

Toward new energy-rich molecular systems: from N_{10} to N_{60}

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Abstract

The electronic structure calculations locate the local minima for bicyclic N_{10} and the fullerene analog N_{60} , both as high-energy density species. The bridging N—N bond in N_{10} is quite remarkably strong ($\Delta E [N_{10} \rightarrow 2N_5] = 93$ kcal/mol), yet flexible to allow a facile rotation of one ring with respect to the other. This property could permit N_{10} to serve as a building block for specific clustering into the nitrogen buckminsterfullerene structure. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In contrast to the same group elements (phosphorus and arsenic), nitrogen has thus far resisted transformation from its basic molecular diatomic phase. The possible existence of polymeric forms of nitrogen, in which the strong triple bond of the diatom is transformed and replaced by single or single and double bonds, is of particular interest due to the energetic properties associated with these materials. As potential high-energy density materials from an abundant natural source, they become leading candidates for alternative energy storage media.

The prospect of destabilizing the strong $N \equiv N$ triple bond under high pressure invited several experimental [1,2] and theoretical [3–5] attempts to locate and characterize bulk polymeric phases. These studies, however, appeared to be contradictory. Calculations suggested polymeric regimes to exist below 100 GPa, at 70 and 50 GPa, while

the diamond-anvil-cell experiments failed to record a transition from the diatomic form for pressures up to 180 GPa. A non-static, shock compressed nitrogen experiment [6] recorded an anomaly at pressure above 30 GPa that was later interpreted as a dissociation to dense atomic phase [7].

Quantum chemical-based computational studies at various levels of theory [8–12] have shown that N_4 and N_8 are metastable species, having (several) local minima on their respective potential energy surfaces. Coupled cluster calculations, CCSD(T), by Lee and Rice [10] showed the energy difference $\Delta E (N_4 - 2N_2)$ to be 186 kcal/mol, and an energy barrier to decomposition of 61 kcal/mol. Later work examined reaction pathways to other structures [11], and determined the lowest-energy conformation of N_4 to be an open-chain triplet [13] with a dissociation barrier of 63 kcal/mol [14]. The results suggested tetrahedral N_4 to have a reasonably long lifetime, and could be trapped and studied by matrix isolation techniques.

Computational studies on polyazacubane [15,16] indicated that the high-energy content of

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these species, $\Delta E(N_8-4N_2) = 423$ kcal/mol for cubic N_8 using DZP CCSD(T) [12], is not due to strain energy but rather to a weak N–N single bond. Five isomers of N_8 have been determined to be metastable [12,17] using highly correlated methods. In order to guide laboratory synthesis, protonated structures of N_4 and N_8 have been optimized and harmonic vibrational frequencies were also calculated [18]. Recent studies reported 10 Hartree–Fock and MP2 isomers of N_8 corresponding to analogous CH structures [19], and the isomerization reaction of N_8 cubane to planar bicyclic (pentalene-like) structure with multiconfigurational self-consistent field and second-order perturbation theory (CASPT2) treatment [20]. Nine single-bonded structures of N_x ($x = 8-24$) were also considered [21] at the DFT(B3LYP)/6-31G** level of computation. Similar computational studies should eventually lead to a viable pathway for the experimental characterization and production of some form of polymeric nitrogen.

We are tempted to address the following: (a) Could a nitrogen fullerene analog, N_{60} be a possible candidate, and (b) if so, what is the reasonable building block for such a cluster. A more general theme for our subsequent work is that computational methods are currently mature enough to help guide experimental efforts in establishing new polymorphs of nitrogen, through a combination of electronic structure and molecular dynamics calculations.

In this Letter, several computational methods are employed to locate the extrema of bicyclic N_{10} . Hartree–Fock self-consistent field (SCF), second-order Møller–Plesset (MP2), quadratic configuration interaction with single and double substitution (QCISD), and density functional (B3LYP) are used as implemented in GAUSSIAN 98 [22] and the parallel NWChem [23] packages of codes. Two correlation consistent basis sets of Dunning [24], cc-PVDZ and cc-PVTZ were used in the expansion of the electronic wave functions. We also report single-point QCISD(T) calculations in which approximate triples' contributions to energy are included. Geometry search, not constrained by symmetry, located a planar structure (D_{2h} symmetry) as a saddle point and an orthogonal

structure (D_{2d} symmetry) as a local minimum. Only 3–6 kcal/mol, depending on the level of computation, separate the two structures. This molecule is postulated herein to serve as a building block for yet a super-high-energy content N_{60} cluster, which is shown to be a local minimum at the AM1 [25] and SCF levels of theory. Harmonic vibrational frequencies of N_{10} and infrared active modes of N_{60} are reported.

