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Besides N_2, What Is the Most Stable Molecule Composed Only of Nitrogen Atoms?[†]

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Polynitrogen molecules have been studied systematically at high levels of *ab initio* and density functional theory (DFT). Besides N_2, the thermodynamically most stable N_n molecules, located with the help of a newly developed energy increment system, are all based on pentazole units. The geometric, energetic, and magnetic criteria establish pentazole (**2**) and its anion (**3**) to be as aromatic as their isoelectronic analogues, e.g., furan, pyrrole, and the cyclopentadienyl anion. The bond lengths in **2** and **3** are equalized; both have large aromatic stabilization energies (ASE) and also substantial magnetic susceptibility exaltations (Λ). The C_s symmetric azidopentazole (**14**), a candidate for experimental investigation, is the lowest energy N_8 isomer but is still 196.7 kcal/mol higher in energy than four N_2 molecules. Octaazapentalene (**12**) with 10 π electrons also is aromatic. The D_{2d} symmetric bispentazole (**21**) is the lowest energy N_{10} minimum but is 260 kcal/mol higher in energy than five N_2 molecules. For strain-free molecules, the average deviation is ±2.6 kcal/mol between the DFT energies and those based on the increment scheme. The increment scheme also provides estimates of the strain energies of polynitrogen compounds, e.g., tetraazatetrahedrane (**8**, 48.2 kcal/mol), octaazacubane (**11**, 192.6 kcal/mol), and N_{20} (**27**, 294.6 kcal/mol), and is useful in searching for new high-energy−high-density materials.

Introduction

Can the potential of polynitrogen compounds as high-density−high-energy materials be realized? Since N_2 is likely to be much more stable than any higher nitrogen molecule, it is understandable that the pertinent experimental investigations[2−7] are far outnumbered by the theoretical literature.[7−24] However, none of the theoretical studies have been comprehensive and systematic. The present survey compares many N_n species and

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[†] We dedicate this paper to Prof. Dr. Rolf Huisgen (75th birthday) and to Prof. Dr. Ivar Ugi (65th birthday) in commemoration of their pioneering joint investigation of pentazoles 40 years ago.

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(27) The experimental dissociation energies (at 0 K) of the C−C (ethane),[28a] C=C (ethylene),[28b] and C≡C (acetylene)[28b] bonds are 87.6, 171.0 ± 1.2, and 228.8 ± 0.7 kcal/mol, respectively. The experimental values of the N−N (hydrazine),[28a] N=N (*trans* diimide),[28c] and N≡N (dinitrogen)[28a] bond dissociation energies are 65.4 ± 0.8, 122.1 ± 0.3, and 225.0 kcal/mol, respectively.

(28) (a) Calculated from the experimental data given in: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl 1. (b) Erwin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; Depuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750. (c) Biehl, H.; Stuhl, F. *J. Chem. Phys.* **1994**, *100*, 141.

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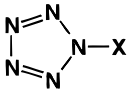
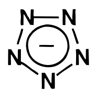
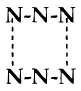
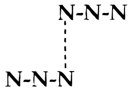
identifies pentazole derivatives as being the thermodynamically most stable polynitrogen compounds.

Pentazole derivatives were first prepared by Huisgen and Ugi;[2] by working under careful temperature control, they succeeded where earlier investigations had failed in reacting the azide anion, N_3^-, with diazonium ions, ArN_2^+. The aryl pentazole products readily lost N_2, but the dimethylanilino derivative **1** ($X = p$-$C_6H_4NMe_2$) was stable enough to allow an X-ray crystal structure determination.[3] While the parent pentazole, 2 ($X = H$), has never been prepared, Roberts et al.[4] mentioned the pentazole anion (**3**), N_5^-, as a possible intermediate in the ^{15}N scrambling reactions involving *p*-toluenesulphonyl azide with the azide ion. Other experimental attempts to obtain polynitrogen compounds also have involved N_3^- and/or the N_3 radical. A recent paper describes the observation of the N_6^- (**4**) radical anion,[5] and there are earlier reports on the possible preparation of a neutral N_6 species.[6] However, the latter probably involves an open chain NNN−NNN form, rather than a cyclic benzene-like structure.

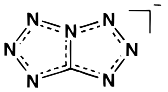

1 X = p-$C_6H_4NMe_2$; **2** X = H

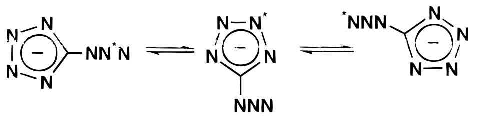

3 D_{5h}


4a


4b

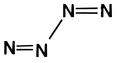
On the basis of theoretical, ^{15}NMR, and IR studies,[7] **5** (N_7C^-), isoelectronic with the pentalene dianion, was considered as an intermediate in the interamolecular isotope-exchange process, **6** → **6a** → **6b**.

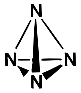

5


6 6 a 6 b

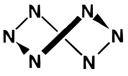
Many polynitrogen and nitrogen-rich systems have been investigated extensively at various levels of theory, e.g., N_4,[8−11] N_4^+,[12] N_5^-,[13−15] N_5H,[14,15] N_6,[10,17,18b,19] N_8,[7,10,18,20] N_{10},[21b] N_{20},[20,22,23] the set of CN_7^-, $N(N_3)_3$, $HN(N_3)_2$, $N(N_3)_2^-$ molecules and anions,[24] and carbon/nitrogen cubanoids $[(CH)_{8-n}N_n]$.[18c]

At high theoretical levels, the lowest energy N_4 species has the triplet open-chain structure (**7**).[11] The lowest energy cyclic N_6 minimum is not the benzene-like D_{6h} **9** but the D_2 twist-boat form **10**.[17] Furthermore, the most stable isomer of N_6 has an open-chain NNN−NNN (**10a**) structure.[17] Therefore, there is no structural analogy between benzene, $(CH)_6$, and hexazine, N_6.

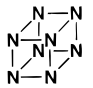

7 C_{2h} (^3B_u)

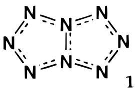

8 T_d

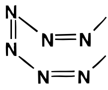

9 D_{6h}

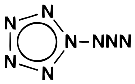

10 D_2

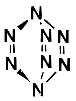
Calculations of N_8 isomers, e.g., octaazacubane (**11**), octaazacyclooctatetraene (**12**) and octaazapentalene (**13**) also have been carried out.[7,10,18,20] While all three are minima, **12** has the lowest energy.[7,20] The possible aromatic character[29,30] of **12** which has 10 π electrons may contribute to its stability.[20]

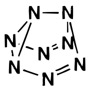

11, O_h

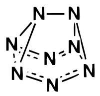

12, D_{2h}


13, D_{2d}


14, C_s

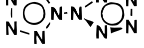

15, D_{3h}


16, C_s

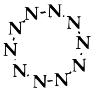

17, C_{2v}

NN-NN-NN-NN

18, C_{2h}

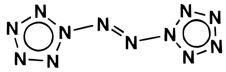

21, D_{2d}

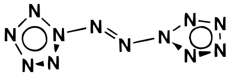

22, D_2


23, D_{10h}

NN-NN-NN-NN-NN

24, C_{2h}


26 a, C_{2h}


26 b, C_{2h}

Organic aromatic compounds are generally more stable than their nonaromatic, open-chain analogues due to the cyclic electron delocalization.[29−31] Polynitrogen or nitrogen-rich systems are known to behave differently. For example, octaazapentalene (**12**) was calculated at HF/4-31G[7] to be 26.2 kcal/mol *higher* in energy than the open-chain isomer **18**; however, azidopentazole (**14**) is 6.6 kcal/mol lower in energy than **18**.

