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Strain Energies in Homoatomic Nitrogen Clusters N_4, N_6, and N_8

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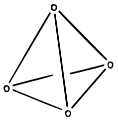
Strain energies and resonance energies can be obtained as the energy changes for appropriate homodesmotic reactions using *ab initio* calculated total energies as the energies of the reactants and products involved. Homodesmotic reactions conserve bond types and preserve valence environments at all atoms, requirements that favor the cancellation of basis set and electron correlation errors in the *ab initio* energies. In this paper we calculate strain energies and resonance energies for N_4, N_6, and N_8 clusters in a number of chemically significant but, for nitrogen, hypothetical structural forms. The nitrogen cluster strain energies are generally of the same order of magnitude as those of isostructural hydrocarbon clusters, and individual differences can be explained by using the ring strain additivity rule and recognizing the effect of the presence of lone pairs of electrons on nitrogen clusters but not on the hydrocarbons. Resonance energies of the nitrogen clusters are much smaller than those of the comparable aromatic hydrocarbons. The differences can be rationalized by considering the relative strengths of CC and NN single and double bonds. Strain and resonance energies of nitrogen clusters are compared with those previously reported for homoatomic clusters of phosphorus and arsenic. Trends through the series are remarkably similar, but strain energies for clusters from lower periods are progressively smaller. Strain and resonance have been important organizing concepts in organic chemistry for many years. Estimates of corresponding parameters for inorganic analogs are only now becoming available.

Introduction

There has been considerable recent interest in the homoatomic nitrogen clusters N_4, N_6, and N_8.[1−13] Reports of the preparation of N_6 gave motivation to theoretical investigations to predict the structure of the proposed N_6 molecule.[14,15] Because N_2 is exceptionally stable, any N_{2n} structures that might actually be realized could be expected to be thermodynamically unstable with respect to decomposition into nN_2 fragments. If any homoatomic nitrogen clusters turned out to be metastabilized behind reasonably high activation barriers, then those structures might be convenient and useful receptacles for the storage of energy. But there is a more fundamental reason to study the stabilities of nitrogen clusters. N_4, N_6, and N_8 are isoelectronic with the hydrocarbons $(CH)_4$, $(CH)_6$, and $(CH)_8$. Many of the concepts of chemical valence theory are based on the properties, known or anticipated, of these hydrocarbons. An appreciation of the similarities and differences among the properties of otherwise isoelectronic molecules should lead to a better grasp of the concepts we use to describe structure and bonding. In this paper we report calculations of strain energies of N_{2n} clusters and compare them with similarly calculated quantities for $(CH)_{2n}$ using the familiar chemical concepts of average bond energies, strain energies of individual rings, and resonance energies.

Consider the structures **1**−**11**. Glukhovtsev and Schleyer have reported geometry-optimized *ab initio* calculations for nitrogen clusters **1**−**8** at both RHF and MP2 levels of theory with the 6-31G* basis set.[2,3] Independently, Engelke has performed identical calculations for **3** and **5**−**8**.[4,5] Leininger, Sherrill, and Schaefer have published calculations for **9**−**11** with a slightly different basis set.[6] In order to make comparisons among the whole series at the same levels of theory, we have carried out calculations for **9**−**11** at the RHF and MP2 approximations using the 6-31G* basis set. We have also performed calculations for several acyclic reference structures required for the estimation of strain and resonance energies as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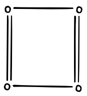
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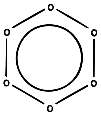
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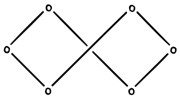
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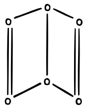
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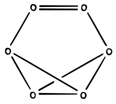
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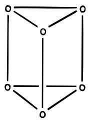
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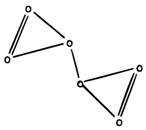
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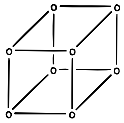
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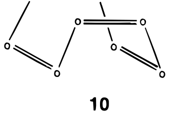
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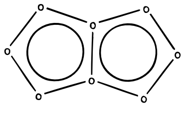
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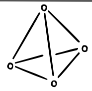
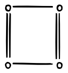
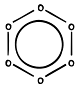
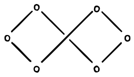
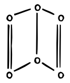
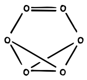
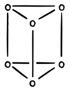
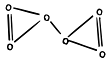
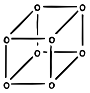
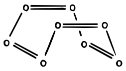
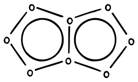
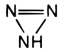
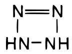
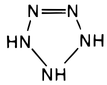
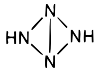
Table 1. Total Energies *E* (hartrees) for N_{2n} Structures,[a] and in parentheses, Relative Energies (kcal/mol) among Isomeric Structures of Equal *n*

Structure		RHF	MP2
1: T_d		−217.53385 (9.0)	−218.23543 (0)
2: D_{2h}		−217.54818 (0)	−218.21572 (12.4)
3: D_{6h}		−326.44896 (0)	−327.44209 (2.5)
4: D_2		*b*	−327.44606 (0)
5: C_{2v}		−326.37686 (45.2)	−327.38894 (35.8)
6: C_{2v}		−326.35456 (59.2)	*c*
7: D_{3h}		−326.23076 (136.9)	−327.25768 (118.2)
8: C_{2h}		−326.38095 (42.7)	−327.39534 (31.8)
9[a]**:** O_h		−434.94916 (226.4)	−436.30038 (233.6)
10[a]**:** D_{2d}		−435.24219 (42.5)	−436.58806 (53.0)
11[a]**:** D_{2h}		−435.30997 (0)	−436.67258 (0)

[a] This work: **9-11**; others from Refs 2-5. [b] The D_2 structure **4** optimizes to D_{6h}, **3**. [c] Upon optimization, **6** dissociates toward $N_2 + N_4$.

Table 2. Total Energies *E* (hartrees) of Acyclic Reference Structures and Cyclic Fragments, and in Parentheses, Relative Energies (kcal/mol) of Various Rotational Conformers

Structure		RHF	MP2
trans,C_{2h} — HN=NH		−110.00123	−110.34033
gauche,C_2 — H_2N–NH_2		−111.18352	−111.54331
C_3 — $N(NH_2)_3$		−221.18863	−221.89619
C_s — $HN(NH_2)_2$		−166.18458	−166.71744
trans,C_2 — H_2N-N=N-NH_2		−220.03344 (0)	−220.72508 (1.3)
cis,C_2 — H_2N-N=N-NH_2		−220.03012 (2.1)	−220.72715 (0)
cis,trans,cis,C_{2h} — HN=N-N=NH		−218.82802 (1.7)	−219.49820 (0)
all trans — HN=N-N=NH		−218.83079 (0)	
12: C_s		−163.78221	−164.29350
13: C_s		−218.78826	−231.46819
14: C_s		−273.80446	−274.65477
15: C_{2v}		−218.70944	−219.40838
16: C_1 — $H_2NN(NH)_2$		−219.98471	−220.69545

energy changes for homodesmotic reactions and for some cyclic molecules that occur as fragments in several of the nitrogen clusters.