2. Results and discussion

2.1. N_{10}

Table 1 lists the optimized geometry of the minimum and transition state structures of N_{10} cluster at various levels of computational treatment, as depicted in Fig. 1. The bond lengths in the two structures are very similar except in the bridging bond, R_2 , where it is stretched by about 0.02 Å in the transition state structure from that of the equilibrium. SCF treatment invariably provided shorter bond lengths by as much as 0.04 Å than the higher level methods. Bond angles, however, are consistent in all levels of treatment. Remarkable agreement should be noted between the DFT(B3LYP) and QCISD results. The cc-PVDZ basis seems to provide adequate values when compared with the cc-PVTZ basis. Furthermore, the geometry and frequencies for the minimum structure are in good agreement when compared with the unpublished B3LYP results of Bartlett and Fau [26] using the augmented cc-PVDZ basis.

One expects single and double N–N bonds to exist in the N_{10} molecule. The bond distances in Table 1 show that R_1 , R_2 and R_4 have similar magnitudes, while the R_3 bond is much shorter. Typical experimental bond lengths for N–N single is 1.449 Å and for N=N double 1.252 Å [27]. The calculated bonds R_1 , R_2 and R_4 are very close to the averaged experimental single and double bonds, indicative of substantial charge delocalization in this system. The R_3 bond, however, is distinctly close to the N=N bond value. The absence of purely single-bonded N–N moiety, and the existence of higher bond order in this system are encouraging for the stabilization effect, since N–N

Table 1
Optimized molecular geometry of N_{10} minimum and transition state structures as in Fig. 1 at various levels of theory^a

	SCF	B3LYP	MP2	QCISD
R₁	1.309 (1.305) 1.298 (1.293)	1.346 (1.338) 1.335 (1.328)	1.342 (1.322) 1.339 (1.319)	1.345 1.333
R₂	1.332 (1.332) 1.354 (1.353)	1.353 (1.350) 1.371 (1.369)	1.357 (1.344) 1.370 (1.356)	1.351 1.374
R₃	1.246 (1.242) 1.259 (1.256)	1.281 (1.275) 1.294 (1.288)	1.316 (1.304) 1.323 (1.309)	1.282 1.296
R₄	1.346 (1.345) 1.325 (1.322)	1.378 (1.373) 1.359 (1.355)	1.362 (1.344) 1.354 (1.337)	1.388 1.362
α_1	111.9 (111.8) 112.9 (112.9)	112.5 (112.3) 113.5 (113.3)	114.4 (114.5) 114.9 (114.9)	112.6 113.8
α_2	109.3 (109.2) 109.4 (109.4)	109.6 (109.5) 109.8 (109.6)	109.8 (109.7) 110.0 (109.8)	109.4 109.6
α_3	124.0 (124.1) 123.5 (123.5)	123.7 (123.8) 123.2 (123.3)	122.8 (122.8) 122.5 (122.5)	123.7 123.1

^a Distances are in Å, and angles in degrees. Calculated parameters for the transition state structure are below that of the minimum. Results using cc-PVTZ basis set are in parenthesis.

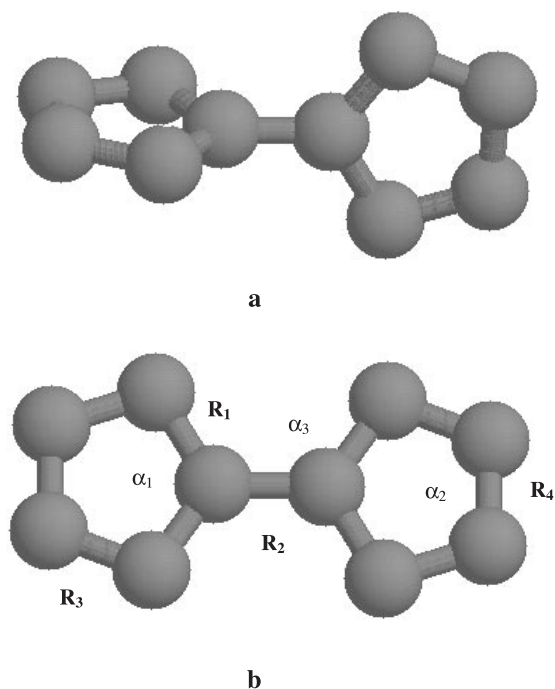


Fig. 1. (a) The minimum and (b) the transition state structures with molecular parameters of N_{10} .

single bonds are in general weak, with greater likelihood to entice decomposition.