In this paper, we first compare our density functional theory (DFT) computational data on N_4 and N_6 systems with recent high-level *ab initio* results[11,17] and then discuss a set of N_8 isomers. These include **11**−**13** and azidopentazole (**14**), octaazabarrelene (**15**), and octaazasemibullvalene (**16**, **17**) as well as the all-*trans* open-chain form (**18**) in order to identify aromatic compounds which may be tangible targets for experimental study. In addition, we provide evidence for the aromaticity of pentazole (**2**), the pentazole anion (**3**), and azidopentazole (**14**) as well as octaazapentalene (**12**). The aromatic character of pentazole-ring systems also is reflected in the dipentazole molecule (N_{10}, **21**); this is compared with its monocyclic (**22**, **23**) and open-chain (**24**) systems. The N_{12} isomers (**26a** and **26b**) also have two aromatic pentazole rings. Furthermore, we have developed an energy increment scheme for the polynitrogen and nitrogen-rich systems. This was used to predict the energies of addition N_n molecules and to estimate the strain energies of tetraazatetrahedrane (**8**), octaazacubane (**11**), and dodecahedral N_{20} molecule (**27**).

Computational Details

Ab initio and DFT computations were carried out with the Gaussian 92/DFT program package.[32] Geometries were optimized using analytic

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Table 1. Total (hartrees) and Relative Energies (kcal/mol) of Tetraazatetrahedrane (**8**), Tetrazete (**8a**, D_{2h}), and Open-Chain (C_{2h}) Structure (**7**) as Well as Two Nitrogen Molecules Calculated at the Becke3LYP/6-311+G(3df) Level and Using G2 Theory

	$E_{\text{tot.}}$[a]	ZPVE (NIMAG)[b]	E_{rel}[c]	E_{rel}(G2)[d]
tetraazatetrahedrane, **8**	−218.845 50	8.36 (0)	182.8	177.4
tetrazete, D_{2h} (**8a**)	−218.846 00	8.95 (0)	183.1	180.1
open-chain N_4 triplet, **7**	−218.904 93	7.34 (0)	144.5	156.5
two N_2	−219.134 74	7.02(0)	0	0

[a] At Becke3LYP/6-311+G(3df). [b] At Becke3LYP/6-31G*. [c] At Becke3LYP/6-311+G(3df) + ZPVE (Becke3LYP/6-31G*). [d] G2 values taken from ref 40.

gradient techniques[33] at HF/6-31G*, MP2(fu)/6-31G*,[34,35] Becke3LYP/6-31G*,[36] and at Becke3LYP/6-311+G* for N_8 as well as at Becke3LYP/6-311+G(3df) for estimating the strain energy of N_4 (T_d, **8**). Harmonic vibrational frequencies were computed at HF/6-31G*, Becke3LYP/6-31G* and, in some cases, at Becke3LYP/6-311+G** levels. Relative energies were obtained at HF/6-31G*, MP2(fu)/6-31G*, Becke3LYP/6-31G*, and Becke3LYP/6-311+G* levels (only for N_8), as well as at Becke3LYP/6-311+G(3df). Single-point Becke3LYP/6-311+G**//Becke3LYP/6-31G* energies were used to evaluate the energy increments. Spin-projected PMP2 energies are given for triplet states.[37] Magnetic properties were computed using the IGLO method with the basis II and Becke3LYP6-31G* geometries (IGLO/II//Becke3LYP/6-31G*).[38]

Results and Discussion

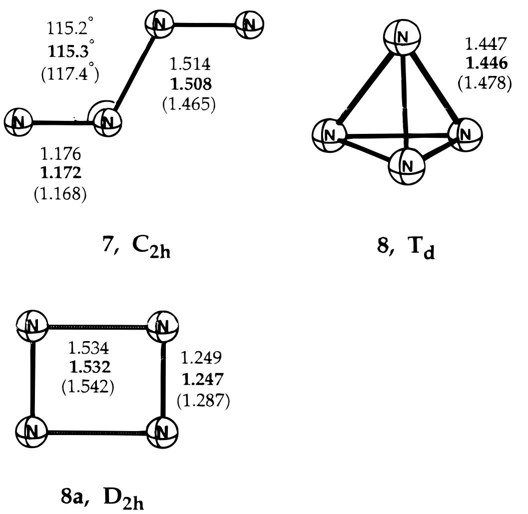

Figure 1. Optimized geometries for N_4 isomers (**7**, **8**, and **8a**) at Becke3LYP/6-31G*, Becke3LYP/6-311+G* (in bold), and MP2(fu)/6-31G* (in parentheses).

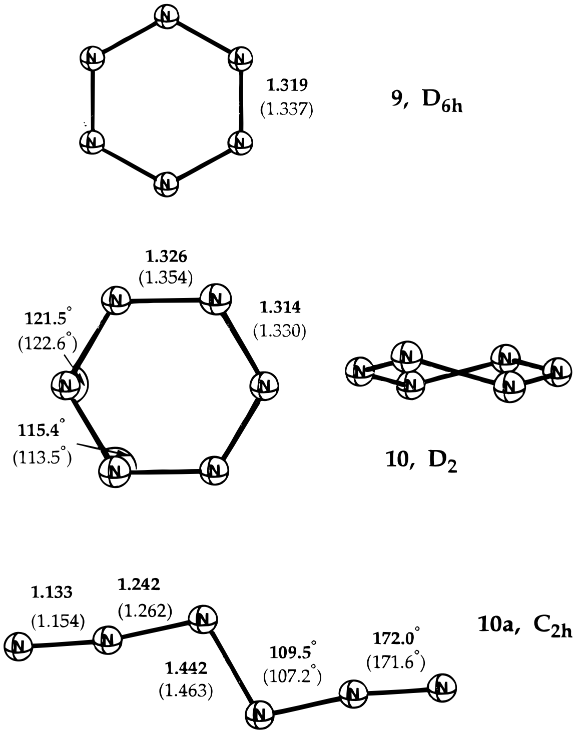

Figure 2. Optimized geometries for N_6 isomers **9**, **10**, and **10a** at Becke3LYP/6-311+G* (in bold) and MP2(fu)/6-31G* (in parentheses).

(A) N_4 and N_6 Isomers. Since N_4 and N_6 isomers have been considered in detail in recent publications,[11,17] only evaluation of performance of our DFT computations and comparison of some properties with these of larger N_n molecules are relevant to our present study. The relative energies of the N_4 isomers calculated at Becke3LYP/6-311+G(3df) agree well with those using G2 theory (which approximates QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31G(d) + HF/6-31G(d) scaled zero-point energies and higher level corrections, Table 1).[39,40] Furthermore, the Becke3LYP N_4 (**8**) → $2N_2$ energies of dissociation, computed with various basis sets, converge to the G2 value (Table 2).

In agreement with the MP4/6-311+G* results,[11] the open-chain C_{2h} triplet **7** is the lowest energy N_4 isomer at Becke3LYP/6-311+G(3df). At Becke3LYP/6-31G*, **7**, **8**, and **8a** are minima (Table 1). For N_6, both **10** and the open-chain NNN−NNN isomer (**10a**) are minima, but **9** has two imaginary frequencies ($\nu(e_{2u}) = 272i$ cm^{-1}) at Becke3LYP/6-311+G*. Compound **10** (D_2) is 32.1 kcal/mol higher in energy than **10a** but is 1.5 kcal/mol lower in energy than **9** (D_{6h}) at Becke3LYP/6-311+G* + ZPE(Becke3LYP/6-311+G*) (Table 3).

Table 2 shows that the Becke3LYP/6-311+G* + ZPE (Becke3LYP/6-31G*) data provide reliable estimates of the dissociation energy of N_4 (T_d) into two N_2. The bond lengths (Figure 1) at the DFT and MP2 levels agree within 0.04 Å or better.

