energy Changes[a]

reaction	ΔE (kcal/mol)	nm	ηnm	δL
1 + $[PH_4]^+ \rightarrow [H_2P(NH_2)_2]^+ + [PH_2]^+$	68.06	2	104.79	0.595
2 + $[NH_4]^+ \rightarrow [H_2N(NH_2)_2]^+ + [NH_2]^+$	153.06	2	215.75	0.934
4 + $2[PH_4]^+ \rightarrow$ [**4**$-H_4]^{2+} + 2[PH_2]^+$	92.55	4	209.58	0.638
5 + $2[NH_4]^+ \rightarrow$ [**5**$-H_4]^{2+} + 2[NH_2]^+$	140.36	4	431.50	1.594
7 + $3[PH_4]^+ \rightarrow$ [**7**$-H_6]^{3+} + 3[PH_2]^+$	145.64	9	471.55	1.280
8 + $3[NH_4]^+ \rightarrow$ [**8**$-H_6]^{3+} + 3[NH_2]^+$	256.93	9	970.87	2.152
10[b] + $2[PH_4]^+ \rightarrow$ [**10**$-H_4]^{2+} + 2[PH_2]^+$	122.90			1.050
11[b] + $2[NH_4]^+ \rightarrow$ [**11**$-H_4]^{2+} + 2[NH_2]^+$	255.09			1.973
12 + $2[PH_4]^+ \rightarrow$ [**12**$-H_4]^{2+} + 2[PH_2]^+$	129.48	8	419.15	1.155
13 + $2[NH_4]^+ \rightarrow$ [**13**$-H_4]^{2+} + 2[NH_2]^+$	247.41	8	863.00	1.825
$NH_2PH^+ + [PH_4]^+ \rightarrow NH_2PH_3^+ + [PH_2]^+$	52.39	1	52.39	0.458
$NH_2NH^+ + [NH_4]^+ \rightarrow NH_2NH_3^+ + [NH_2]^+$	107.87	1	107.87	0.760

[a] [**4**$-H_4]^{2+}$, [**5**$-H_4]^{2+}$ and so on represent the cations hydrogenated at the atoms having the vacant valence shell orbital. For instance, $[H_2P(NH_2)_2]^+$ is shown by [**1**$-H_4]^+$. n, m, and η are the number of lone-pair atoms directly connected to the atom having a vacant orbital, the number of atoms with vacant valence shell orbitals, and the lone-pair π-conjugation factor, respectively. δL is the total lone-pair deviation. See the text for further details. [b] The presence of the BH unit in these systems hinders the full calculation of the conjugation energy.

corresponding angles in **8** and **9**. This can be ascribed to the smaller hybridization of the phosphorus atom mentioned previously.

To study further multiply charged systems with six lone-pair electrons, the structures of cationic systems **10** and **11** are also optimized at B3LYP/6-31G(d). Their planar geometries are minima. The HN$-$X bonds (X = P in **10** and X = N in **11**) in these systems are shorter than the N$-$X bonds in the other systems, indicating that stronger conjugation takes place. As a consequence the N$-$B bonds in **10** and **11** are elongated as compared to any other N$-$B bonds obtained in this study. In other words, N$-$P and N$-$N lone-pair electron sharing may be more favorable than N$-$B sharing. This is presumably because of the fact that the P and N atoms having a positive charge are more electron withdrawing than the neutral B atom.

Doubly charged cations **12** and **13** and the neutral molecule **14** have eight electrons from the four nitrogen lone pairs for a cyclic conjugation. Only the planar geometry of cation **13** is a minimum. The planar geometries of **12** and **14** have one and two imaginary frequencies, respectively, and the minimum-energy structures of them are slightly distorted from planarity (cf. Figure 1). However, the distorted geometries do not show any significant change in the bond lengths and bond angles as compared to the planar geometries. In the nonplanar structure of **12** the sum of the three angles around each nitrogen atom is 360°, indicating a locally planar conformation. Similarly, the minimum-energy conformation of **14** shows a small amount of pyramidalization at nitrogen atoms, and all the ring atoms lie more or less in the same plane. The distorted geometries of **12** and **14** show only a marginal increase in stability when compared with the planar structures (0.68 and 3.67 kcal/mol, respectively, for **12** and **14**).

According to Hückel's theory,[26] the situation in which $4n$ ($n = 2$) electrons are involved in conjugation may lead to an unstable antiaromatic state. To avoid this instability, the HN$-$NH bonds in **12**, **13**, and **14** are much longer than the HN$-$N bonds in **8** for instance, and their bond lengths are close to the single bond distance. In **12**, the absence of large pyramidalization and the P$-$N bond distance of 1.65 Å, which is shorter than a single bond distance, confirm the presence of local N$-$P$-$N lone-pair π-conjugation. Thus, **12** may be described as two phosphenium cation moieties such as **1** connected through two N$-$N single bonds. In the same way, two nitrenium cationic moieties such as **2** and two HN$-$BH$-$NH moieties connected by two N$-$N bonds lead to **13** and **14**, respectively. The planar structures of the HN$-$X$-$NH moieties kept by the local conjugation result in all the ring atoms being nearly coplanar.

Lone-Pair π-Conjugation Energies. Isodesmic reactions[27] are the reactions in which the number and type of bonds are conserved. The reactions reported in Table 1 belong to this category, and in addition to the bond conservation, the charges on similar groups are also conserved. The ΔE values reported in Table 1 were calculated assuming maximum conjugation in the planar structures irrespective of the nature of the stationary structures. Moreover, the reactions of two additional cations, NH_2NH^+ (N$-$N = 1.229 Å) and NH_2PH^+ (N$-$P = 1.621 Å), not mentioned in the previous discussions, are included in Table 1, to complete the following analysis.