Calculations

Table 1 collects the geometry-optimized total energies for **1**−**11** at both RHF and MP2 approximations with the 6-31G* basis set.[16] This basis set has a split or double-ζ valence shell and includes a set of d-type polarization functions on each nitrogen atom. For our calculations, we used the GAUSSIAN 92 program package.[17] Glukhovtsev and Schleyer and Engelke report that calculated vibrational frequences for **1**−**3** and **5**−**8** are all real for the RHF calculations, indicating that these structures are relative minima at this level of theory.[2−5] The twist-boat D_2 ring **4** flattens to the D_{6h} regular hexagon **3** on RHF optimization. But at the MP2 level, structures **3** and **6** are no longer minima.[3,5] On the MP2 energy surface, the D_2 ring **4** becomes a local minimum, 2.5 kcal/mol lower in energy than the planar hexagon **3**. The benzvalene structure **6** dissociates toward $N_2 + N_4$. Schaefer and co-workers, using a double-ζ plus polarization basis set that is somewhat better than 6-31G*, found that the three N_8 structures **9**−**11** are relative minima at both RHF and MP2 levels.[6] We assume these structures are also minima for the 6-31G* basis set.

The bicyclopropenyl hydrocarbon $(CH)_6$ **8** is known to have the trans C_{2h} structure,[18] and indeed, the N_6 analog has a minimum energy in this same conformation. One can imagine this structure as having lone pairs of electrons trans to each other at either end of the central N−N bond. The structure is reminiscent of hydrazine H_2N−NH_2, which appears to have a very shallow minimum in the trans,C_{2h} conformation but a still lower minimum in the gauche,C_2 conformation in which the nitrogen lone pairs are rotated approximately 90° apart — an arrangement said to be stabilized by the well-known *gauche effect*.[19−21] We thought bicyclopropenyl might also have a gauche conformation. A fixed-geometry energy surface scan for rotation from cis,C_{2v} ($\theta = 0°$) to trans,C_{2h} (180°) produced a curve with a maximum at $\theta = 0°$ and an extremely flat portion for $\theta > 120°$. Subsequent attempts at RHF optimization in this region led to the trans structure, but on the MP2 surface we found a gauche minimum at 130.5° — only 0.1 kcal/mol below the trans minimum reported by Glukhovtsev and Schleyer.[3] Such small energy differences between minima, as well as the minute barrier separating them, are well below the noise level of zero-point vibrational energies, which we have ignored in this study.

At this point, it is interesting to compare the relative energies of $(CH)_{2n}$ and N_{2n} isomers. Hess and Schaad found that $(CH)_4$ tetrahedrane **1** is higher in energy than cyclobutadiene **2** by 23−27 kcal/mol.[22] Using the same 6-31G* basis set, Glukhovtsev and Schleyer found N_4 isomers **1** and **2** to be much closer together, with **2** above **1** by 12.5 kcal/mol at the MP2 level.[2] Schulman and Disch published the energies of the valence isomers of benzene $(CH)_6$, **3** and **5**−**8**, calculated with the 6-31G* basis set.[23] For both sets of isomers, $(CH)_6$ and N_6, the range of relative energies is about the same, 120−130 kcal/mol, with the hexagonal ring **3** (or **4**) being the lowest in each set. A notable order difference between the two sets is the position of the bicyclopropenyl isomer **8**, which is the highest energy $(CH)_6$ isomer but the second most stable structure among N_6 isomers, ∼35 kcal/mol above **3** or **4**.

Table 2 contains the total energies of the acyclic structures involved in the homodesmotic reactions to be described in the next section. Also in Table 2 are the energies of several cyclic structures that serve as models in the discussion of strain energies of larger N_{2n} clusters. For these hydrogen-containing reference structures, we used the 6-31G** basis set, which includes a set of three p-type polarization functions

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(16) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(17) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92,* Revision C.4; Gaussian Inc: Pittsburgh, PA, 1992.

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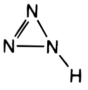
(23) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 5059.

for each hydrogen atom as well as the d-type polarization functions on the nitrogens. At both RHF and MP2 levels we find that planar, trans HN=NH is more stable than the planar, cis isomer and that H_2N-NH_2 is most stable in the gauche conformation compared to the trans or cis form. The situation is more complicated for N_4H_4 and N_4H_2. At the RHF level, $H_2N-N=N-NH_2$ is more stable in the trans,C_2 conformation than in the cis,C_2 by 2.1 kcal/mol, while at the MP2 level the cis conformation is more stable than trans by 1.3 kcal/mol. With the RHF approximation, HN=N−N=NH in the planar, all-trans arrangement is more stable than the cis,trans,cis chain by 1.4 kcal/ mol, but with MP2, the planar, cis,trans,cis chain is more stable than the corresponding gauche conformation by 0.4 kcal/mol. Structures **5**, **6**, and **8** contain fragments resembling **12**−**15**. Since the strain energies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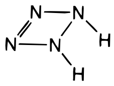
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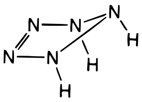
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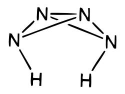
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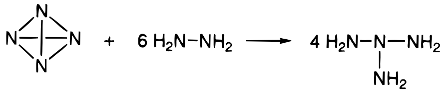
of these fragments are useful in rationalizing the strain energies of the larger homoatomic clusters, we have performed *ab initio* calculations for them in the specific conformations illustrated and with restricted symmetries: C_s for **12**−**14** and C_{2v} for **15**. Total energies appear in Table 2.

Strain Energies and Resonance Energies

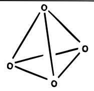
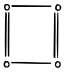
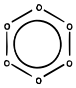
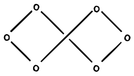
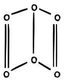
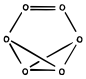
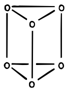
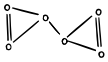
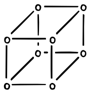
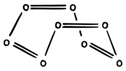
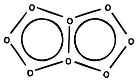
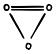
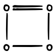
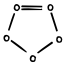
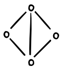
Equation 1 converts tetrahedral N_4 **1** into the pyramidal but acyclic product $N(NH_2)_3$. This reaction is said to be *homodesmotic* in that it conserves numbers of N−N and N−H bonds


(1)

and preserves the valence environment around each nitrogen atom.[24] Since bond types are conserved, the bond additivity model predicts an energy change of zero for eq 1. But we recognize that the 60° bond angles at each nitrogen in N_4 are severely displaced from the 109.5° angles preferred by sp^3-hybridized nitrogen, making tetrahedral N_4 highly strained. The resulting product $N(NH_2)_3$, with NNN angles of 110.0°/109.2° (RHF/MP2), is presumably unstrained. Therefore, we anticipate that the reaction will actually be exothermic by an amount that we can attribute to the *strain energy* of tetrahedral N_4. We calculate the energy change for eq 1 using *ab initio* calculated total energies of reactants and products from Tables 1 and 2. As expected, the reaction is exothermic. The negative energy change is reported as a positive strain energy in Table 3. Comparable homodesmotic reactions can be written to include **7** and **9**.

