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T_h-Symmetrical $N_8(C{=}C)_6$ and $P_8(C{=}C)_6$; an Extraordinary Contrast in Heterofullerene Stability

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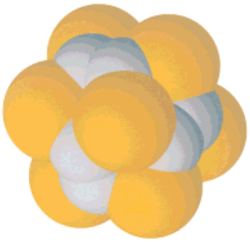
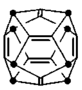
ABSTRACT

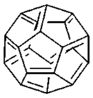


T_h-symmetrical $P_8(C{=}C)_6$, 1, is predicted to be a remarkably stable small heterofullerene with carbon atoms less pyramidal than in C_{60}. T_h-$N_8(C{=}C)_6$, 2, in sharp contrast, is strongly destabilized relative to T_h-$(HC)_8(C{=}C)_6$. The causes of this extraordinarily large difference (nearly 1000 kJ mol^{-1}) between 1 and 2 are explained.

The smallest fullerene that satisfies Euler's theorem is C_{20}, **3**, but this is highly strained relative to its saturated analogue, dodecahedrane **4**, as a result of the extreme pyramidalization of the double bonds.



1, • = P
2, • = N



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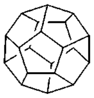

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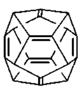

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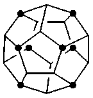

6, • = P
7, • = N

Nevertheless, the generation of **3** has been reported recently by Prinzbach, Scott, and co-workers.[1] We now show that T_h-symmetrical $P_8(C{=}C)_6$, **1**, should be a stable, cube-shaped, heterofullerene analogue of **3** with double bonds that are actually less pyramidal than those in C_{60}. The nitrogen analogue, **2**, on the other hand, is extraordinarily unstable, and we identify the novel structural effects that are the cause of this.

We chose **1** in the expectation that conventional strain relative to the all-carbon analogue **5** would be low. Since phosphorus(III) tolerates small bond angles and P−C bonds are longer than C−C, flatter C=C double bond environments can be expected in **1**. Based on Benson's 1993 aliphatic CH group enthalpy equivalent (−10.0)[2] and the experimental heat of formation (76.1 kJ mol^{-1}),[3] the strain energy of **4** is 277 kJ mol^{-1} (all the CH bonds are eclipsed). The strain energy of **5** is calculated[4] to be much higher, 839 kJ mol^{-1}.[5] A considerable part of this huge strain is relieved in **1**; isodesmic reaction 1 is evaluated (data in Table 1) to be

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† University of Bristol.
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[1] Prinzbach, H.; Weller, A.; Landenberger, P.; Wahl, F.; Worth, J.; Scott, L. T.; Gelmont, M.; Olevano, D.; von Issendorff, B. *Nature* **2000**, *407*, 60. See also: Hirsch, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 1195.
[2] Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419.
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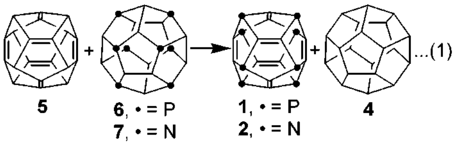
Table 1. Computed Total and Zero-Point Energies (B3LYP/6-311G*, in au) for $C_{12}P_8$ (T_h) **1** and Related Systems

	E_{tot}	E_{tot} + ZPE
$C_{12}P_8$ (T_h) **1**	−3188.14083	−3188.06007
$C_{12}N_8$ (T_h) **2**	−894.77506	−894.66435
$C_{20}H_{20}$ (I_h) 4	−774.33116	−773.97295
$C_{20}H_8$ (T_h) **5**	−766.74059	−766.52807
$C_{12}H_{12}P_8$ (T_h) **6**	−3195.58901	−3195.36542
$C_{12}H_{12}N_8$ (T_h) **7**	−902.60899	−902.34506
$C_{19}H_7P$ (C_3)	−1069.41325	−1069.21750
$C_{19}H_7N$ (C_3)	−782.75606	−782.55608
$C_{19}H_{19}P$ (C_{3v})	−1076.98870	−1076.64684
$C_{19}H_{19}N$ (C_{3v})	−790.36801	−790.02144

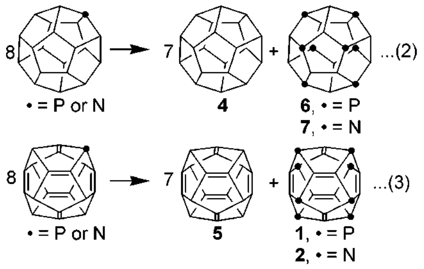
exothermic by 366 kJ mol^{-1} when $\bullet$ = P. Other factors have profound effects on the stability of these cage species, however. T_h-$N_8(C{=}C)_6$, **2**,[6] is strongly destabilized not only relative to **1** but even relative to **5**: isodesmic reaction 1 is 619 kJ mol^{-1} endothermic when $\bullet$ = N!