The harmonic vibrational frequencies for the minimum structure are reported in Table 2. SCF modes exhibit tendencies toward producing higher frequencies, consistent with the calculated shorter bond distances at this level of treatment. The B3LYP and MP2 calculations are in more general agreement with one another. The strongest IR bands are exhibited in the B_2 mode at 856 (969) and 1082 (1070) wavenumbers at the B3LYP (MP2) computational levels. Again, use of the larger cc-PVTZ basis set did not seem to substantially alter the results as determined by the SCF and B3LYP methods.

The planar, D_{2h} symmetry, structure (Fig. 1b) was confirmed to be a saddle point with the imaginary (negative) frequency being 93, 76, and 75 cm^{-1} at the cc-PVDZ SCF, B3LYP and MP2 levels, respectively. This mode is associated with a rocking motion of one ring with respect to the other, and intrinsic reaction coordinate (IRC) calculations at the B3LYP level proved this internal motion. Bonding in this structure does not differ, as expected, from the minimum D_{2d} structure except in about 0.02 Å stretch for the ring-

Table 2
Harmonic vibrational frequencies (in cm^{-1}) and IR intensities (in km/mol) of N_{10} minimum structure (D_{2d} symmetry) at various levels of theory from cc-PVDZ basis

Mode	SCF	B3LYP	MP2
B_1	82 (0.0)	60 (0.0)	37 (0.0)
E	116 (3.8)	105 (3.2)	109 (3.6)
A_1	487 (0.0)	427 (0.0)	427 (0.0)
E	495 (0.9)	430 (0.8)	438 (0.9)
E	747 (0.3)	669 (0.1)	670 (0.0)
A_2	828 (0.0)	739 (0.0)	733 (0.0)
B_1	850 (0.0)	765 (0.0)	755 (0.0)
A_1	1022 (0.0)	834 (0.0)	948 (0.0)
B_2	1028 (120.0)	856 (55.0)	969 (44.5)
E	1196 (2.5)	1051 (0.1)	1047 (1.4)
B_2	1254 (21.1)	1082 (66.9)	1070 (29.1)
A_1	1288 (0.0)	1088 (0.0)	1080 (0.0)
E	1337 (23.8)	1126 (1.9)	1140 (3.1)
B_2	1383 (3.8)	1132 (0.0)	1157 (0.0)
A_1	1507 (0.0)	1269 (0.0)	1180 (5.9)
B_2	1551 (19.0)	1319 (13.4)	1228 (4.9)
E	1714 (3.6)	1448 (8.0)	1312 (4.7)
A_1	1776 (0.0)	1512 (0.0)	1519 (0.0)

connecting bond, \mathbf{R}_2 . Energetically, the saddle point is placed 4.5, 3.3, 6.1 and 5.4 kcal/mol higher than the minimum structure using the cc-PVDZ B3LYP, MP2, QCISD, and QCISD(T) methods, respectively. The triple-zeta basis, cc-PVTZ does not change these values appreciably, giving 4.9 and 3.2 kcal/mol for B3LYP and MP2 treatment, respectively. Further calculations at the MP2 and B3LYP levels showed that there is no other barrier separating these two structures, indicative of the flexibility of this bond with respect to rotation.