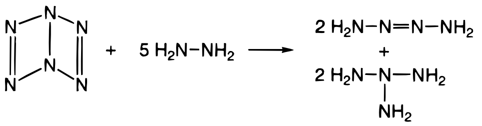
Because eq 1 preserves atomic valence environments as well as bond types, we can hope that basis set and electron correlation energy errors inherent in the calculations may largely cancel when we take differences among *ab initio* calculated energies.[25] Experience with a number of related systems indicates that this assumption is a good one.[26−30]

Table 3. Calculated Strain and Resonance Energies (kcal/mol) for Homoatomic Nitrogen Clusters, Various Structural Reference Fragments, and Their Hydrocarbon Analogs

		Strain or Resonance Energy	
Structure		Nitrogen (RHF/MP2)	Hydrocarbon
1: T_d		75.0 / 56.1	$129^{a,b}$ 137^{b} 140^{c} 141^{d}
2: D_{2h}		95.2 / 95.4	
3: D_{6h}		24.9 / 19.8	-24.7^{e}
4: D_2		— / 17.3	—
5: C_{2v}		93.9 / 88.6	63.6^{f}
6: C_{2v}		93.3 / —	81.3^{f}
7: D_{3h}		156.5 / 144.1	145.3^{d} 148.9^{f}
8: C_{2h}		91.4 / 84.6	107.2^{f}
9: O_h		224.4 / 219.4	158.6^{d}
10: D_{2d}		98.8 / 92.8	2.1^{h}
11: D_{2h}		−23.8 / −20.1	-43^{i}
12: C_s		43.2 / 40.5	54.5^{j}
13: C_s		40.0 / 40.1	30.6^{j} 34.0^{j}
14: C_s		30.5 / 32.3	6.8^{j} 6.9^{j}
15: C_{2v}		74.9 / 64.2	66.5^{j}

[a] Ref 32. [b] Ref 35. [c] Ref 33. [d] Ref 34. [e] Ref 31. [f] Ref 23. [g] Ref 38. [h] Ref 36, calculated from experimental heats of formation given therein. [i] Ref 45, but see text. [j] Ref 40.

Equation 2 is a homodesmotic reaction that converts the Dewar benzene structure **5** into acyclic products. We include it here to demonstrate the disposition of the double bonds and


(2)

sp^2-hybridized nitrogens from **5** to the product $H_2N-N=N-NH_2$. Analogous reactions involve **2**, **6**, **8**, and **10**.

Exothermic energy changes are reported as positive strain energies in Table 3. In calculating strain energies with eq 2, we used the lowest energy conformer of the $H_2N-N=N-NH_2$ product, which is different under RHF and MP2 approximations. Because of the chemical significance of the benzvalene structure **6**, we include its strain energy from RHF calculations in Table 3. No corresponding MP2 result is possible because **6** is not a minimum on this surface, even under constraints of C_{2v} symmetry.

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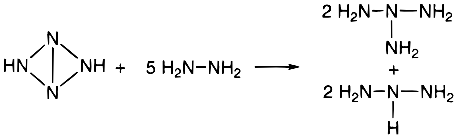
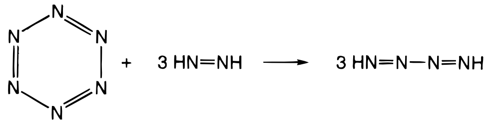
(24) George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1036. George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Ibid.* **1976**, 1222. George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.
(25) Disch, R. L.; Schulman, J. M.; Sabio, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1904.
(26) Zhao, M; Gimarc, B. M. *J. Phys. Chem.* **1993**, *97*, 4023.
(27) Warren, D. S.; Gimarc, B. M. *J. Phys. Chem.* **1993**, *97*, 4031.
(28) Gimarc, B. M.; Zhao, J. *J. Phys. Chem.* **1994**, *98*, 1596.
(29) Zhao, M.; Gimarc, B. M. *J. Phys. Chem.* **1994**, *98*, 7491.
(30) Gimarc, B. M.;. Zhao, M. *Phosphorus, Sulfur, Silicon* **1994**, *93−94*, 231.

Homodesmotic reactions that give strain energies of hydrogenated reference structures **12**−**15** involve the product $H_2N(NH)NH_2$, the structure and energies of which we have reported previously.[29] For convenience, we recall those energies in Table 2. Equation 3, including the bicyclobutane butterfly **15**, is typical of the homodesmotic reactions for this set of fragments.


(3)

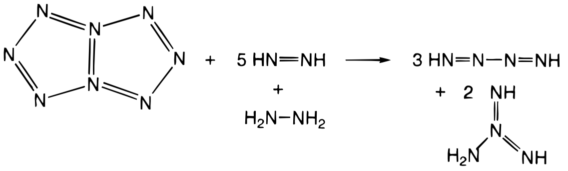
Equation 4 is the homodesmotic reaction involving the planar hexagonal structure **3**, drawn here as one of its Kekulé structures with alternate single and double bonds to emphasize the transfer of those bonds to the conjugated product HN=N−N=NH and the conservation of bond types.[31]

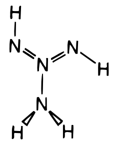

(4)

Of course, geometry-optimized calculations show that the planar hexagon prefers a regular structure of 6 equivalent NN bonds of length intermediate between normal NN single and double bonds, not the arrangement in the Kekulé benzene structure in eq 4. The conjugated product HN=N−N=NH is included to allow the possibility for the transfer of the effects of π electron delocalization from the ring **3** to product. If we can assume N_8 cyclooctatetraene **10** to be the model of a structure with nonconjugated single and double bonds (MP2: 1.429 and 1.267 Å, respectively), then NN single and double bonds in HN=N−N=NH (1.522 and 1.242 Å, respectively) show little conjugation. Compare these values with the N⋯N "aromatic" bond in **3**, 1.337 Å. Thus, the homodesmotic requirement of conservation of bond types does not strictly hold for eq 4. The 120° interior angles in **3** are exactly those required by sp^2-hybridized nitrogen, making **3** completely free of strain. Furthermore, from our experience with benzene $(CH)_6$, the 6 electrons delocalized around the N_6 ring in π MOs are expected to confer an added stability normally described as aromatic or resonance stabilization. Equation 4 should be endothermic by an amount called the *resonance energy*. Indeed, for the reaction that parallels eq 4 but involves $(CH)_6$ benzene and appropriate hydrocarbon reactants and products, Hess and Schaad found the energy change to be endothermic by 24.7 kcal/mol.[31] But with nitrogen compounds, Glukhovtsev and Schleyer found eq 4 to be exothermic by 20 kcal/mol, indicating that N_6 **3** is less stable than expected.[3] Since we report (destabilizing) strain energies as positive quantities, Table 3 lists the destabilizing resonance energy of **3** as positive also, while the stabilizing resonance energy of $(CH)_6$ benzene is negative. In calculating energy changes for eq 4, we used the lowest energy conformer of HN=N−N=NH; these are different for RHF and MP2 results.