Reaction energies (kJmol^{-1}): P = -366; N = +619

The stability trends for **1**, **2**, and **5** are nicely illustrated by comparison of their hydrogenation enthalpies with that of $Me_2C{=}CMe_2$ (experimental 108;[7] computed 101 kJ mol^{-1}). Hydrogenation of **5** to form **4** is exothermic by 1169 kJ mol^{-1}, i.e. by 195 kJ mol^{-1} per double bond. Hexahydrogenation of **1** is computed to be exothermic by only 134 kJ mol^{-1} per C=C bond, whereas for **2**, the corresponding energy is 298 kJ mol^{-1} per C=C bond. We will first explain the extraordinary destabilization of **2**, before returning to explore the properties of **1**.

The extreme contrast, nearly 1000 kJ mol^{-1}, in the energies of reaction (1, P vs N) is not due to anomeric or other special effects associated with saturated species **6** and **7**. Thus, reaction 2, which assesses additivity, is only mildly endothermic (+41.5) for $\bullet$ = N, and slightly exothermic (−3.5 kJ mol^{-1}) for $\bullet$ = P. On the other hand, reaction 3 (corresponding to reaction 2 for the unsaturated species) is strongly endothermic for $\bullet$ = N (230.6) but only mildly exothermic for $\bullet$ = P (−43.6 kJ mol^{-1}). It is clear that there is a strong nonadditive destabilization of **2**.

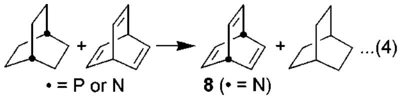


Reaction (2) energies (kJmol^{-1}): P = -3.5; N = +41.5

Reaction (3) energies (kJmol^{-1}): P = -43.6; N = +231

Perhaps **1** is aromatic and **2** is antiaromatic. Computed nucleus-independent chemical shifts (NICS)[8,9] were −15 for **1** and 0 for **2**. Thus, **1** is (mildly) aromatic and **2** is nonaromatic. Although NICS values cannot be directly related to energy differences, it seems unlikely that aromaticity accounts for very much of the huge differences in the energies of reaction 1.

The major reason for the destabilization of the unsaturated nitrogen systems, which do not benefit from strain relief by N/CH replacement, is electronic. The lack of effective vinylic delocalization between the nitrogen lone pair and the adjacent double bonds in **2** and $C_{19}H_7N$ (as well as in 1,4-diazabarrelene **8**, see eq 4) is indicated directly by the long C(sp^2)−N distances in these compounds (e.g., **2**, 1.481 Å; $C_{19}H_7N$, 1.475 Å; 1,4-diazabarrelene **8**, 1.480 Å; compare the (computed) bond length in vinylamine, 1.391 Å, and the 1.474 Å C(sp^3)−N length in the *saturated* $C_{12}H_{12}N_8$, **7**). The resulting destabilization in the unsaturated 1,4-diazabarrelene cage system **8** is illustrated by eq 4, which is 19 kJ mol^{-1} exothermic for the phosphorus analogue, $\bullet$ = P, but is 44.4 kJ mol^{-1} endothermic for $\bullet$ = N. The enforced pyramidality of the nitrogen atom environments is largely responsible for these remarkable effects. The long cage C−N bonds in **2** and **8** are weaker than the C−N bonds in the saturated reference systems. The large number (24) of such weaker C−N bonds in **2** results in the remarkable endothermicity of eq 1 ($\bullet$ = N).



Reaction Energies (kJmol^{-1}): P = -19; N=+44.4

Simple computational experiments on the parent vinylamine reveal the basis for the cage behavior. Rotation of the amino group into a C_s conformation like that in **8** raises

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(4) All calculations were performed using the B3LYP hybrid density functional as implemented in Gaussian 98 (M. J. Frisch et al.; Gaussian, Inc.: Pittsburgh, PA, 1998). Vibrational frequency computations confirmed that the fully optimized structures were indeed minima and provided harmonic zero-point energies. Energies discussed in the text are at the B3LYP/6-311G*//B3LYP/6-311G* + ZPE level, except for reaction 4 and the model vinylamines, where a slightly larger basis was used (B3LYP/6-311+G**). The reaction energies are not very sensitive to the level of theory used; AM1 and MP2/6-311G*//B3LYP/6-311G* calculations give very similar values.

