New Isomers of N_8 without Double Bonds

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Quantum mechanical methods have been used to examine isomers of N_8. In addition to the previously studied octaazacubane structure (O_h symmetry, **1**), we have investigated two new structures, of D_{2h} (**2**) and C_{2v} (**3**) symmetry, without N═N double bonds. The C_{2v} structure may be designated octaazacuneane. The following basis sets and methods have been employed to optimize geometries: (1) (SCF, CISD, CCSD)/DZP; (2) (SCF, MP2, B3LYP, B3P86, BHLYP)/6-31G*; (3) B3LYP/6-311+G*. The single-point energies have also been estimated at the CISD+Q/DZP level of theory with CISD/DZP geometries and at the CCSD(T)/DZP level with CCSD/DZP geometries. The harmonic vibrational frequencies and their infrared intensities have also been predicted with the SCF, MP2, and DFT methods. The results show that the two new isomers are both minima on the N_8 potential energy hypersurface and of higher energy than isomers containing N═N double bonds. Among the three isomers with only single bonds, the ones with the higher symmetry have higher energies.

1. Introduction

The intense scientific and popular interest in the C_{60} molecule has naturally raised the question whether other important cluster species have been systematically overlooked. N_n clusters are reasonable candidates for the following two reasons. First, a number of $(CH)_n$ clusters have been synthesized, which are isoelectronic with N_n. It is posible that these nitrogen structures will show analogous stability. Second, N_n clusters would be high energy density materials (HEDM). The dissociation energy of N_2 (N≡N triple-bond energy) is 225 kcal/mol, while the standard N═N double-bond energy is 100 kcal/mol and that of the N−N single bond is about 40 kcal/mol.[1] Since the N≡N triple-bond energy (225 kcal/mol) is much more than three times the single-bond energy ($3 \times 40 = 120$ kcal/mol), this argument suggests that the N_n clusters with N−N single bonds may release significant amounts of energy when they dissociate into N_2 molecules. For instance, the cluster N_{2n}, which has $3n$ single N−N bonds (each nitrogen atom connecting to three other nitrogen atoms with single bonds), will release as much as $225n - 40 \times 3n = 105n$ kcal/mol energy when it decomposes into nN_2 molecules. Also since the N═N double-bond energy (100 kcal/mol) is still larger than that of two single bonds ($2 \times 40 = 80$ kcal/mol), the ideal HEDM candidates are those clusters containing only N−N single bonds. This rough estimation of the decomposition energy may be compared with the results of recent high-level theoretical studies. For tetraazatetrahedrane N_4 ($105 \times 2 = 210$ kcal/mol), the relative energy to N_2 was reported as 191 kcal/mol at the TZ2P CCSD level of theory[2] or 183 kcal/mol at the 6-311+G(3df) Becke3LYP level.[3] For octaazacubane N_8 ($105 \times 4 = 420$ kcal/mol), the analogous relative energy was reported as 450 [TZ2P CCSD],[2] 442 [6-311+G(3df) BeckeLYP],[3] or 423 kcal/mol [DZP CCSD(T)],[4] respectively.

The potential for the existence of N_n ($n > 2$) clusters has been examined theoretically.[2−11] However, much of the published work is concentrated on N_4 and N_6,[5−7] in part because of the limitation of computer resources. The early studies on the N_8 molecule were limited to the cubic structure (**1**). The first (1981) theoretical paper on the N_8 cubane structure was due to Trinquier *et al*. and used the SCF/DZ level.[8] Next, Engelke and Stine reported N_8 cubane to be a minimum by SCF vibrational analyses with basis sets up to 4-31G*.[9] They also reported single-point energies at the MP4 level. Lauderdale *et al*. optimized the N_8 structure on the MP2 energy hypersurface with a DZP basis set and reported the single-point energy at the CCSD level.[2] In 1993, Engelke reported a uniform set of carbon/nitrogen cubanoids with the formula $(CH)_{8-n}N_n$, where $0 \le n \le 8$, at 10 different levels of theory.[10]