The cyclobutadiene analog N_4 **2** deserves special consideration. Glukhovtsev and Schleyer found that **2** has a planar, rectangular structure of alternate single and double bonds (MP2: 1.542 and 1.287 Å, respectively), not a system of four equivalent aromatic NN bonds.[2] The 90° angles in **2** are much smaller than the preferred 120° angles for sp^2-hybridized nitrogen, suggesting destabilization by strain. Therefore, we used a reaction similar to eq 2 for **2**, rather than one related to eq 4, to give the cyclobutadiene strain energy shown in Table 3.

We propose eq 5 as a homodesmotic reaction involving **11**, the N_8 analog of the pentalene dianion. It is not possible to draw a classical structure for **11**. The illustration included here has 5 bonds around each of the two nitrogens that form the common edge of the two fused pentagons. One can imagine each of these nitrogens as having a pair of electrons in a p AO perpendicular to the molecular plane, while each of the other 6 nitrogens has only a single electron in its perpendicular p AO for a total of 10 electrons in the π electron system of **11**. The product $H_2NN(NH)_2$ is isoelectronic with the trimethylenemethyl dianion $C(CH_2)_3^{2-}$, a planar structure with a system of 6 π electrons. $C(CH_2)_3^{2-}$ has been variously described as being stabilized by cross conjugation, Y-delocalization, and even Y-aromaticity.[32,33] Our low-energy conformation for $H_2NN(NH)_2$ is **16**, in which the $-NH_2$ group is pyramidal and the four nitrogens are slightly noncoplanar. Calculated single- and double-bond distances in **16** (MP2: 1.421, 1.294, 1.295 Å) show little evidence of delocalization compared to those of cyclooctatetraene **10**. In contrast, our calculated N⋯N bond distances in **11**, ranging from 1.334 to 1.368 Å, indicate extensive delocalization. The energy change for eq 5 is endothermic, indicating resonance stabilization of **11**. The corresponding resonance energy given in Table 3 is negative. We know of no examples in which resonance energies of polycyclic aromatic hydrocarbons have been calculated using *ab initio* energies and homodesmotic reactions.


(5)


16

If RHF and MP2 estimates of strain energies and resonance energies are similar, then we can assume that correlation energies are effectively canceling in the energy differences for homodesmotic reactions. Except for the tetrahedron **1**, for which RHF and MP2 strain energies differ by 19 kcal/mol, and the triangular prism, where the difference is 12 kcal/mol, differences between estimates at the two levels of theory are 7 kcal/mol or less. In the following discussion, we use MP2-calculated energies throughout, except for the case of benzvalene **6**, for which only RHF results are available.

Table 3 displays estimates of $(CH)_{2n}$ cluster strain energies from a variety of sources[23,31,34−40] for comparison with results

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[31] Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7500.

[32] Klein, J.; Medlik, A. *J. Chem. Soc., Chem. Commun.* **1973**, 275.

[33] Gund, P. *J. Chem. Educ.* **1972**, *49*, 100.

[34] Maier, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 309.

[35] Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

[36] Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 329. Nagase, S. *Polyhedron* **1991**, *10*, 1299.

[37] Schulman, J. M.; Venanzi, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 4739.

[38] Eaton, P. E.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 724.

[39] Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

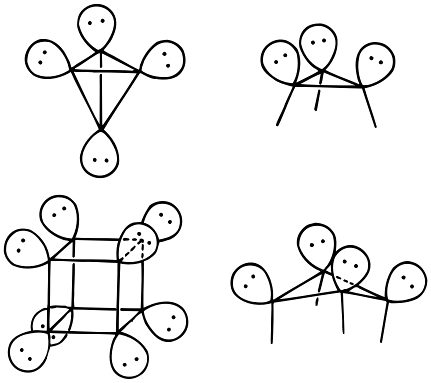


Figure 1. Disposition of lone pairs around tetrahedral N_4 and cubic N_8 and their corresponding $(NH)_3$ and $(NH)_4$ rings. The monocycles are not in their lowest energy conformations.

for N_{2n}. For the tetrahedron **1**, the N_4 cluster is much less strained than $(CH)_4$ in the same form. The N_6 and $(CH)_6$ triangular prisms **7** have comparable strain energies, and the N_8 cube **9** is much more strained than $(CH)_8$ cubane. These differences can be rationalized with the help of the *ring strain additivity rule*, which has been applied to hydrocarbons.[40−43] The rule notes that the strain energy of a polycyclic system is approximately equal to the sum of the strain energies of the individual component rings. The ring strain additivity rule can be applied in reverse to the nitrogen clusters. For example, tetrahedral N_4 **1** is composed of four 3-membered rings. Therefore, the strain energy of each 3-membered ring must be $56.1/4 = 14.0$ kcal/mol. Similarly, the cube **9** consists of six 4-membered rings, each of which must have a strain energy of $219.4/6 = 36.6$ kcal/mol. With these cluster component ring strain energies, we can use the additivity rule again to calculate the strain energy of the N_6 triangular prism **7** as composed of two 3-membered and three 4-membered rings. The strain energy of **7** should be $2 \times 14.0 + 3 \times 36.6 = 137.8$ kcal/mol, compared with 144.1 kcal/mol for **7** from Table 3.

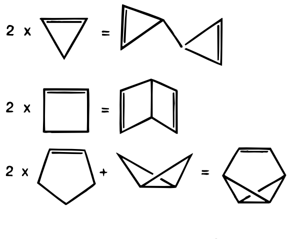
The strain energies of 3- and 4-membered rings derived above are not what one might have expected. Although its ring angles have expanded, the 4-membered ring has a larger strain energy than the 3-membered ring. However, this observation is consistent with our result for calculations of strain energies of $(NH)_n$ rings.[29] We have attributed the larger strain energy for the 4-membered nitrogen ring to larger numbers of nearest neighbor and next nearest neighbor lone pair−lone pair repulsions. The 3-membered ring has three sets of nearest neighbor lone pair−lone pair repulsions, while the 4-membered ring has four sets of nearest neighbor repulsions plus two sets of next nearest neighbor repulsions. The cycloalkanes $(CH_2)_n$ have no lone pairs at all, and the 4-membered ring is less strained than the 3-membered ring − although only slightly so. Figure 1 illustrates the arrangement of lone pairs in the N_4 tetrahedron **1**, the N_8 cube **7**, and the corresponding $(NH)_3$ and $(NH)_4$ cycloazines. The monocycles shown in Figure 1 are not the lowest energy conformers of these rings, but their strain energies can be calculated from the data in ref 28: 42.0 kcal/mol for the C_{3v} conformation of $(NH)_3$ and 57.8 kcal/mol for the C_{2v} conformation of $(NH)_4$. These quantities have the right order, 3-membered ring less strained than 4-, but the values are much larger than those we estimated above by decomposing strain energies of polyhedral clusters using the ring strain additivity rule: 14 kcal/mol for 3- and 37 kcal/mol for 4-. The smaller strain energies for the polyhedral cluster rings must be due to the averaging of nearest neighbor lone pair−lone pair repulsions over several adjacent faces. In the N_4 tetrahedron, 6 pairs of nearest neighbor lone pair−lone pair repulsions, one pair along each bond, are averaged over 4 rings or faces, or 1.5 pairs per 3-membered ring. In the N_8 cube, 12 nearest neighbor sets of lone pair−lone pair repulsions are averaged over 6 rings, or 2.0 sets per 4-membered ring. Lone pair repulsions in $(NH)_3$ and $(NH)_4$ are confined to the individual rings.