The energy change in each reaction (ΔE) can be considered to be mainly due to the destruction of the nitrogen lone-pair π-conjugation. Although the ΔE values include the energy due to hybridization change (changes in σ bond energies) and strain energy, we can expect that the ΔE values are a good measure of the lone-pair π-conjugation energy in each cation. Since in all the isodesmic reactions the reactant side and the product side contain the same number of P and/or N atoms with sp^2 and sp^3 hybridization, the energy contribution due to hybridization change could be neglected. The strain energy is not very important because the cyclic nature of the cations is retained in both sides of the reaction. Only the six-membered hydrogenated cations show drastic change in the planarity of the hexagonal skeleton (they have chair conformations). However, the ΔE values obtained for **12** and **13** are almost double that obtained for the strain-free systems **1** and **2**, respectively (cf. Table 1), suggesting that the strains in **12** and **13** do not much affect the ΔE values (it was already seen that the cations **12** and **13** are composed of two phosphenium moieties such as **1** and two nitrenium moieties such as **2**, respectively).

Interestingly, comparing the species having the same number of lone pairs, all the phosphenium cations give smaller ΔE values as compared to the nitrenium cations. For instance, the ΔE values for **8** and **7** are 257 and 146 kcal/mol, respectively. This result further supports Kutzelnigg's observation[21] that the valence orbitals of third-row atoms are much less efficient in sharing their orbital space with another atom as compared to those of second-row elements. Unfortunately, formulation of

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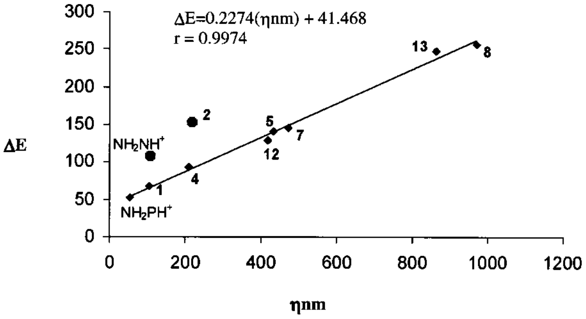

Figure 3. Total lone-pair deviation versus the energies of isodesmic reactions.

such comparable reactions involving neutral boron-containing molecules is impossible.

We have also obtained a simple empirical equation (cf. Figure 3) that relates the ΔE values with the number of lone pairs (n) and the number of vacant orbitals (m) involved in conjugation and a conjugation factor (η). The conjugation factor η is defined separately for the N$-$N$^+$ bond and N$-$P$^+$ bond. They are taken as the ΔE value obtained for the isodesmic reactions of cations NH_2NH^+ and NH_2PH^+, respectively (107.87 and 52.39 kcal/mol, respectively). For these cations "*nm*" is unity. There is a good linear correlation between ΔE and "ηnm".[28] Two points corresponding to acyclic nitrenium cations NH_2NH^+ and **2** are much deviated from the fitted line. Since acyclic and cyclic phosphenium cations are nearly on the line, we may conclude that the difference in the structures of the phosphenium cations does not affect the conjugation energies, but it indeed does those of nitrenium cations.

NBO Analysis. We have performed natural bond orbital (NBO) analysis[29] for NH_2NH^+, NH_2PH^+, and all the cationic systems reported in Figure 1. Except the dipositively charged cation **5**, all the systems showed strongly delocalized structures when the orbital occupancy threshold was at 1.90. The calculations showed that the occupancy of each lone-pair orbital perpendicular to the molecular plane (i.e., the valence p_z orbital of the nitrogen atom) is smaller than the maximum occupancy of two electrons. The difference between the maximum occupancy and the original occupancy of a lone pair (lone-pair deviation) acts as a measure of the delocalization of that lone pair in a cation. The sum of all such lone-pair deviations of a cation designated here as the total lone-pair deviation (δL) is considered as a measure of the extent to which all the lone-pair electrons are involved in the conjugation (cf. Table 1). Since there is no conjugated species in the product side of all the isodesmic reaction, it is meaningful to compare the δL values with the corresponding ΔE values. There is a good linear correlation between the two quantities of total lone-pair deviation (δL) and ΔE as shown in Figure 4. This strongly suggests that the ΔE values indeed represent a stabilizing effect due to the lone-pair π-conjugation.

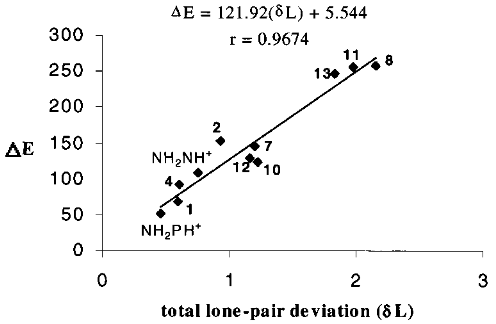

Figure 4. Lone-pair π-conjugation term versus the energies of isodesmic reactions.

Concluding Remarks

On the basis of structural, energetic, and orbital analysis data, the existence of nitrogen lone-pair π-conjugation in phosphenium and nitrenium cations is brought out. Although highly positive ΔE values were obtained for the isodesmic reactions of these cations, especially for multiply charged cations, they do not indicate the existence of such cations as stable species. But the underlying fact is that the nitrogen lone-pair π-conjugation, which is mainly responsible for the endothermicity of these reactions, can be utilized for any attempt to synthesize stable multiply charged cations.[30]

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(28) We note here that this is not a unique equation as suggested by one of the reviewers of this paper. The relation could be $\Delta E \propto \eta nq$, where q is the charge of the cation, or $\Delta E \propto \eta nm^2/q$, etc. This happens because m and q are identical for these cations.

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