In 1995, Leininger, Sherrill, and Schaefer (LSS) studied two new isomers: an all-nitrogen analogue of cyclooctatraene with D_{2d} symmetry and a planar bicyclic structure octaazapentalene with D_{2h} symmetry.[4] Using the DZP basis set accompanied by the SCF, MP2, CISD, and CCSD methods, they reported optimized geometries and harmonic vibrational frequencies for these structures. High-quality estimates of the energy differences between these N_8 structures and $4N_2$ were determined using the CCSD(T) method. In 1996, Gamarc and Zhao studied the strain energies and resonance energies of these three N_8 clusters using *ab initio* methods.[11] The nitrogen cluster strain energies are generally of the same order of magnitude as those of isostructural hydrocarbon clusters, and resonance energies of nitrogen clusters are much smaller than those of the comparable aromatic hydrocarbons. Recently, Glukhovtsev, Jiao, and Schleyer (GJS) investigated N_n clusters more systematically.[3] The number of the structures (including two saddle points) for N_8 clusters in their paper has reached as many as eight.

However, all the previously investigated isomers, except the cubic structure, contain N═N double bonds. For the purpose of searching for HEDM candidates, we wanted to limit our

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attention to isomers with only N−N single bonds. With the help of graph theory, we have found two new previously univestigated isomers, which have only N−N single bonds. One has D_{2h} symmetry (**2**), and the other, analogous to cuneane, has C_{2v} symmetry (**3**).

2. Theoretical Methods

Ab initio and density functional theory (DFT) methods were applied with three basis sets. The DZP basis set involves Dunning's double-zeta contraction[12] of Huzinaga's primitive sets[13] plus a set of six d-like polarization functions with $\alpha_d(N) = 0.80$. This basis set is designated as (9s5p1d/4s2p1d). The standard 6-31G* basis set is of double-zeta contraction quality plus six d-like polarization functions, which may be designated (10s4p1d/3s2p1d).[14] The 6-311+G* basis set is of triple-zeta valence quality plus diffuse plus five d-like polarization functions and may be designated (12s6p1d/5s4p1d).[15]

In conjunction with the DZP basis set, geometries were optimized with analytic gradient techniques using the self-consistent field (SCF),[16] single- and double-excitation configuration interaction (CISD),[17] and coupled-cluster (CCSD) methods.[18] In conjunction with the 6-31G* basis set, the geometry optimization was carried out with the SCF, second-order Møller−Plesset perturbation theory (MP2),[19] and using hybrid Hartree−Fock/DFT methods with Becke's three parameter exchange functional along with the Lee−Yang−Parr nonlocal correlation functional (B3LYP),[20,21] B3 in conjunction with Perdew's 1986 correlation functional (B3P86),[22] and Becke's half-and-half exchange functional (BH) along with the correlation functional of LYP.[23]

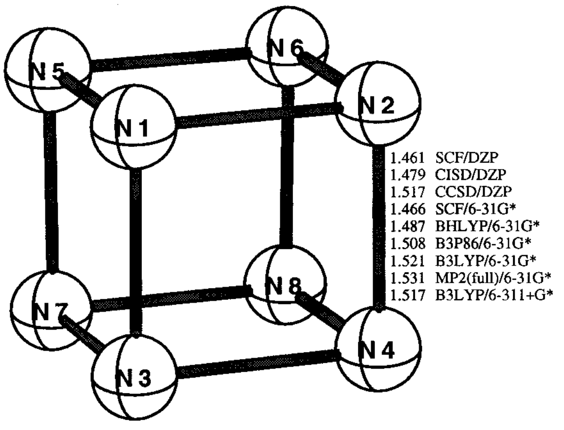
The single-point energies for the CISD+Q/DZP method at CISD/DZP stationary point geometries and for CCSD(T)/DZP at CCSD/DZP stationary point geometries have also been evaluated. The analytic second-derivative technique was employed to predict the harmonic vibrational frequencies and infrared intensities with the SCF, MP2, and hybrid Hartree−Fock/DFT methods.[24]

The SCF, CI, and CC computations were carried out with the PSI program package.[25] For the CISD and CCSD methods, eight core orbitals were frozen (double occupied) and the eight highest virtual orbitals (core counterparts) were deleted from the procedures. The total number of configurations with the CISD method for the C_{2v} structure is 424 889. That for the D_{2h} structure is 214 535. The hybrid Hartree−Fock/DFT and MP2(full) computations were carried out with the Gaussian94 program package.[26] The fine grid (75, 302) was used for evaluating integrals numerically in the DFT methods.