Another effect might also make the cluster component ring strain energies smaller than those of the cyclic azines. Homodesmotic reactions for polyhedral clusters and individual monocycles involve different unstrained reference structures. The monocycles are converted into unbranched chains, but the polyhedral clusters become branched chains which may themselves be somewhat strained. Although NNN angles in these branched structures turn out to be very close to those required for sp^3 hybridization, the spatial disposition of nearest neighbor and next nearest neighbor lone pairs may not be in the optimum arrangements that are available in the unbranched chain. This effect would give polyhedral clusters smaller apparent strain energies, which would then make the cluster component ring strain energies smaller than values obtained for the monocycles.

For the cycloalkanes $(CH_2)_3$ and $(CH_2)_4$, strain energies derived from thermodynamic data are 28.3 and 27.4 kcal/mol, respectively.[39] These values are bracketed above and below by the cluster-derived strain energies of the 3- and 4-membered nitrogen cluster rings. Following the ring strain additivity rule, the cycloalkane ring strain energies give the following polyhedral cluster strain energies: $(CH)_4$, **1**, 113.2 kcal/mol; $(CH)_6$, **7**, 138.8 kcal/mol; $(CH)_8$, **8** 164.45 kcal/mol − results which are acceptable approximations to other estimates for the polyhedral hydrocarbons given in Table 3.

Now we are equipped to compare strain energies of polyhedral hydrocarbon and nitrogen clusters. For the tetrahedral structure **1**, N_4 has considerably less strain energy than $(CH)_4$ because of the smaller ring strain energy of the nitrogen 3-membered cluster ring compared to that of the hydrocarbon. The larger strain energy of the nitrogen 4-membered cluster ring gives the N_8 cube **9** higher strain energy than $(CH)_8$ cubane. In the N_6 triangular prism **7**, the larger strain energy of the nitrogen 4-membered ring offsets the smaller strain energy of the nitrogen 3-membered ring to give approximately equal strain energies for N_6 and $(CH)_6$ prisms.

For the hydrocarbons $(CH)_6$ **8**, **5**, and **6**, the ring strain additivity rule produces remarkably accurate estimates of strain energies expressed as combinations of strain energies of appropriate cycloalkene fragments.[40] Estimated values (in kcal/mol) are in essentially quantitative agreement with those from other sources (shown in brackets):



8: 2 × 54.5 = 109 [107.2]

5: 2 × (30.6; 34.0) = 61.2; 68.0 [63.6]

6: 2 × 6.8 + 66.5 = 80.1 [81.3]

Additivity rule estimates for the corresponding N_6 clusters show larger deviations from values (shown below in brackets)

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(40) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

(41) Benson, S. W. *Thermochemical Kinetics,* 2nd ed.; Wiley: New York, 1976.

(42) Kybett, B. D.; Carroll, S.; Natalis, P.; Bonnell, D. W.; Margrave, J. L.; Franklin, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 626.

(43) Gasteiger, J.; Dammer, O. *Tetrahedron* **1978**, *34*, 2939.

calculated directly as energy changes for homodesmotic reactions (Table 3):

$$\mathbf{8}: \quad 2 \times 40.5 = 81.0\ [84.6]$$

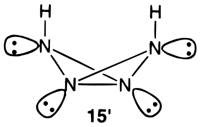
$$\mathbf{5}: \quad 2 \times 40.1 = 80.2\ [88.6]$$

$$\mathbf{6}: \quad 2 \times 32.3 + 64.2 = 128.8\ [93.3]$$

The estimates for **8** and **5** are within 10% of direct values, but that for **6** is unacceptably large. The failure of the additivity rule here must result from its failure to account for the averaging of lone pair−lone pair repulsions over the several adjacent faces of the benzvalene structure. If we replace the strain energy of the N_4H_2 bicyclobutane fragment by twice the strain energy of a 3-membered ring from N_4 tetrahedrane, we obtain:

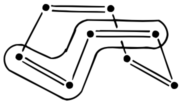
$$\mathbf{6}: \quad 2 \times 32.2 + 2 \times 14.0 = 92.6\ (93.3)\ \text{kcal/mol}$$

in excellent agreement with the directly calculated value. This result is consistent with the following analysis of the strain energy of the N_4H_2 bicyclobutane butterfly **15**. As illustrated by **15′** the butterfly structure has five sets of nearest neighbor lone pair−lone pair repulsions averaged over only two 3-membered rings, or 2.5 repulsions per ring compared with 3.0 repulsions per face for $(NH)_3$ and 1.5 repulsions per face for N_4 tetrahedrane **1** (see Figure 1). The directly calculated strain energy of **15** (64.2 kcal/mol) is less than twice the strain energy of $(NH)_3$ (2 × 42 = 84 kcal/mol) but much larger than twice the 3-membered cluster ring strain energy derived from tetrahedrane (2 × 14 = 28 kcal/mol).

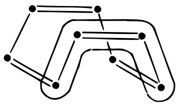


15′

The strain energy of N_8 cyclooctatetraene **10** (92.8 kcal/mol) is much larger than that of the corresponding hydrocarbon (2.1 kcal/mol; from the energy change of a homodesmotic reaction using experimental heats of formation[39]). Angle strain in N_8 **10** is probably relatively low because NNN bond angles (115.7°) are not far from optimal angles of 120° preferred by sp^2-hybridized nitrogen. Torsional displacements are significant. The cyclooctatetraene **10** exhibits two types of torsional or conformational displacements delineated by the envelopes in **10′** and **10″**, each of which involves a sequence of four nitrogen atoms. We can model these sequences with chain-type structures: HN═N−N═NH for **10′** and H_2N−N═N−NH_2 for **10″**. Energies of the most stable conformations of these chains appear in Table 2. Single-point calculations for these model chain structures assuming the cyclooctatetraene dihedral (76.6°) show that the conformation represented in **10′** is 8.1 kcal/mol higher than planar, C_{2h}, while that of **10″** is 6.5 kcal/mol above cis, C_2. Each conformational displacement occurs four times in **10**, for a total of 58.4 kcal/mol, accounting for roughly two-thirds of the strain energy of **10**. NNN angle strain provides an additional component to the total strain energy.



10′



10″

Average Bond Energies

We have used deviations from the bond additivity rule as the basis for estimating strain energies and resonance energies of nitrogen clusters. Ignoring the effects of strain and resonance, the bond additivity model assumes that we can estimate relative stabilities of molecules from the differences in the numbers of different kinds of bonds. Table 4 contains average bond energies of CC and NN single, double, and triple bonds.[44] Trends in bond energy with bond order for carbon and nitrogen are strikingly different.

Table 4. Average Bond Energies *D*(X−X) (kcal/mol)[a]

D(C−C)	83	*D*(N−N)	38
D(C═C)	146	*D*(N═N)	100
D(C≡C)	200	*D*(N≡N)	226

[a] Reference 44.