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Table 2. Energies (kcal/mol) of the Dissociation of Tetraazatetrahedrane, N_4 (**8**), into Molecular Nitrogen Calculated at Various Computational Levels

computational levels	E_{diss}	E_{diss}/N_2
Becke3LYP/6-31G* + ZPE(Becke3LYP/6-31G*)[a]	172.6	86.3
Becke3LYP/6-311+G* + ZPE(Becke3LYP/6-31G*)[a]	180.9	90.5
MP4SDTQ/6-31+G*//MP2/6-31G* + ZPE(MP2/6-31G*)	188.5[c]	94.3
QCISD(T)/6-311+G*//MP2/6-31G* + ZPE(MP2/6-31G*)	187.9[c]	94.0
MP4SDTQ/6-311G(2df)//MP2/6-31G* + ZPE(MP2/6-31G*)	178.8	89.4
Becke3LYP/6-311+G(3df) + ZPE(Becke3LYP/6-31G*)	182.8	91.4
G2	177.4[d]	88.7

[a] Total energies (hartrees) for N_4 (**8**): −218.775 36 (Becke3LYP/6-31G*) and −218.827 77 (Becke3LYP/6-311+G*). [b] For N_4 (**8**), ZPE(MP2/6-31G*) = 7.53 kcal/mol (unscaled; scaling factor[41] is 0.9646). [c] Taken from ref 11. [d] Taken from ref 40.

Table 3. Energies (kcal/mol) of Dissociation of the N_6 Lowest Energy Cyclic (**10**, D_2) and Open-Chain (**10a**, C_{2h}) Isomers into Molecular Nitrogen, Calculated at Various Computational Levels

structure	computational level	ΔE	ΔE per N_2
N_6, D_2	MP4SDTQ/6-31G*//MP2/6-31G* + ZPE(MP2/6-31G*)	214.3[a]	71.4
N_6, D_2	Becke3LYP/6-311+G* + ZPE(Becke3LYP/6-311+G*)[b,c]	195.5	65.2
N_6, C_{2h}	MP4SDTQ/6-31G*//MP2/6-31G* + ZPE(MP2/6-31G*)	188.3[a]	62.8
N_6, C_{2h}	Becke3LYP/6-311+G* + ZPE(Becke3LYP/6-311+G*)	163.4	54.5

[a] Taken from ref 17. [b] The ZPE for N_6 (D_2), N_6 (C_h), and N_2 are 14.0, 15.1, and 3.5 kcal/mol, respectively, at Becke3LYP/6-311+G*. [c] The N_6 planar D_{6h} structure **9** (R_{NN} = 1.319 Å) is a second-order saddle point and has a 2.6 kcal/mol higher energy than the D_2 twist-boat structure **10** at Becke3LYP/6-311+G*. For **9**, ZPE(Becke3LYP/6-311+G*) is 13.5 kcal/mol.

Table 4. Total Energies (with Reverse Sign, in hartrees), Number of Imaginary Frequencies (NIMAG), and Zero-Point Vibrational Energies (ZPE, kcal/mol) for N_8 Structures Calculated at Various Computational Levels

	HF/6-31G*	ZPE(NIMAG)[a]	MP2(fu)/6-31G*	Becke3LYP/6-31G*	ZPE (NIMAG)[b]	Becke3LYP/6-311+G*
11, O_h	434.949 16	27.3 (0)	436.300 38	437.428 46	21.6 (0)	437.524 27
12, D_{2h}	435.309 97	27.6 (0)	436.672 58	437.776 43	23.7 (0)	437.886 47
13, D_{2d}	435.242 19	25.5 (0)	436.588 06	437.709 57	20.6 (0)	437.819 79
14, C_s	435.344 16	25.9 (1)	436.694 87	437.798 57	22.8 (0)	437.914 40
15, D_{3h}	435.215 67	25.2 (0)	436.580 98	437.691 35	18.7 (2)	437.799 18
16, C_s				437.653 11	19.9 (0)	437.757 95
17, C_{2v}				437.650 16	19.4 (1)	437.754 11
18, C_{2h} (^1A_g)	435.318 73	23.7 (0)	436.664 19	437.777 75	21.2 (0)	437.902 16
18a, C_2 (^3B)	435.324 51	17.6 (0)	(436.758 39)[c]			
four N_2	435.775 80		437.046 28	438.096 52	14.0 (0)	438.227 92

[a] At HF/6-31G*. [b] At Becke3LYP/6-31G*. [c] At UMP2/6-31G*, the C_2 symmetric **18** "collapses" into the N_4 C_{2h} triplet (^3B_u) and two N_2 upon geometry optimization; the total energy given is the PMP2 single-point energy at the HF geometry.

Table 5. Relative Energies (kcal/mol) for N_8 Isomers Calculated at Various Computational Levels

compounds	HF/6-31G* [a]	MP2(fu)/6-31G* [b]	Becke3LYP/6-311+G* [c]	Becke3LYP/6-31G* [d]
11, O_h	249.1	246.3	243.4	231.0
12, D_{2h}	23.3	14.9	18.4	14.8
13, D_{2d}	63.3	64.8	57.2	53.5
14, C_s [e]	0.0 (270.9)	0.0 (220.5)	0.0 (196.7)	0.0 (187.0)
15, D_{3h}	80.4	67.4	68.2	63.2
16, C_s			95.3	88.4
17, C_{2v}			97.2	89.7
18, C_{2h} (^1A_g)	14.0	17.7	6.1	11.5
18a, C_2 (^3B)	5.0	180.7[f]		

[a] At HF/6-31G* + ZPE (HF/6-31G*). [b] At MP2(fu)/6-31G* + ZPE (Becke3LYP/6-31G*). [c] At Becke3LYP/6-311+G* + ZPE (Becke3LYP/6-31G*). [d] At BeckeLYP3/6-31G* + ZPE (Becke3LYP/6-31G*). [e] The relative energy to four N_2 molecules are given in parentheses. [f] PMP2//UHF/6-31G* value relative to four N_2.

(B) N_8 Isomers. (1) Relative Stability and Geometries. Table 4 summarizes the computational data on N_8 isomers, obtained at various levels of theory. The relative energies are given in Table 5. The Becke3LYP/6-311+G* + ZPE (Becke3LYP/6-31G*) results are discussed; and data at other levels are given for comparison. The N_8 geometries optimized at various levels are given in Figure 3.

In agreement with the earlier computations, octaazacubane (**11**),[10] octaazapentalene (**12**),[7] and octaazacyclooctatetraene (**13**)[20] as well as the azidopentazole (**14**)[7] are minima at the Becke3LYP/6-31G* level. Octaazasemibullvalene (**16**, C_s) and the all-*trans* open-chain isomer (**18**, C_{2h}) also are minima. The C_{2v} **17**, as expected, is the transition structure for the degenerate Cope rearrangement in octaazasemibullvalene. The D_{3h} symmetric **15** is a second-order saddle point (two imaginary frequencies).

The Becke3LYP geometries for **11**−**13** agree well with the CCSD optimized parameters.[20] At Becke3LYP, the structural parameters[42] of the pentazole ring in azidopentazole (**14**) agree with the measured X-ray data.[3] Taken together with the computational results on the N_4 and N_6 molecules (see section A) gives us confidence in application of the Becke3LYP functional to calculations of larger N_n molecules.

The relative energies at Becke3LYP/6-311+G* + ZPE (Becke3LYP/6-31G*) for **12**, **13**, and **11** (0.0, 224.9, and 38.8 kcal/mol) are similar to those at CCDS/DZP (0.0, 198, and 35

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(42) For example, the NN bond lengths of 1.323−1.347 and 1.303−1.305 Å are very close to the measured 1.321−1.327 and 1.309 Å.