3. Results and Discussion

The geometric structures of the three N_8 clusters with only N−N single bonds (**1**, **2**, and **3**) are shown in Figures 1−3, respectively.

The octaazacubane (O_h symmetry, **1**) has been examined in many previous studies.[2−4,8−11] LSS reported that electron correlation (CI and CC) increases the N−N bond lengths, but MP2 significantly overestimates the effect.[4] They anticipated that the true equilibrium bond lengths lie somewhere in between those determined at the CISD/DZP and CCSD/DZP levels of theory.[27] The present study with DFT methods draws the same conclusion. Figure 1 shows that the N−N bond lengths of octaazacubane (**1**) at the SCF/6-31G* level of theory are 1.466 Å, while they increase to 1.508 Å at the B3P86 level and to 1.521 Å at the B3LYP level. Note that the DFT results are close to those of CCSD/DZP (1.517 Å). The bond lengths from the BHLYP method are 1.487 Å, which is in between. This is expected since half of the BHLYP exchange functional is that of the SCF method. The MP2 method gives too long of N−N bond distances (1.531 Å) similar to the results reported by LSS.



1 (O_h)

Figure 1. Geometry of structure **1** (Q_h symmetry).

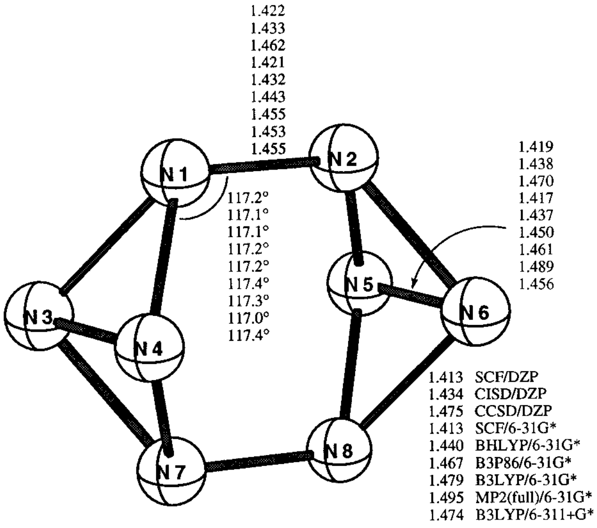
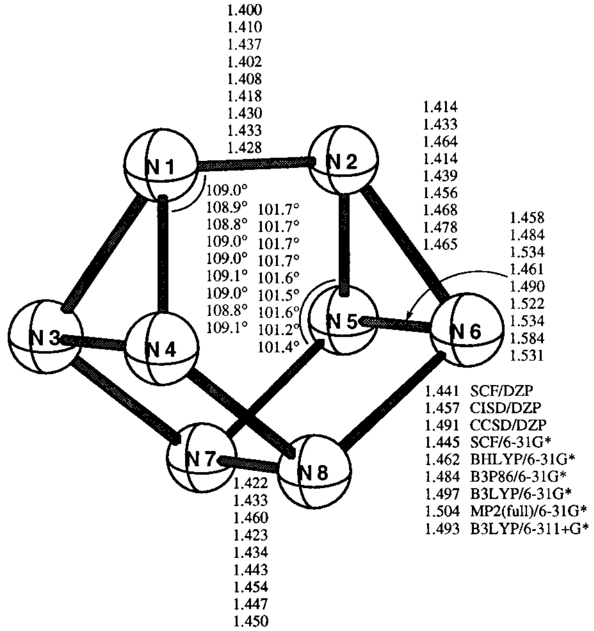


Figure 2. Geometry of structure **2** (D_{2h} symmetry).



3 (C_{2v})

Figure 3. Geometry of structure **3** (C_{2v} symmetry).