CC multiple bonds are weaker than the product of bond order and single-bond energy: *D*(C═C) = 1.76*D*(C−C); *D*(C≡C) = 2.41*D*(C−C). For nitrogen, the trend is reversed; multiple bonds are much stronger than the product of bond order and single-bond energy: *D*(N═N) = 2.63*D*(N−N); *D*(N≡N) = 5.95*D*(N−N). The $(CH)_4$ and N_4 isomers **1** and **2** each have six cluster bonds. For $(CH)_4$, average bond energies favor the tetrahedron **1**, with six single bonds, over the planar rectangle **2**, containing two double bonds and two single bonds, by 6 × 83 − 2(83 + 146) = 40 kcal/mol. But *ab initio* results of Hess and Schaad for $(CH)_4$ place **2** more stable than **1** by 23 kcal/mol at the MP2 level.[22] Therefore, the difference between strain energies of **1** and **2** must be 23 + 40 = 63 kcal/mol. If the strain energy of **1** is 141 kcal/mol (Table 3, from ref 34), then the strain energy of **2** is 141 − 63 = 78 kcal/mol. These quantities and relative stabilities are displayed in Figure 2. The relative stabilities of the corresponding N_4 isomers at the bond additivity level should be just the reverse of those for $(CH)_4$. For N_4 structures, **2** should be more stable than **1** by 2(38 + 100) − 6 × 38 = 48 kcal/mol. The *ab initio* results of Glukhovtsev and Schleyer[2] (Table 1; MP2 results) show that **2** is indeed more stable than **1**, but by only 12.4 kcal/mol. Thus, the strain energy of **2** must be larger than that of **1** by 48 − 12 = 36 kcal/mol. Calculated individual strain energies (Table 3) give a difference very close to that amount: 95 − 56 = 39 kcal/mol. Relative energies and strain energies of N_4 isomers appear in Figure 2.

The bond additivity model suggests that the larger the number of N═N double bonds a structure has, the more stable that structure should be. The exercise above for N_4 demonstrated that the rule worked because the difference in strain energies of the two structures was smaller than their bond energy differences. Indeed, the orders of relative stabilities of N_{2n} isomers established by *ab initio* calculations and displayed in Table 1 at least qualitatively follow the double-bond rule. Among the N_6 isomers, most stable is **3**, with three double bonds—at least in its Kekulé structure. Next come **5** and **8**, each with only two double bonds, followed by **6** (RHF level only), with one double bond. Highest of all N_6 isomers is **7**, with all N−N single bonds. It turns out that strain energies (or destabilizing resonance energy in the case of **3**) follow the same order: least for **3**; higher but nearly equal values for **5**, **6**, and **8**; and greatest for **7**. Among N_8 isomers, **11** is the most stable. Although a classical Lewis structure is not feasible for **11**, a compromise structure has as many as five N═N double bonds. Higher in energy is **10**, with four N═N double bonds. Highest is **9**, with all N−N single bonds.

Finally, consider N_6 **3**, with a destabilizing resonance energy of 20 kcal/mol, and N_8 **11**, which has a stabilizing resonance energy of −20 kcal/mol. For these two nitrogen clusters, the

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(44) Reger, D. L.; Goode, S. R.; Mercer, E. E. *Chemistry: Principles and Practice*; Saunders: New York, 1993.

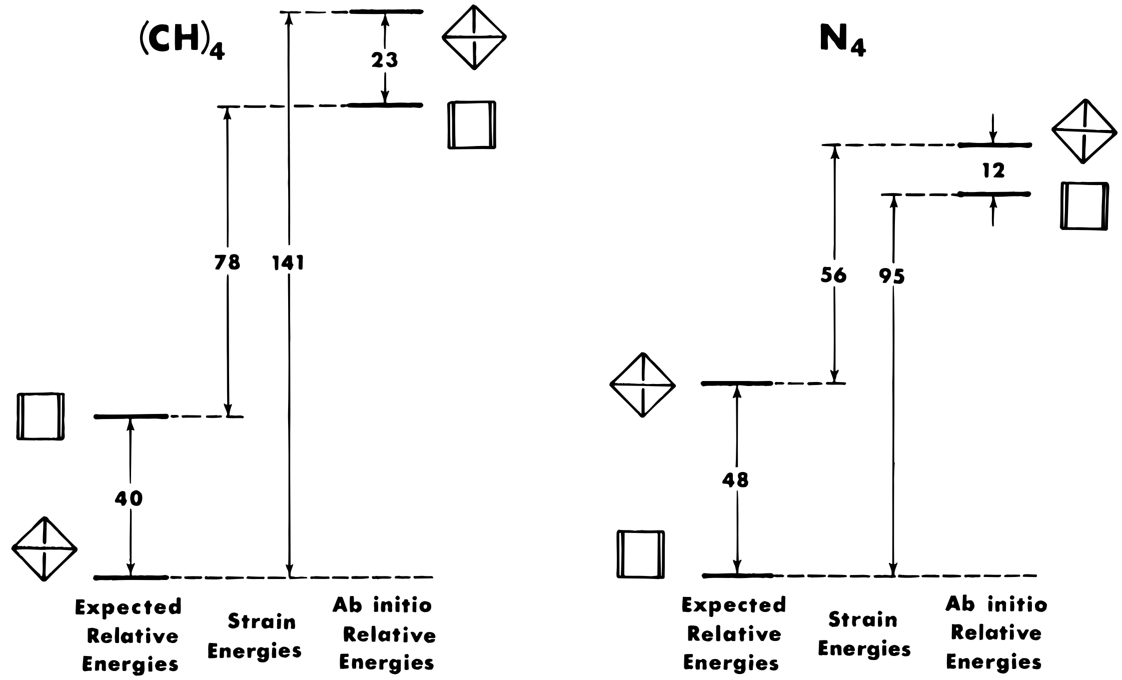


Figure 2. Comparisons of relative energies (kcal/mol) of tetrahedrane and cyclobutadiene forms of (CH)$_4$ and N$_4$. Expected relative energies are based on energy differences between single and double bonds (Table 4). *Ab initio* relative energies are results of *ab initio* calculations (Table 1; from refs 2 and 22). Strain energies are from Table 3.

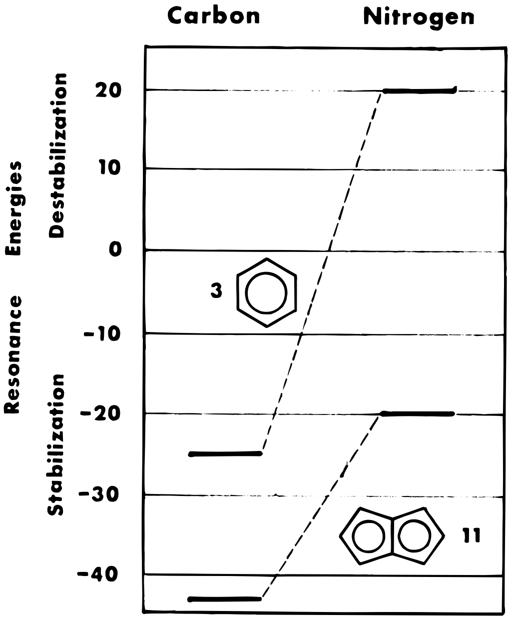
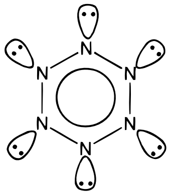