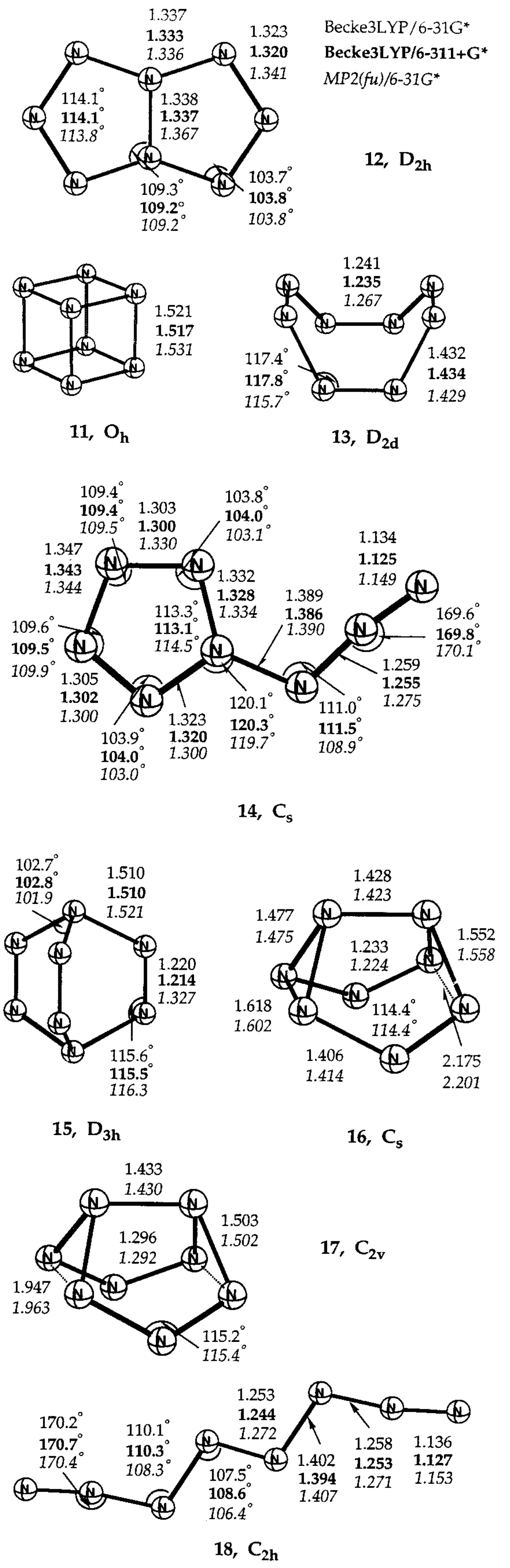

Figure 3. Optimized geometry parameters (bond lengths and bond angles are in angstroms and degrees, respectively) for N_8 isomers (**11**–**18**) at the Becke3LYP/6-31G*, Becke3LYP/6-311+G* (in bold), and MP2(fu)/6-31G* (in italics) levels.

kcal/mol, Table 5).[20] These reflect the aromatic character of **12** with its 10 π electrons. Bicyclic **12** may be compared with its aromatic isoelectronic hydrocarbon analogue, the pentalene dianion.[30,43,44] Both species have D_{2h} symmetry, in contrast to the neutral antiaromatic pentalene,[30] which is has a C_{2h} ground state geometry with alternating bond lengths.[45,46]

The computed activation energy for the degenerate Cope rearrangement in octaazasemibullvalene (**16**) is only 1.9 kcal/mol [Becke3LYP/6-311+G* + ZPE (Becke3LYP/6-31G*)] and is even lower than that of semibullvalene itself (4.1 kcal/mol, at MP2(fu)/6-31G* + ZPE (HF/6-31G*); the measured value is 4.8 ± 0.2 kcal/mol).[47]

Since the *trans* open-chain structure of N_6 is lower in energy than the *cis* form,[17] we only considered the *trans* open-chain N_8 isomer. At correlated levels (MP2 and Becke3LYP), singlet **18** is a minimum but the N_8 open-chain triplet structure (**18a**, a minimum at UHF/6-31G*) "collapses" into triplet N_4 and two N_2 during the geometry optimizations. The relative energy at PMP2 using the HF geometry of **18a** toward four N_2 is 180.7 kcal/mol.

The C_s symmetric azidopentazole (**14**) is the lowest energy N_8 isomer we have found, and this is true at various computational levels (Table 5). The relative energies of N_8 isomers **12**–**18** are listed in Table 5. Azidopentazole (**14**) is the most stable N_8 polynitrogen molecule but is still 196.7 kcal/mol higher than four N_2 molecules. A possible way to get **14** experimentally could be via the reaction between N_5Li (if this can be made) and the known N_3X (halides).[25]

(2) Aromaticity. Evidence from Geometric, Energetic, and Magnetic Criteria. Why is **14** more stable than the other N_8 isomers? Is aromaticity responsible? How aromatic is the parent pentazole molecule, N_5H (**2**)? The geometric, energetic, and magnetic criteria show that the isoelectronic analogues of pentazole, such as furan, pyrrole, and the cyclopentadienyl anion are aromatic.[48] In order to evaluate the aromatic character of pentazole (**2**), its anion (**3**), and azidopentazole (**14**) as well as that of octaazapentalene (**12**) with formal 10 π electrons, we analyzed the geometric, energetic, and magnetic criteria of aromaticity for pentazole and the magnetic criteria for **12** and **14**.

$$\mathbf{2} + N_2H_4\,(\mathbf{20}) \rightarrow H_2NN{=}NNHN{=}NNH_2\,(\mathbf{19}) \qquad (1)$$

$$\mathbf{2} + N_2H_4\,(\mathbf{20}) \rightarrow H_2NN{=}N\bar{N}N{=}NNH_2\,(\mathbf{19a}) \qquad (2)$$

The homodesmotic reaction 1 was used to estimate an aromatic stabilization energy (ASE = 16.0 kcal/mol) of **2** (Becke3LYP/6-311+G**//MP2(fc)/6-31G*). The NN bond lengths in **2** of 1.329, 1.32, and 1.348 Å are close to the average value (1.330 Å) of the single and double NN bond lengths in **19**; this fulfills the geometric criterion of aromaticity.[29,49]

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(49) Since the pentazole ground state structure has C_{2v} symmetry and is an energy minimum at both HF and MP2, we only optimized the C_{2v} structure **19** with a skeleton similar to that of pentazole.

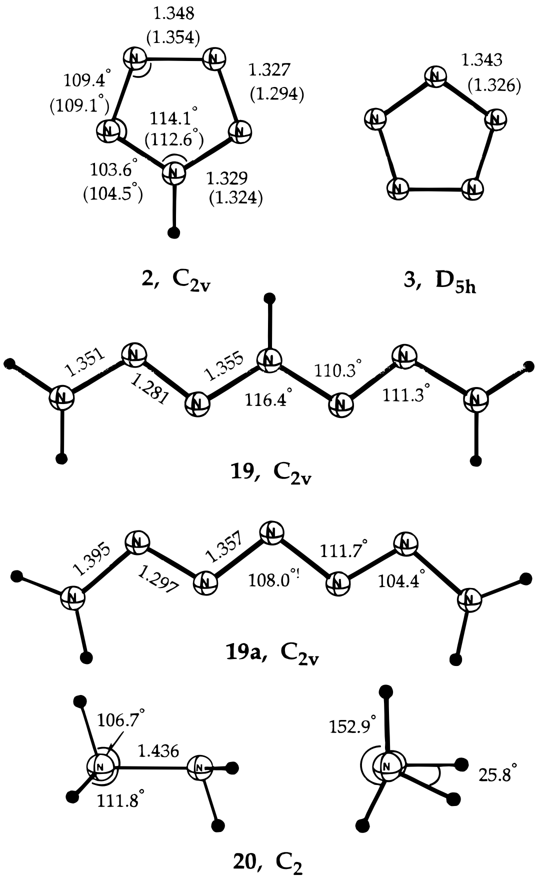

Figure 4. MP2(fc)/6-31G* optimized geometry parameters (bond lengths and bond angles are in angstroms and degrees, respectively) for **2**, **3**, **19**, **19a**, and **20** (the Becke3LYP/6-311+G* values for **2** and **3** given in parentheses).