TABLE 1: Total Energies (hartrees) and Energies Relative to $4N_2$ and to Octaazacubane (1) (kcal/mol, in Parentheses) of the N_8 Isomers without N=N Double Bonds

level	O_h (**1**)[a]	D_{2h} (**2**)	C_{2v} (**3**)	$4N_2$
SCF/DZP	−435.054 757 (490.1, 0.0)	−435.105 014 (458.5, −31.6)	−435.157 144 (425.9, −64.2)	−435.835 856 (0.0)
CISD/DZP	−436.055 002 (450.6, 0.0)	−436.111 083 (415.5, −35.1)	−436.162 522 (383.2, −67.4)	−436.773 154 (0.0)
CISD+Q/DZP[b]	−436.258 123 (440.8, 0.0)	−436.314 993 (405.2, −35.6)	−436.365 019 (373.8, −67.0)	−436.960 642 (0.0)
CCSD/DZP	−436.375 146 (434.4, 0.0)	−436.432 064 (398.7, −35.7)	−436.478 903 (369.3, −65.1)	−436.067 464 (0.0)
CCSD(T)/DZP[c]	−436.439 961 (423.2, 0.0)	−436.501 923 (384.3, −38.9)	−436.547 588 (355.6, −67.6)	−437.114 346 (0.0)
SCF/6-31G*	−434.949 163 (518.7, 0.0)	−435.009 461 (480.9, −37.8)	−435.056 839 (451.2, −67.5)	−435.775 796 (0.0)
BHLYP/6-31G*	−437.152 655 (442.1, 0.0)	−437.214 327 (403.4, −38.7)	−437.262 771 (373.0, −69.1)	−437.857 156 (0.0)
B3P86/6-31G*	−438.431 247 (394.4, 0.0)	−438.501 833 (350.1, −44.3)	−438.547 221 (321.6, −72.8)	−439.059 689 (0.0)
B3LYP/6-31G*	−437.428 314 (419.3, 0.0)	−437.496 316 (376.6, −42.7)	−437.539 719 (349.3, −70.0)	−438.096 514 (0.0)
MP2(full)/6-31G*	−436.300 384 (468.1, 0.0)	−436.391 752 (410.7, −57.4)	−436.433 705 (384.4, −83.7)	−437.046 297 (0.0)
B3LYP/6-311+G*	−437.524 593 (448.2, 0.0)	−437.598 653 (401.7, −46.5)	−437.639 355 (376.1, −72.1)	−438.238 773 (0.0)

[a] Some of the results for the O_h structure were taken from ref 4. [b] Single-point energy at the optimized geometry of CISD/DZP. [c] Single-point energy at the optimized geometry of CCSD/DZP.

When the B3LYP method is used in conjunction with a somewhat larger basis set (6-311+G*), the N−N bond lengths are 1.517 Å, which is idential to the CCSD/DZP prediction.

The optimized geometry for the D_{2h} structure **2** demonstrates the same general trends in the effects of correlation methods on equilibrium bond lengths. There are three independent N−N bonds due to the D_{2h} symmetry. The changes of the three kinds of N−N bond lengths are similar to each other as a function of the theoretical method. It is convenient to discuss the average values of the bond lengths. Similar to structure **1**, the CI (1.435 Å) and CC (1.472 Å) methods increase the average N−N bond length from the SCF (1.416 Å) method by about 0.19 and 0.56 Å, respectively. The average bond lengths predicted by the B3LYP and B3P86 methods (1.460 and 1.472 Å, respectively) are between those from the CISD and CCSD methods, which are regarded as close to the true values. BHLYP yields results almost halfway from the SCF to the B3P86 or B3LYP method. MP2, again, overestimates the N−N bond lengths (average 1.487 Å). With a larger basis set, the average bond length from B3LYP/6-311+G* (1.467 Å) is slightly longer than that from B3LYP/6-31G*. The B3LYP results fall between the results from the CISD/DZP (1.435 Å) and CCSD/DZP (1.472 Å) methods. The bond angles are insensitive to the different levels of theory. The angle $N_2-N_1-N_3$ falls within a small range (117.0°−117.4°) at the various levels of theory.