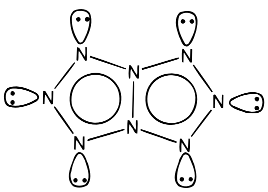
Figure 3. Resonance energies (kcal/mol) for aromatic hydrocarbon and nitrogen clusters. Resonance stabilization of the hydrocarbons is much greater than that for the hypothetical nitrogen analogs. The energy gap between **3** and **11** is much larger for nitrogen clusters than for the hydrocarbons.

obvious hydrocarbons for comparison are benzene (CH)$_6$ and the pentalene dianion $C_8H_6^{2-}$. Trinajstic and co-workers[45] have calculated topological resonance energies for both benzene (0.27β) and pentalene dianion (0.46β). These quantities are reported in units of an unspecified value of the resonance integral β. Equating 25 kcal/mol as the resonance energy for benzene (Table 3) and 0.27β gives a value of β that we can use to convert the topological resonance energy of pentalene dianion into 43 kcal/mol. Figure 3 compares the resonance energies of the hydrocarbons with those of the nitrogen clusters. The figure reveals two significant differences between hydrocarbon and nitrogen systems: (i) the hydrocarbons are much more effectively stabilized by resonance than are the nitrogen clusters and (ii) the difference between the resonance energies of N$_6$ **3** and N$_8$ **11** is twice that between hydrocarbons **3** and **11**. We propose the following arguments to rationalize these differences.

N=N double bonds are preferred to pairs of N−N single bonds, whereas pairs of C−C single bonds are favored compared to C=C double bonds. In whatever compromise is required in the formation of the delocalized structures of **3** and **11**, loss of N=N double-bond character is destabilizing in nitrogen clusters, whereas development of C−C single-bond character is stabilizing. The larger gap (compared to the case of hydrocarbons) between resonance energies of N$_6$ **3** and N$_8$ **11** may be a result of differences in numbers of nearest neighbor lone pair−lone pair repulsions. Each structure has six lone pairs as described in **3′** and **11′**, but **3′** has six sets of nearest neighbor lone pair repulsions while **11′** has only four sets. Therefore, we could expect a larger splitting between the resonance energies of N$_6$ **3** and N$_8$ **11** compared to benzene and the pentalene dianion, which have no lone pairs.



3'



11'

If the bond additivity model gives the relative energies of structures but lacking strain or resonance, then we can reconstruct the average bond energy relative energies by taking the *ab initio* calculated relative energies and subtracting out the strain or resonance energies—as we have done in Table 5, which contains two sections: an upper one devoted to RHF results and a lower part for MP2. In each section, the top line (A) sets out the calculated relative energies of **1**−**3** and **5**−**11** from

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[45] Gutman, I.; Milun, M.; Trinajstic, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692.

Table 5. Relative Stabilities (kcal/mol) of N_{2n} Clusters at the Level of the Bond Additivity Model

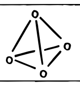
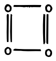
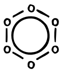
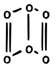
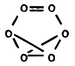
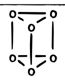
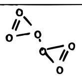
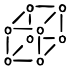
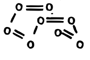
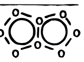
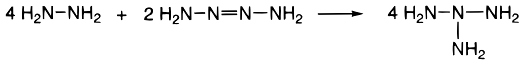
Structure										
RHF:										
A. Relative energy	9.0	0	0	45.2	59.2	136.2	42.7	226.4	42.5	0
B. Strain energy	75.0	95.2	24.9	93.9	93.3	156.5	91.4	224.4	98.8	−23.8
A–B. Bond additivity	−66.0	−95.2	−24.9	−48.7	−34.1	−19.6	−48.7	2.0	−56.3	+23.8
A–B+C. Renormalized bond additivity	29.2	0	23.8	0	14.6	29.1	0	58.3	0	80.1
MP2:										
A. Relative energy	0	12.4	0	33.3	—	115.7	29.3	233.6	53.0	0
B. Strain energy	56.1	95.4	19.8	88.6		144.1	84.6	219.4	92.8	−20.1
A–B. Bond additivity	−56.1	−83.0	−19.8	−55.3		−28.4	−55.3	14.2	−39.8	+20.1
A–B+C. Renormalized bond additivity	26.9	0	35.5	0		26.9	0	54.0	0	59.9

Table 1. The second line (B) recalls the corresponding strain or resonance energies from homodesmotic reactions from Table 3. The third line (A − B) presents the relative energies as they would have been without strain or resonance—*i.e.*, the relative energies at the level of the bond additivity model. To make these quantities easier to interpret, we add back in the most negative relative energy (−C) for each cluster size $2n$. These renormalized relative energies appear in the third line (A − B + C) in each section of Table 5. Ignore the delocalized structures **3** and **11**, which do not contain normal NN double and single bonds. At the RHF level, all structures **1**, **2**, and **5**−**10** differ in energy by an amount $m\Delta$, where m is the number of double bonds and $\Delta = D(\mathrm{N{=}N}) - 2D(\mathrm{N{-}N}) = 14.6$ kcal/mol at the RHF level. The same relationship holds at the MP2 level, with $\Delta = 13.45$ kcal/mol. Both values of Δ are smaller than the result 24 kcal/mol implied by the average bond energies in Table 4, but the sense is correct, $D(\mathrm{N{=}N}) > 2D(\mathrm{N{-}N})$, and the differences are remarkably consistent for clusters of different size—N_4, N_6, and N_8. If we take $D(\mathrm{N{=}N}) = 100$ kcal/mol from Table 4, and $\Delta = 14$ kcal/mol, an average of the two quantities derived above, then $D(\mathrm{N{-}N}) = (100 - 14)/2 = 43$ kcal/mol—a single-bond energy only 5 kcal/mol greater than the value in Table 4.

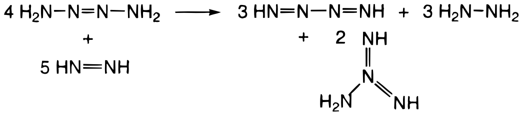
The consistency of isomer energy differences at the bond additivity level and their relations to bond energy differences is not accidental. Line A in Table 5 is the energy of a particular isomer R relative to that of the lowest energy isomer S at the *ab initio* level: A = R − S. This is the energy change for an isomerization reaction that converts S into R. Isomerization is an example of an *isogyric* reaction that conserves numbers of electron pairs — in these cases, number of bonds and lone pairs but not bond types and atomic valence environments. Line B contains the strain energy (or resonance energy) of isomer R as the energy change of a homodesmotic reaction, B = −(P − Q − R), where P is the sum of total energies of reaction products and Q is the sum of energies of supplemental reactants as in eqs 1−5. The minus sign before the parenthesis makes strain energies positive quantities. Line A−B represents the reduction of relative stabilities to those at the bond additivity level by subtracting the strain energy out of the *ab initio* relative energy (or adding back in the resonance energy): A − B = R − S + (P − Q − R) = P − Q − S. The total energy of isomer R cancels out of A − B. The next step is to compare relative energies of different isomers at the level of the bond additivity model. Suppose that isomer T has the lowest energy (lowest value of A − B) at the bond additivity level. Call the isomer energy difference at this level $m\Delta = (\mathrm{A} - \mathrm{B})_\mathrm{R} - (\mathrm{A} - \mathrm{B})_\mathrm{T} = \mathrm{P_R} - \mathrm{Q_R} - \mathrm{S} - (\mathrm{P_T} - \mathrm{Q_T} - \mathrm{S}) = \mathrm{P_R} - \mathrm{P_T} - (\mathrm{Q_R} - \mathrm{Q_T})$. The energy of isomer S, lowest among the *ab initio* energies, drops out and $m\Delta$ depends only on energy differences between products P and supplemental reactants Q for isomers R and T. Although energies of the isomers themselves have disappeared from the energy difference, their structural features have established the numbers and kinds of products and supplementary reactants that are included in the $m\Delta$ expression. For example, among N_4 clusters, R = **1**, T = **2**, and $m\Delta$ is the energy change for eq 6. This is an isogyric reaction that