We considered the decomposition of N_{10} into two rings, $\text{N}_{10} \rightarrow 2\text{N}_5$, and optimized the N_5 ring radical at the cc-PVDZ QCISD configuration interaction with single and double excitations (CISD), MP2 and B3LYP. The C_{2v} symmetry-optimized structure for the single ring has similar bonding in \mathbf{R}_1 and \mathbf{R}_4 as in N_{10} . The significant difference is that the \mathbf{R}_3 bond is now more reminiscent of a purely single bond, $\mathbf{R}_3 = 1.607$, 1.568, and 1.536 Å at the QCISD, CISD, and B3LYP levels, respectively. MP2 optimizations tended toward opening of the ring, and thus, a highly stretched (non-bonded) \mathbf{R}_3 distance. Furthermore, energy second-derivative calculations at all the above levels confirmed that the optimized struc-

ture is a first-order saddle point, so that it is unlikely to be stable and further decomposition is expected. The reaction energy, $\Delta E (\text{N}_{10} \rightarrow 2\text{N}_5)$ was calculated to be 93 and 84 kcal/mol at the QCISD and B3LYP levels, indicative of a remarkably strong connecting (\mathbf{R}_2) bond. For the purpose of comparison, we note that the C—N and N—N bond energies in model energetic materials such as nitromethane ($\text{H}_3\text{C—NO}_2$) and nitramine ($\text{H}_2\text{N—NO}_2$) are 60 and 45 kcal/mol, respectively. Finally, we determined the reaction energy $\Delta E (\text{N}_{10} \rightarrow 5\text{N}_2)$ to be 286, 270, and 224 kcal/mol at the QCISD, MP2, and B3LYP levels, respectively. These values are reflective of the interest in polynitrogen as high-energy density materials.

The relative stability of the N—N (\mathbf{R}_2) bond and the internal rotation flexibility in N_{10} as shown above afford a plausible avenue for the synthesis of such materials. The only stable molecular forms of nitrogen known to date are the diatomic N_2 and the azide ion N_3^- , although the synthesis of the ion N_5^+ (C_{2v} symmetry) in a complex with As_xF_y anion seems to have been successful [28]. A stable ring structure of N_5^- ion (D_{5h} symmetry) with bond lengths of 1.329 Å has been determined with coupled cluster (CCSD(T)) theory [26]. Combination of these two ions might prove fruitful towards the synthesis of bicyclic N_{10} .

2.2. N_{60}

The surprising discovery of icosahedral C_{60} [29] as a new allotropic form of carbon not only opened the door to new technological advances in the field, but also directed the search for new exotic molecular structures. From the electronic structure perspective, there is no reason in principle why the three-dimensional π -bonding system in C_{60} cannot be extended to other elements that exhibit similar bonding such as nitrogen and boron. The electron delocalization in C_{60} , albeit, would give way to (weaker) singly bonded N—N or B—B structures. The metastability of N_{60} would establish this hypothetical molecule as a super-high-energy containing material.

Table 3 lists the equilibrium bond distances and IR active vibrational frequencies of N_{60} as determined at the SCF and AM1 levels of theory. The

Table 3

Equilibrium bond distances (in Å) and IR active vibrational frequencies (in cm^{-1}) of N_{60} from AM1 and SCF methods^a

	\mathbf{R}_1	\mathbf{R}_2	Frequencies
SCF/cc-PVDZ	1.430	1.437	251 (3), 483 (1), 1298 (0.6)
SCF/6-31G*	1.430	1.436	
AM1	1.441	1.482	608 (56), 701 (94), 1153 (4)

^a \mathbf{R}_1 refers to pentagonal bonds, and \mathbf{R}_2 to bonds shared in six-member rings. IR intensities are in parenthesis.

6-31G* basis set was used in an optimization procedure without symmetry constraints. The two basis sets provide the SCF results that are in very close agreement; with the pentagonal bond (\mathbf{R}_1) being 0.006 Å shorter than the bonds shared in the six-member rings (\mathbf{R}_2). In the case of C_{60} , SCF treatment provided comparable bond lengths ($\mathbf{R}_1 = 1.450$, $\mathbf{R}_2 = 1.375$) [30] to those obtained from MP2 calculations ($\mathbf{R}_1 = 1.451$, $\mathbf{R}_2 = 1.412$) [31] using double-zeta plus polarization (DZP) basis set. Both these results were in close agreement with the experimental determinations ($\mathbf{R}_1 = 1.432$, $\mathbf{R}_2 = 1.388$) [32]. We expect the same trend for N_{60} , and will report the results of MP2 and DFT calculations being currently conducted on parallel platforms in future publication. We note that the AM1 bond distances in Table 3 are somewhat larger than the corresponding SCF ones, particularly in the case of the \mathbf{R}_2 bond, which experienced an almost 0.05 Å stretch. More important, however, is that both the SCF and AM1 calculations confirm that the order of the bond lengths in N_{60} has been switched from that of C_{60} : whereas \mathbf{R}_2 is the delocalized (type- π) shorter bond in C_{60} , and it becomes the slightly longer one in N_{60} . This should not be surprising due to the fact that in N_{60} a p -type orbital of all nitrogen atoms is the dominant contribution to bonding.