Table 6. Calculated Anisotropy (χ_{anis}) and Magnetic Susceptibility Exaltation (Λ) as Well as Aromatic Stabilization Energy (ASE) for Pentazole (**2**) Pentazolyl Anion (**3**), Compared with the Values for Furan, Pyrrole, and Cyclopentadienyl Anion as Well as Azidopentazole (**14**) and Octaazapentalene (**12**)

compounds	χ_{anis}[a]	Λ[a]	ASE
pentazole (**2**, N_5H)[b]	−55.3	−7.7[c] (−8.8)[d]	16.0
pentazolyl anion (**3**, N_5^-)[b]	−61.0	−10.6[e]	52.4
furan[f]	−36.2	−9.1	19.8
pyrrole[f]	−41.8	−12.1	25.5
cyclopentadienyl anion[f]	−45.8	−17.2	28.8
azidopentazole (**14**), C_s	−46.0	−5.9[g]	
octaazapentalene (**12**), D_{2h}	−78.5	−7.8[g]	

[a] At IGLO/II/Becke3LYP/6-31G* (ppm cgs). [b] Becke3LYP/6-311+G* total energies for molecules involved in homodesmotic reactions 1 and 2: −274.335 20 (**2**); 273.821 42 (**3**); −386.219 92 (**19**); −285.748 07 (**19a**); −111.910 20 (**20**). [c] From eq 1. [d] Relative to the value for the open-chain isomer. [e] From eq 2. [f] Taken from ref 48. [g] Relative to the value for the open-chain N_8 isomer.

ASE = 52.4 kcal/mol is calculated using the homodesmotic reaction 2 for the pentazolyl anion (N_5^-, **3**) (Becke3LYP/6-311+G**//MP2(fc)/6-31G*). The higher symmetric **3** (D_{5h}) possesses larger aromatic stabilization than the neutral pentazole (**2**) itself. The MP2(fc)/6-31G* optimized geometries for **2**, **3**, **19**, **19a**, and **20** are shown in Figure 4, and the computed total energies are summarized in Table 6.

The magnetic criteria of aromaticity are based on ring current effects which result in magnetic susceptibility exaltations (Λ), large magnetic susceptibility anisotropies (χ_{anis}), and abnormal chemical shifts.[46,48,50−53] The magnetic susceptibility exaltation (Λ) is defined as the difference between the measured bulk magnetic susceptibility (χ_M) of a molecule and the value (χ_M) evaluated using an increment system derived from the reference molecules without cyclic electron delocalization.[51] For pentazole (**2**) and its anion (**3**), the magnetic susceptibility exaltations were deduced from eqs 1 and 2. The values of −7.7 and −10.6 ppm cgs for **2** and **3** are similar to those for the isoelectronic furan, pyrrole, and the cyclopentadienyl anion. The magnetic susceptibility anisotropies, also listed in Table 6, document the aromaticity of **2** and **3**. Since pentazole itself is aromatic, azidopentazole (**14**) also should be aromatic. The magnetic susceptibility exaltations for azidopentazole (**14**) and octaazapentalene (**12**) also can be based on the value of the *trans* open-chain isomer **18**. The Λ values of −5.9 and −7.8 ppm cgs for **14** and **12** characterize the aromaticity of these molecules.

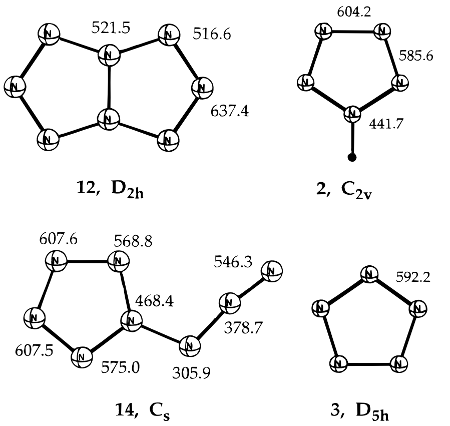

Figure 5. IGLO/II calculated ^{15}N chemical shifts for **2**, **5**, **12**, and **14** (H_3CNO_2 as standard).

Table 7. Becke3LYP/6-31G* Calculated Harmonic Vibrational Frequencies (cm^{-1}) and Their Intensities (KM/mol) for Azidopentazole (**14**) and Octaazapentalene (**12**)

14		12	
frequencies	intensities	frequencies	intensities
41 (0)	967 (52)	245 (10)	1027 (67)
156 (0.6)	1037 (0.5)	376 (0)	1048 (0)
267 (3.4)	1116 (2)	468 (0.5)	1115 (2)
403 (2)	1146 (1.4)	683 (0)	1182 (0)
494 (6)	1205 (37)	690 (0)	1185 (2)
543 (0)	1243 (1.3)	697 (0.1)	1294 (0)
683 (0.6)	1376 (16.5)	699 (0)	1318 (11)
747 (0)	1409 (65.2)	845 (0)	1321 (9)
784 (8)	2267 (384)	964 (5)	1400 (0)

For assistance in the possible experimental identification of **12** and **14**, the calculated vibrational frequencies with intensities are summarized in Table 7 and the computed ^{15}N chemical shifts[54] for **12**, **14**, as well as **2** and **3** are shown in Figure 5.

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Table 8. Total ($E_{tot.}$, hartrees) and Relative (E_{rel}, kcal/mol) Energies with the Zero-Point Vibrational Energies and the Number of Imaginary Frequencies (NIMAG) for N_{10} Isomers, N_{12} Forms, N_{20}, and N_2H_2 Reference Molecules

compound	$E_{tot.}$[a]	ZPE-(NIMAG)[a]	$E_{tot.}$[b]	E_{rel}[c]
21, D_{2d}	−547.262 25	29.7(0)	−547.403 48	0.0 (260.0)[d]
22, D_2	−547.042 87	24.1(2)	−547.180 50	134.3
23, D_{10h}	−546.765 70	21.8(7)	−546.911 70	300.7
24, C_{2h}	−547.216 46	26.8(0)	−547.370 84	17.6
25a, C_{2h}	−110.637 42	17.6(0)[e]	−110.679 37	0.0
25b, C_{2v}	−110.627 91	17.2(0)[e]	−110.668 87	6.2[f]
26a, C_{2h}	−656.705 69	35.3(0)	−656.873 71	0.0 (308.0)[g]
26b, C_{2h}	−656.683 54	34.9(2)	−656.853 46	12.3
27, I_h	−1093.890 22		−1094.151 40	(888.5)[h]

[a] At Becke3LYP/6-31G*. [b] At Becke3LYP/6-311+G**//Becke3LYP/6-31G*. [c] At Becke3LYP/6-311+G**//Becke3LYP/6-31G* + ZPE /Becke3LYP/6-31G*). [d] Relative to five N_2. [e] At Becke3LYP/6-311+G**. [f] At Becke3LYP/6-311+G** + ZPE(Becke3LYP/6-311+G**). The energy difference between **25a** and **25b** is 5.0 kcal/mol at the G2 level.[39c] [g] Relative to six N_2 molecules. [h] Relative to ten N_2.