$$4\,\mathrm{H_2N{-}NH_2} + 2\,\mathrm{H_2N{-}N{=}N{-}NH_2} \longrightarrow 4\,\mathrm{H_2N{-}N(NH_2){-}NH_2} \qquad (6)$$

converts two N=N double bonds into four N−N single bonds. From the bond additivity approximation, $m\Delta = 2[D(\mathrm{N{=}N}) - 2D(\mathrm{N{-}N})]$. If Δ is the expression within the brackets, then $m = 2$, the difference in number of double bonds between T and R. Therefore, in the paragraph above, our estimate of energy differences between a double bond and a pair of single bonds is the energy change for an isogyric reaction. Since neither bond types nor atomic valence environments are conserved, conditions for cancellation of basis set and correlation errors are less favorable than in homodesmotic reactions. Nevertheless, *ab initio* energies have been used to provide reasonable estimates of energy changes for isogyric reactions.[16]

Reactions resulting from comparisons involving the potentially aromatic structures **3** (or **4**) and **11** are more complicated than eq 6. As an example, eq 7 is the reaction associated with



$$4\,\mathrm{H_2N{-}N{=}N{-}NH_2} + 5\,\mathrm{HN{=}NH} \longrightarrow 3\,\mathrm{HN{=}N{-}N{=}NH} + 3\,\mathrm{H_2N{-}NH_2} + 2\,\mathrm{HN{=}N(NH_2)(NH)} \qquad (7)$$

the energy difference $m\Delta$ for R = **11** and T = **10**. At the bond additivity level, this corresponds to the conversion of two N−N single bonds into one N=N double bond—a process that should be exothermic. Instead, using MP2 energies from Table 2, the reaction is endothermic, $\Delta = 59.9$ kcal/mol. We can only conclude that those comparisons are not appropriate for potentially aromatic systems. In particular, the product $\mathrm{H_2NN(NH)_2}$ does not have a proper Lewis structure, and therefore its connection with the bond additivity model is tenuous. Furthermore, NN bond distance comparisons (MP2) in $\mathrm{H_2N{-}N{=}N{-}NH_2}$ (1.3969, 1.2687 Å) and $\mathrm{HN{=}N{-}N{=}NH}$ (1.5220, 1.2423 Å) indicate significant differences in bonds of the same type.

Conclusions

The N_{2n} clusters on the whole have strain energies that are comparable in magnitude to those of isostructural $(\mathrm{CH})_{2n}$

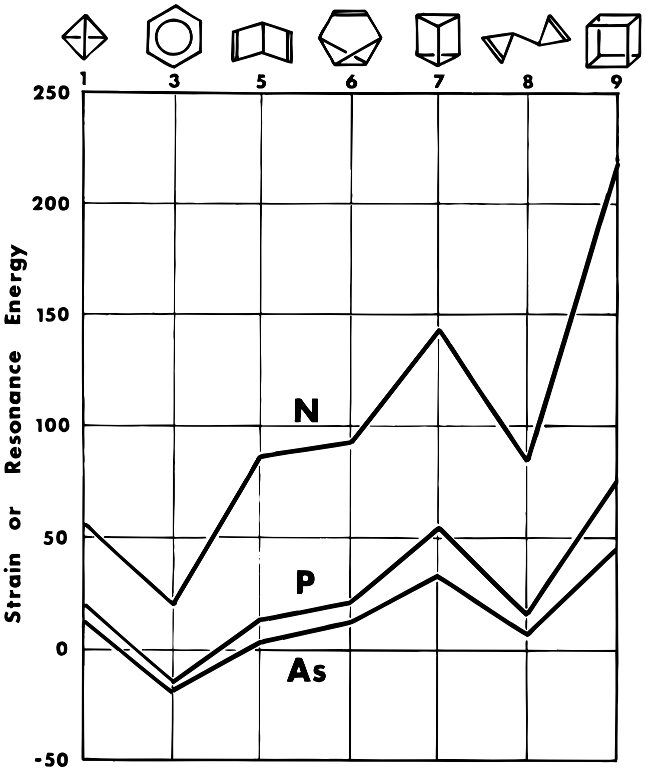


Figure 4. Strain energies (and resonance energies for **3**) of some group 15 homoatomic clusters. Strain energies decline with lower position in the group, but values for the nitrogen clusters are much larger than those for P and As.

analogs. Differences between hydrocarbons and nitrogen for particular structures can be rationalized in terms of strain energies of individual component rings and the presence of lone pairs of electrons on nitrogens but not on carbons. Resonance energies of aromatic-like nitrogen clusters are much smaller and, indeed, in the case of the hypothetical N_6 planar hexagon, even destabilizing compared to the corresponding aromatic hydrocarbons.

Strain and resonance have been important organizing concepts in organic chemistry for many years. Only recently have estimates of corresponding parameters for inorganic analogs become available. In contrast to hydrocarbon and nitrogen clusters, the homoatomic clusters of lower rows of the periodic table have much smaller strain energies. In earlier work, we used *ab initio* total energies and homodesmotic reactions to estimate strain energies and resonance energies of P_{2n} and As_{2n} clusters in the forms **1**, **3**, and **5**−**9**.[46−48] The trends in strain energies for these homoatomic clusters appear in Figure 4. Smaller strain energies and weaker bonds are anticipated trends as we move down a group in the periodic table and encounter atoms whose valence MOs are made from AOs of larger principal quantum number. The horizontal trends are remarkably similar. Although the resonance energy for N_6 **3** is destabilizing (and therefore a positive quantity in our convention) rather than stabilizing as one might have expected, the position of N_6 **3** in Figure 4 appears to be quite in accord with strain and resonance energies associated with other N, P, and As heteroatom clusters.

Among the clusters illustrated in Figure 4, only P_4 and As_4 are known molecules, but elements from the lower periods of group 15 form many homoatomic but ionic clusters—examples of which include P_4^{2-}, As_4^{2-}, P_5^{-}, P_6^{4-}, As_6^{4-}, P_7^{3-}, As_7^{3-}, P_{11}^{3-}, and As_{11}^{3-}. How strain energies and resonance energies affect the relative stabilities of these and other homoatomic clusters will be the subject of future studies.

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