The SCF infrared active low modes listed in Table 3 differ significantly from those obtained from the AM1 theory. All the modes have T_{1u} symmetry character. The difference could be attributed to the difference in the optimized bond lengths. Due to incorrect description of bond dissociation, SCF calculated frequencies are known to be usually up to 15% as high as the experimental ones. MP2 results with more extensive basis sets are usually more accurate [33] and will be compared to those obtained in this study once available.

The production of new forms of polynitrogen can be achieved through direct synthetic methods or through high pressure-induced transformation. An intriguing possibility of creating N_{60} from six unit blocks of N_{10} is inviting (Fig. 2). A conformation in a cell containing these basic units can be

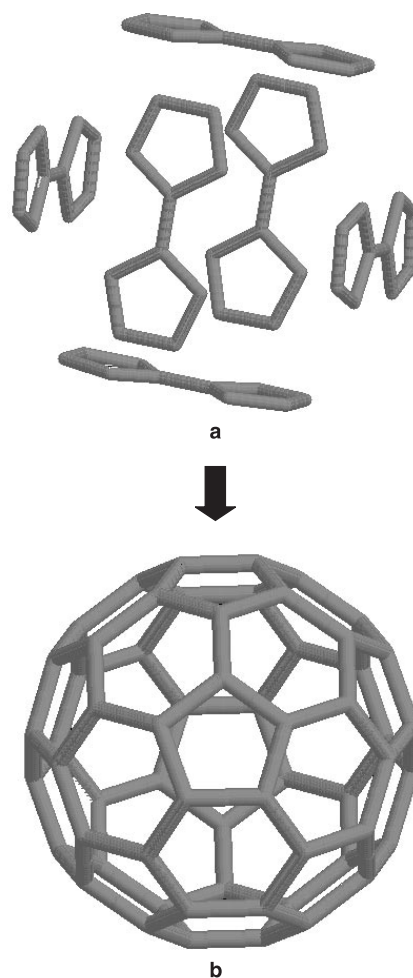


Fig. 2. (a) Combination of molecular unit blocks of N_{10} to form (b) nitrogen fullerene, N_{60} .

envisioned to undergo a transformation to N_{60} as intermolecular bonds are compressed under high pressure loading, either static (diamond anvil cell) or dynamic (shock compression). Ab initio-based methods in combination with molecular dynamics simulations under these extreme conditions are currently being conducted to investigate the feasibility of these processes and will be reported elsewhere. Such an event might be considered minute and involve considerable energy and entropy constraints. It is, however, the rare events that distinguish chemical research, such as the synthesis of one particular toxin isomer out of 5×10^{21} available configurational choices in the case of palytoxin $C_{129}H_{223}N_3O_{54}$ [34,35]. Pending more reliable calculations with correlated methods, the reaction energy of $N_{60} \rightarrow 6N_{10}$ is estimated at the HF/cc-pVDZ level to be -2430 kcal/mol. Finally, calculations on chemical reaction mechanism involving the known basic units of nitrogen that could lead to the formation to N_{10} are currently underway.

3. Summary

In this Letter, several computational methods were employed to locate the extrema of bicyclic N_{10} , a high-energy density molecule, and the minimum structure of N_{60} . SCF, DFT, MP2, and QCISD methods located a planar bicyclic structure (D_{2h} symmetry) as a saddle point for N_{10} , and a corresponding orthogonal structure (D_{2d} symmetry) as the equilibrium structure. Only 3–6 kcal/mol separated the two structures, without any further barrier. The structure is remarkably stable with respect to ring connecting bond homolysis. This molecule is postulated herein to serve as a building block for yet a super-high-energy content N_{60} cluster, which is shown to be a local minimum at the AM1 and SCF levels of theory. Harmonic vibrational frequencies of N_{10} and infrared active modes of N_{60} are reported. This study is the first in a series with the purpose of identifying possible synthetic and physical routes for N_{10} from the known forms of nitrogen, and for the possibility of producing N_{60} from a combination of N_{10} units under extreme conditions.

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