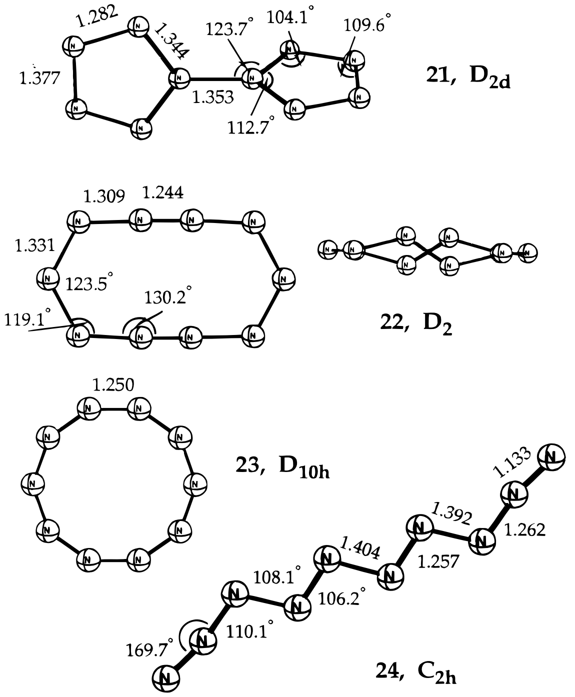

Figure 6. Becke3LYP/6-31G* optimized geometries parameters (bond lengths and bond angles are in angstroms and degrees, respectively) for N_{10} isomers **21**−**24**.

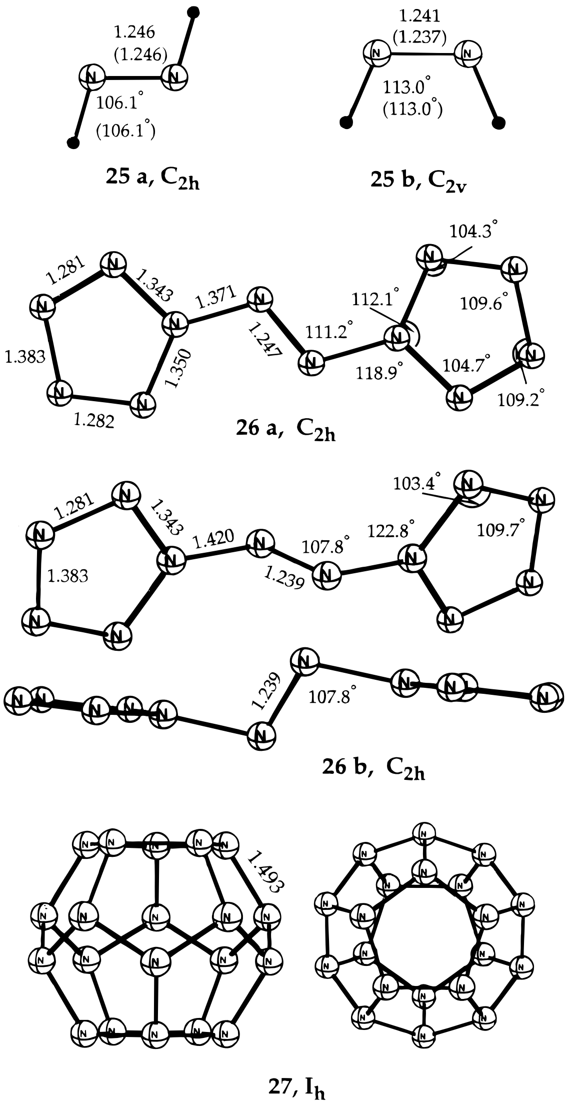

Figure 7. Becke3LYP/6-31G* optimized geometry parameters (bond lengths in angstroms and bond in degrees, respectively) for **25** (the Becke3LYP/6-311+G** values in parentheses), **26**, and **27**.

(C) N_{10} Isomers. Recently, [10]annulene isomers have been investigated theoretically.[56] The D_{10h} form is not a minimum and is high in energy. However, a nearly planar C_s isomer, in which one of the C−H bonds is directed toward to the ring center, is a minimum.[56b] Both the D_{10h} and the C_s forms are aromatic, as evident from the geometric, energetic, and magnetic criteria.[56b] Hence, we calculated bispentazole (**21**, D_{2d}), monocyclic **22** (twisted, D_2), and **23** ($D10h$) as well as the *trans* open-chain **24** (C_{2h}). Table 8 summarizes the computational results, and the optimized geometries are shown in Figure 6.

Bispentazole (**21**) is indeed the lowest energy N_{10} minimum (Becke3LYP/6-31G*, Table 8). The highest symmetry (D_{10h}) structure **23** is 300 kcal/mol higher in energy and has *seven* imaginary frequencies! Twisted **22** is not favorable either. It has two imaginary frequencies and is 134.3 kcal/mol less stable than **21**. At Becke3LYP/6-31G*, the N_{10} C_{2h} symmetric open-chain structure **24** is a minimum and "only" 17.6 kcal/mol less stable than **21** at Becke3LYP/6-311+G*//Becke3LYP/6-31G* + ZPE (Becke3LYP/6-31G*). Attempts to optimize a N_{10} ring in lower symmetry led to a C_2 minimum at HF/6-31G*. However, this dissociated into five N_2 on attempted reoptimization at Becke3LYP/6-31G*, and it seems unlikely than any ten membered N_{10} ring can exist. The relative stability of **21** is due to the aromatic pentazole rings; even so, this structure is still 260 kcal/mol higher in energy than five N_2 molecules (Table 8)!

(D) N_{12} Isomers and N_{20} I_h Dodecahedral Structure. At Becke3LYP/6-311+G** + ZPE (Becke3LYP/6-311+G**), *trans*-diazene, HN=NH (**25a**), is 6.2 kcal/mol more stable than

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(53) Benson, R. C.; Flygare, W. H. *J. Am. Chem. Soc.* **1970**, *92*, 7523.

(54) As liquid nitromethane is the experimental standard, the IGLO ^{15}N chemical shifts are relative to NH_3 (gas) (the experimental $\delta^{15}N$ for NH_3 is 400.9 ppm).[55]

(55) (a) Mitzel, N. W.; Hofmann, M.; Waterstradt, E.; Schleyer, P. v. R.; Schmidbauer, H. *J. Chem. Soc., Dalton Trans.* **1994**, 2503. (b) Jameson, L. J.; Jameson, A. K.; Oppusunggu, D.; Wille, S.; Burrel, P. M.; Mason, J. *J. Chem. Phys.* **1981**, *74*, 81.

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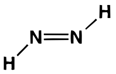
Table 9. Computed Energetic Increments (hartrees) for Polynitrogen Compounds at Becke3LYP/6-311+G**//Becke3LYP/6-31G*

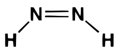
molecules	ZPE[a]	$E_{\text{tot.}}$	increments[b,c]
H_2NNH_2, C_2 (**20**)	33.6	−111.910 26	−55.955 13 [$H_2N-(N_t)$]
$(HN_2)_3N$, C_3 (**28**)	54.5	−222.596 56	−54.731 17 [$N_t-(N_t)_3$]
$(N_3)_3N$, C_3 (**29**)	26.3	−547.341 59	−54.715 25 [$N_t-(N_d)_3$]
N_3N_3, C_{2h} (**10a**)	15.3	−328.417 56	−164.208 78 [$N_3-(N_d)$]
$N_3N{=}NN_3$, C_{2h} (**18**)	21.2	−437.901 54	−109.483 98 [−N=N−, *trans*]
$(NN)_4$, D_{2d} (**13**)	20.6	−437.819 64	−109.454 91 [−N=N−, *cis*]
trans-$H_2NN{=}NNH_2$, C_i (**31**)	39.8	−221.405 33	−55.960 67 [$H_2N-(N_d)$]
N_5N_5, D_{2d} (**21**)	29.7	−547.403 48	−273.701 74 [N_5-, cyclic]

[a] At Becke3LYP/6-31G*. [b] Tricoordinate nitrogen is abbreviated to "N_t". [c] Dicoordinate nitrogen is abbreviated to "N_d".