(5) From computation of the energy of the isodesmic reaction: $C_{20}H_{20} + 6(CH_3)_2C{=}C(CH_3)_2 \rightarrow C_{20}H_8 + 6(CH_3)_2CHCH(CH_3)_2$

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(8) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H. J.; Hommes, N. *J. Am. Chem. Soc.* **1996**, *118*, 6317. Schleyer, P. v. R.; Manoharan, M.; Wang, Z.-X.; Kiran, B.; Jiao, H.; Puchta, R.; Hommes, N. J. R. van E. *Org. Lett.* **2001**, *3*, 2465.

(9) Ths IGLO-PW91/III TZ2P level was used with the deMon program. See: Malkin, V. G.; Malkina, O. L.; Casida, M. E.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898. Malkin, V. G.; Malkina, O. L.; Erikson, L. A.; Salahub, D. R. In *Theoretical and Computational Chemistry*; Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995; Vol. 2, p 273.

the energy by 34.8 kJ mol^{-1}. The resulting loss of conjugation lengthens the C−N bond, but only to 1.440 Å. If, in addition, all the bond angles at N are reduced to 104.9° and the CCN angle is fixed to 113.7° (the values in **8**), the C−N bond lengthens further to 1.479 Å. If the N lone pair-C=C double bond conformation in vinylamine, favoring conjugation, is retained but all the angles at nitrogen are reduced, e.g., to 97°, the CN distance becomes 1.455 Å. This C−N bond distance increase (0.064 Å) is more than the 0.046 Å increase in the C−N length in methylamine due to similar enforced pyramidalization, which changes the hybridization. Even though n−p overlap is possible conformationally in the distorted vinylamine, it is largely eliminated by the outward bending of the nitrogen lone pair. We also find that the energetic cost of constraining the angles around nitrogen to 97° is significantly higher for $CH_2{=}CHNH_2$ (42 kJ mol^{-1}) than for CH_3NH_2 (28 kJ mol^{-1}). The long C−N bonds are therefore not due to strain in the cage of **2**, but are largely a consequence of the small C−N−C angles.

T_h-$N_8(C{=}C)_6$, **2**, has both small C−N−C bond angles (97.6°) *and* long C−N bonds (Table 2). This combination means that there is also very little n−p overlap in **2**, even though C−N−C=C dihedral angles do not preclude it. If the C−N−C bond angles in $(CH_2{=}CH)_3N$, a more closely related model compound, are constrained to 97° but the geometry is otherwise allowed to optimize, a conformation with only one vinyl group oriented to permit n−p overlap is obtained. However, *all* the C−N bonds are much longer (1.491, 1.491, and 1.488 Å) than in the C_3 global minimum (1.401 Å), which is nearly planar at nitrogen. The 97° constrained conformation is 146 kJ mol^{-1} less stable than the global minimum, more than enough to account for the destabilization of **2**.

Table 2. Bond Lengths (Å) and Angles (deg) for **1**, **2**, **6**, and **7** (at the B3LYP/6-311G* Level)

	1	**6**	**2**	**7**
C−C	1.341	1.555	1.330	1.552
C−H		1.091		1.092
C−X	1.878	1.892	1.481	1.473
C−X−C	87.9	99.0	97.6	109.1
X−C−X	113.1	110.2	114.4	108.6
C−C−X	118.5	114.2	113.0	106.6

These effects have clear precedents in the behavior of phosphorus (and other group 15) compounds, where the ca. 95° angles and the high inversion barriers preclude effective n−p overlap and conjugation. The p-lone pair on phosphorus in planar tricoordinate or in dicoordinate environments conjugates nearly as well as nitrogen.[10] The situation here is the obverse: nitrogen in highly pyramidal environments (as in **2**) conjugates just as poorly as pyramidal phosphorus.

Hence, a major cause of the instability of **2** lies in the enforced small C−N−C bond angles (97.6°) that result in long C−N bonds, bond weakening due to a change in hybridization, and loss of conjugation. The CCC angles are deformed as well. These adverse strain and electronic effects are much less pronounced (if not wholly absent, in a relative sense) in the inherently pyramidal phosphorus systems, where additivity is followed closely. The strong exothermicity of eq 1 (• = P) does indeed appear to be due to strain relief at the alkene carbons resulting from the long PC bonds and small bond angles at phosphorus.

The geometry of the optimized structure of T_h-$P_8(C{=}C)_6$, **1**, is intriguing (Table 2). The cube of phosphorus atoms has the C=C units lying only 0.52 Å above each face of the cube, compared with 0.60 Å for **5**. As a result of this cubic flattening of the T_h structure and the larger van der Waals radius of P, heterofullerene **1** presents an almost cubic surface to the outside world (Figure 1).