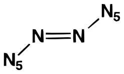
the *cis* minimum (**25b**). The experimental estimate[28a] of the energy difference between *cis*- and *trans*-isomers of HN=NH is 4.8 kcal/mol at 298 K. Hence, we only examine the *trans*-dipentazolyl-substituted diazene forms (**26**) (Table 8 and Figure 7).



25 a



25 b



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At Becke3LYP/6-31G*, **26a** is a minimum, whereas **26b** with two N_5 rings perpendicular to the *trans* N=N double bond is a higher energy second-order saddle point. At Becke3LYP/6-311+G*//Becke3LYP/6-31G* + ZPE (Becke3LYP/6-31G*), **26a** is 12.3 kcal/mol more stable than **26b**. Although **26a** has two aromatic pentazole rings, it is 308.0 kcal/mol higher in energy than six N_2 molecules.

Isoelectronic with dodecahedrane ($C_{20}H_{20}$), the dodecahedral I_h N_{20} structure **27** was optimized at Becke3LYP/6-31G*. At this level, **27** is 888.5 kcal/mol higher in energy than ten N_2 molecules; this energy difference may be compared with the 924 kcal/mol at MP2/DZP.[22]

(E) Energy Increments and Strain Energies. The energies of hydrocarbons can be estimated accurately from increment systems based on their constituent groups.[58] The difference between the measured (or calculated) energy and the evaluated from increment systems can be used to evaluate the strain energy of a molecule. Can this methodology be employed in polynitrogen compounds?

Table 9 summarizes the calculated total energies for the molecules used to evaluated the increment system (energies at Becke3LYP/6-311+G**//Becke3LYP/6-31G*; the Becke3LYP/6-31G* geometries for **28**−**30** are shown in Figure 8). For example, hydrazine (**20**) gave the NH_2 group increment connected with tricoordinate nitrogen (H_2N-N_t); this was employed with triaminoamine [$N(NH_2)_3$, **28**] to give the increment representing a tricoordinate nitrogen (N_t) connected with three tricoordinate nitrogen (N_t) substituents [$N_t-(N_t)_3$]. For the increment for a N_t nitrogen connected with three dicoordinate nitrogen (N_d), [$N_t-(N_d)_3$], we used $N(N_3)_3$ (**29**). The N_3 increment is derived from open-chain N_6 C_{2h} (**10a**). For the *cis* and *trans* −N=N− increments, octaazacyclooctatetraene (**13**, D_{2d}) and the open-chain N_8 (**18**) were used. *Trans* H_2-NN=NNH_2 and the *trans* −N=N− increment gave the H_2N-(N=) grouping. The pentazolyl ring increment (N_5, cyclic) is derived from dipentazole (**21**, D_{2d}).

The increments of Table 9 were tested on some strain-free molecules, such as azidopentazole (**14**). The energy difference between the DFT and the increment value is only 2.3 kcal/mol. A similarly small difference is found for aminoazid (N_3-NH_2, **30**, −1.8 kcal/mol) and for octaazabareilene (**15**, 2.4 kcal/mol).

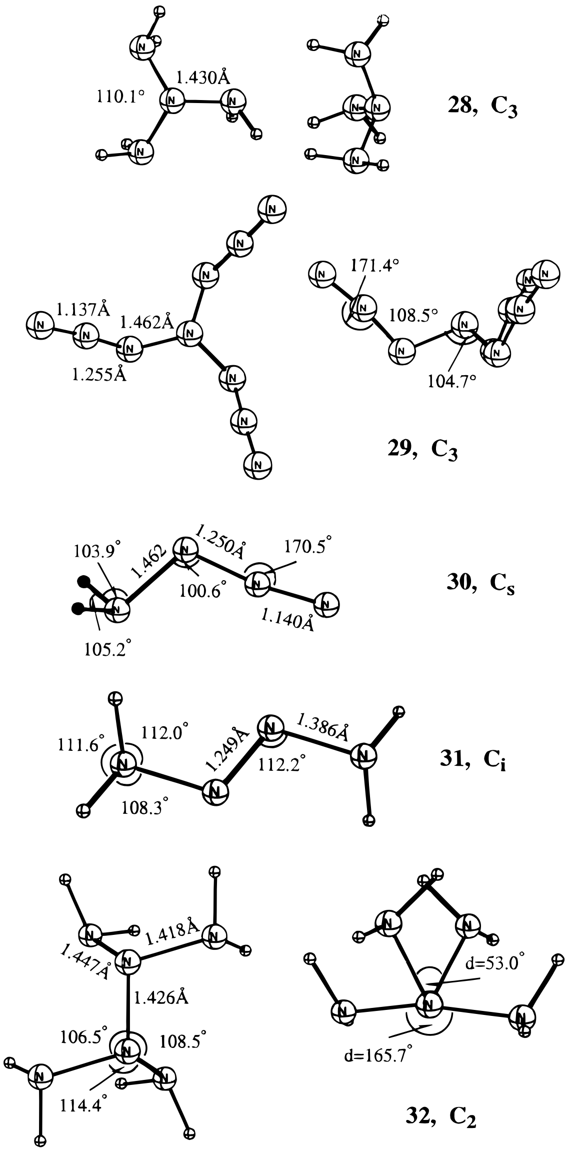

Figure 8. Becke3LYP/6-31G* optimized geometry parameters for **28**−**32**.

The comparison of the DFT energy of the $(H_2N)_2N-N(NH_2)_2$ C_2 structure (*gauche* conformation, in agreement with the GVB-(1,2)/6-31G* calculations[57]) and the increment estimated differ by −3.8 kcal/mol (Table 10). As the average deviation for these three strain-free molecules is ±2.6 kcal/mol, the energetic increments should give reasonably reliable estimates for the energies of strain-free nitrogen-rich and polynitrogen molecules. For *trans* dipentazole diazene (**26a**, $N_5N{=}NN_5$), the increment estimate is −8.6 kcal/mol lower than the DFT energy; this difference is due to the repulsion between the two N_5 rings and the N=N double bond (the central NNN angle in **26a** is wider (111.2°) than that in **18** (107.5°)).

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Table 10. Calculated ($E_{tot.}$(calc)) and Estimated from the Increment Scheme ($E_{tot.}$(inc)) Total Energies as Well as Their Differences ($\Delta E = E_{tot.}$(calc), kcal/mol) for a Set of Polynitrogen Molecules at Becke3LYP/6-311+G**//Becke3LYP/6-31G*

molecules	$E_{tot.}$(calc)	$E_{tot.}$(inc)	ΔE^a
14, C_s	−437.914 14	−437.910 52	+2.3
15, D_{3h}	−437.799 07	−437.795 23	+2.4
N_3NH_2 (**30**, C_s)	−220.166 65	−220.169 45	−1.8
$(H_2N)_2NN(NH_2)_2$ (**32**, C_2)	−333.276 84	−333.282 86	−3.8
26a, C_{2h}	−656.873 71	−656.887 46	−8.6
11, O_h	−437.524 52	−437.849 36	192.6 (24.1)[b]
16, C_s	−437.757 77	−437.787 34	18.6
N_{20}, I_h (**27**)	−1093.151 40	−1094.623 40	296.2 (14.8)
33		−656.834 55	
34		−766.327 51	
35		−875.820 47	
36		−547.394 50	
37		−1204.248 07	
38		−766.276 23	
39		−985.261 15	
40		−985.261 15	

[a] Strain energy for one nitrogen unit is given in parentheses. [b] Using homodesmotic eq 4 and corrected for ZPE (Becke3LYP/6-31G*). [c] Corrected for ZPE (Becke3LYP/6-31G*).