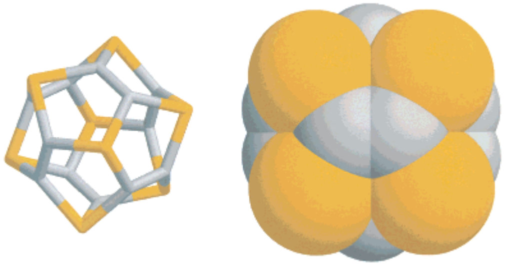

Figure 1. Skeletal and space filling models of **1** (the latter is oriented perpendicular to one cubic face).

The alkene carbon environments in **1** are actually less pyramidal than those in C_{60}. Thus the sum of the bond angles at carbon in **1** is 350.1°, compared with 348° in C_{60} and 340.4° in **2**, and the alkene pyramidalization angle, φ,[11] is 30.0° for **1**, 31.7° for C_{60}, but is much larger for **2** (44.9) and the known dodecahedrene (43.5°).[12]

The relatively small alkene pyramidalization in **1** should not result in high reactivity. Indeed, we predict **1** to have surprisingly normal properties for such an apparently exotic structure. Heterofullerene **1** should be colorless; the electronic spectrum of **1**, calculated with the ZINDO semiempirical program,[13] should show two bands at 207 (180 000) and 260 nm (65 000). The vibrational spectrum is predicted to show only one high-frequency line with nonzero intensity; C−C stretching at 1538 cm^{-1} (T_u, 13.7 km mol^{-1}). There are also lines at 768, 639, 573, 450, 405 and 314 cm^{-1}, with predicted intensities of 23.5, 3.05, 114.1, 4.22, 2.59 and 0.75 km mol^{-1}, respectively.

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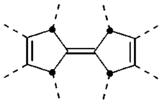
[10] Kapp, J.; Schade, C.; El-Nahas, A.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2236. See also: Schade, C.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1987**, 1399; Nyula'szi, L. *Chem. Rev.* **2001**, *101*, 1229.

[11] Borden, W. T. *Synlett* **1996**, 711. Borden, W. T. *Chem. Rev.* **1989**, *89*, 1095.

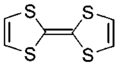
[12] Melder, J. P.; Weber, K.; Weiler, A.; Sackers, E.; Fritz, H.; Hunkler, D.; Prinzbach, H. *Res. Chem. Intermed.* **1996**, *22*, 667.

[13] Zerner, M. C. In *Reviews of Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH Publishing: New York, 1991; Vol. 2, p 313.

The structure of **1** and **2** are built from units **9**, which bear a striking resemblance to tetrathiafulvalene **10** and to the tetraaminoethylenes, and so we wondered if they would have low ionization energies. However, the calculated vertical IPs for **1** (8.26 eV) and **2** (7.66 eV) are quite large,[14] presumably because of the strong pyramidalization of the heteroatoms and the lack of overlap of the lone pairs with the p orbitals.



9, • = P or N



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The T_h-symmetrical structure of **1**, **2**, and **5** is reminiscent of that originally proposed[15] (but no longer accepted[16]) for "met-car" clusters such as $C_{12}Ti_8$. It has been reported[17] that $C_{12}Si_8$ should adopt a T_h structure, although $C_{12}Ge_8$ and $C_{12}Sn_8$ are calculated to prefer quite different D_{2h} and D_2 structures, respectively. However, the silicon atoms in $C_{12}Si_8$ do not provide the same strain relief as the phosphorus atoms in **1**, which results in larger bond angles at the carbon atoms.

While we have not studied the isomers of **1** comprehensively, it should be the lowest energy structure for $P_8(C{=}C)_6$, since all other isomers contain four-membered rings. In fact, **1**, as a minimally strained binary analogue of C_{20}, might be a very interesting ligand for metals in the creation of novel materials. Heterofullerene **1** is surely a worthy target for synthesis. Some binary phosphide cluster ions, including $C_nP_m^-$ were generated during laser ablation of red phosphorus, but few details are available.[18] More directed syntheses are hard to envision, although reactions such as that between $P(CF{=}CF_2)_3$[19] and $P(SiMe_3)_3$ might be worth investigating.

Acknowledgment. We thank the University of Georgia for supporting this work in Athens.

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[14] These values are to be compared to a calculated vertical IP for Ph_3P of 7.46 eV, compared with the experimental value of 7.8 eV. The vertical IEs of **1** and **2** are likely to be underestimated by a similar amount.

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