Table 11. Strain Energy (kcal/mol) of Tetraazatetrahedrane, N_4 (**8**), Calculated Using the Homodesmotic Equation (3) at Various Computational Levels

computational level	E_{strain}	E_{strain}/N
HF/6-31G* + ZPE(Becke3LYP/6-31G*)	66.5	16.6
MP2(fc)/6-31G* + ZPE(Becke3LYP/6-31G*)	54.8	13.7
Becke3LYP/6-31G* + ZPE(Becke3LYP/6-31G*)	61.7	15.4
Becke3LYP/6-311+G** + ZPE(Becke3LYP/6-31G*)	51.1	12.8
Becke3LYP/6-311+G(3df,p) + ZPE(Becke3LYP/6-31G*)	48.2	12.1[a]
G2	49.1	12.3[b]

[a] At Becke3LYP/6-311+G(3df,p), the total energies of molecules involves in the homodesmotic eq 3 are −218.845 50 (N_4, **8**), = −111.916 20 (hydrazine), and −222.608 67 ($N(NH_2)_3$, **28**) hartrees. The ZPE(Becke3LYP/6-31G*) are 8.36 (N_4, **8**), 33.37 (hydrazine), and 54.51 ($N(NH_2)_3$, **28**) kcal/mol. [b] G2 energy was taken from ref 40.

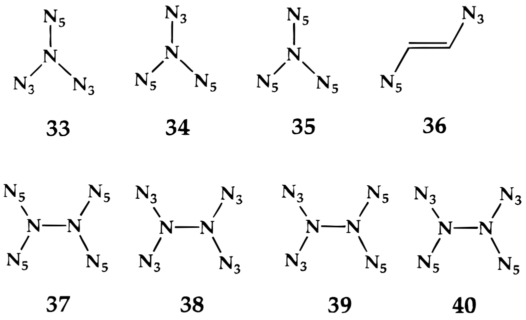

Figure 9. Polynitrogen strain-free molecules **33**−**40**, which total energies were estimated by means of the increment system (Table 10).

Hydrocarbons, such as tetrahedrane, cubane, and dodecahedrane, are highly strained molecules. The same is true for their isoelectronic nitrogen analogues. Consider tetraazatetrahedrane N_4 (T_d, **8**); the increment value estimate is equivalent to the homodesmotic eq 3.

$$4N(NH_2)_3\ (\mathbf{28}) - 6N_2H_4\ (\mathbf{20}) \rightarrow N_4\ (\mathbf{8}) \qquad (3)$$

$$8N(NH_2)_3\ (\mathbf{28}) - 12N_2H_4\ (\mathbf{20}) \rightarrow N_8\ (\mathbf{11}) \qquad (4)$$

Table 11 summarizes the calculated strain energies at various levels for **8**. The strain energies estimated at HF, MP2, and Becke3LYP with the 6-31G* basis set are too high. The Becke3LYP level with much larger basis sets (6-311+G* and 6-311+G(3df) corrected for ZPE (Becke3LYP/6-31G*) gives strain energies of 51.1 and 48.2 kcal/mol, respectively, which are close to the G2 value (49.1 kcal/mol).[40] The strain energies per nitrogen are 12−13 kcal/mol. These indicate again that DFT data with larger basis sets are of quality similar to those at high *ab initio* levels.

Using homodesmotic eq 4, the strain energy for octaazacubane **11** is 192.6 kcal/mol at Becke3LYP/6-311+G*//Becke3LYP/6-31G* + ZPE (Becke3LYP/6-31G*) (Table 10). The strain energy per nitrogen in **11**, 24.1 kcal/mol, is larger than that in **8**. Thus, octaazacubane (**11**) is *more* strained than tetraazatetrahedrane (**8**).

Other strained molecules as given in Table 10; octaazasemibullvalene (**16**) has a strain energy of 18.6 kcal/mol. This strain energy, which is due to a three-membered nitrogen ring, is somewhat larger than one-fourth of the total energy in tetraazatetrahedrane with four three-membered nitrogen rings. Dodecahedral N_{20} (**27**) has a strain energy of 296.2 kcal/mol (14.8 kcal/mol per nitrogen unit) (Table 10) without ZPE correction.

The increments in Table 9 have been used to predict total energies (Table 11) for selected strain-free molecules (**31**−**38**, N_5 is the pentazole ring and N_3 is NNN unit) shown in Figure 9. The increment values of N_5 and N_3 as well as $N_t-(N_d)_3$ were used for **31**−**33**. The increment total energy for **34** comes from N_5, N_3, and a *trans* N═N units. For **35**−**38**, however, "mixed" tricoordinate nitrogens, derived from one-third of the $N_t-(N_t)_3$ and two-thirds of the $N_d-(N_d)_3$ increments, were used. These increment scheme energies may help guide further theoretical and experimental investigations by providing estimates of relative stabilities of unknown nitrogen-rich and polynitrogen compounds. Similar schemes could be developed and applied, e.g., to polyphosphorus and nitrogen−phosphorus clusters and compounds.

Conclusions

This systematic study of polynitrogen molecules at high *ab initio* and DFT levels of theory leads to the following conclusions:

(1) On the basis of the geometric, energetic, and magnetic criteria of aromaticity, pentazole (**2**) and its N_5^- anion (**3**) are just as aromatic as their well-known isoelectronic analogues, e.g., furan, pyrrole, and the cyclopentadienyl anion.[48] Besides the bond length equalization, both have large aromatic stabilization energies (ASE) and substantial magnetic susceptibility exaltations (Λ).

(2) Although 196.7 kcal/mol higher in energy than four N_2 molecules, the C_s symmetric azidopentazole (**14**, C_s) is the lowest energy N_8 isomer and invites possible experimental investigation (*caution!* **14**, like other pentazoles should have a low decomposition barrier). Both **14** with its pentazole ring and octaazapentalene (**12**) with its 10 π electron structure are aromatic as shown by their magnetic properties.

(3) The D_{2d} symmetric bispentazole (**21**) is the most stable N_{10} minimum we investigated but is 260 kcal/mol higher in energy than five N_2 molecules.

(4) In addition we have developed an energy increment scheme (like Benson's[58]) which can be used for polynitrogen and nitrogen-rich compounds. For strain-free molecules, the deviation between the calculated and the evaluated energies is ±2.6 kcal/mol on average. This increment scheme allows the energies of other polynitrogen compounds to be estimated and could be useful in searching new high-energy−high-density materials.

(5) The strain energies of tetraazatetrahedrane (**8**, 48.2 kcal/mol), octaazacubane (**11**, 192.6 kcal/mol), and N_{20} (**27**, 294.6

kcal/mol) were evaluated by means of the increment system (or homodesmotic equations are equivalent). The strain energy of **8** is much lower than the tetrahedrane value (135.6 kcal/mol), but **11** and **27** are more strained than their hydrocarbon analogues, e.g., cubane (153.6 kcal/mol) and dodecahedrane (49.7 kcal/mol) at Becke3LYP/6-31G*.[59]

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(59) (a) The strain energy for tetrahedrane of 135.6 kcal/mol at Becke3LYP/6-31G* was calculated on the basis of the equation 4 isobutane − 6 ethane = tetrahedrane. (b) The strain energy for cubane of 153.6 kcal/mol at Becke3LYP/6-31G* was calculated on the basis of the equation 8 isobutane − 12 ethane = cubane. The experimental strain energies are 140 kcal/mol for tetrahedrane and 154.7 kcal/mol for cubane. See: Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312. (c) The strain energy for dodecahedrane of 49.7 kcal/mol at Becke3LYP/6-31G* was calculated on the basis of the equation 20 isobutane − 30 ethane = dodecahedrane. (d) For a summary of calculated strain energies for dodecahedrane, see: Beckhaus, H.-D.; Rückhardt, C.; Lagerwall, D. R.; Paquette, L. A.; Wahl, F.; Prinzbach, H. *J. Am. Chem. Soc.* **1994**, *116*, 11775. The reported strain energy of 61.4 ± 1 kcal/mol for dodecahedrane is larger than our Becke3LYP/6-31G* value (49.7 kcal/mol).