Figure 3 shows the geometrical parameters for the C_{2v} structure **3**. The C_{2v} structure has five independent N−N bond lengths and two independent bond angles. The N−N bond lengths behave very similarly to structures **1** and **2**. The N−N bonds predicted by the SCF method are too short and those by MP2 too long. The N−N bonds from B3LYP/6-311+G* (average 1.481 Å) are between CISD/DZP (average 1.447 Å) and CCSD/DZP (average 1.482 Å) and close to that of the latter. So they may be regarded as close to the true values. The bond angles are again insensitive to the level of theory. Excluding the MP2 results, the variation in the $N_2-N_1-N_4$ bond angles at different levels of theory is within 0.3°.

The total energies of the three isomers and the energies relative to $4N_2$ molecules and to the cubane structure **1** are shown in Table 1. The energy of N_8 octaazacubane (**1**) relative to $4N_2$ was reported to be quite high at all levels of theory by LSS and GJS.[3,4] At the SCF level of theory, the relative energy is about 490 or 519 kcal/mol with the DZP or 6-31G* basis set. The effects of electron correlation decrease the relative energies. At the CCSD(T)/DZP level of theory assuming the CCSD/DZP equilibrium geometry, the energy of **1** decreases to 423 kcal/mol. A similar result (419 kcal/mol) is predicted at the B3LYP/6-31G* level of theory. With the slightly larger basis set, the relative energy at the B3LYP/6-311+G* level of theory becomes 448 kcal/mol, which is between the results of CISD and CCSD and close to the CISD/DZP result.

Structures **2** and **3** have lower energies than **1**, but their energies relative to $4N_2$ are still quite high. For the D_{2h} structure **2**, the energy relative to $4N_2$ molecules is 459 or 481 kcal/mol at the SCF level of theory in conjunction with the DZP or 6-31G* basis set. It decreases to 384 kcal/mol at the CCSD(T)/DZP level with the CCSD/DZP-optimized geometries. The result from the B3LYP/6-31G* method (377 kcal/mol) is very close. At the B3LYP/6-311+G* level of theory, the relative energy becomes 402 kcal/mol, which is between the predictions from CISD/DZP and CCSD/DZP. For the C_{2v} structure **3**, with the same trend, the relative energy of $4N_2$ molecules is 426 or 451 kcal/mol at the SCF level of theory, and it decreases to 356 kcal/mol at the CCSD(T) level of theory. A similar result is the 349 kcal/mol prediction from the B3LYP/6-31G* level of theory. With the larger basis set, at the B3LYP/6-311+G* level this difference increases to 376 kcal/mol, which again falls between the results of the CISD/DZP and CCSD/DZP methods.

The energies of structures **2** and **3** relative to **1** are fairly insensitive to the theoretical methods. From the SCF/DZP to the CCSD(T)/DZP level of theory, the relative energies of the structures **2** (D_{2h}) and **3** (C_{2v}) relative to **1** (O_h) are nearly constant. They range from −32 to −39 kcal/mol for **2** and from −64 to −68 kcal/mol for **3**. With DFT methods, the deviations from the SCF results (with the same basis set) are also small. The energy of structure **2** relative to structure **1** ranges from −38 (SCF/6-31G*) to −44 kcal/mol (B3P86/6-31G*) and that of structure **3** relative to **1** is from −68 to −73 kcal/mol. However, at the MP2 level of theory, the relative energies of structures **2** and **3** are almost 20 kcal/mol different from the SCF results, being 57 kcal/mol for **2** and 84 kcal/mol for **3**.

TABLE 2: Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol, in Parentheses)

mode	SCF/6-31G*	BHLYP/6-31G*	B3P86/6-31G*	B3LYP/6-31G*	MP2/6-31G*	B3LYP/6-311+G*
O_h (**1**)						
A_{2u}	1334(0)	1223(0)	1123(0)	1117(0)	1055(0)	1009(0)
E_g	1231(0)	1138(0)	1071(0)	1036(0)	995(0)	1034(0)
T_{2u}	1145(0)	1040(0)	964(0)	928(0)	868(0)	927(0)
A_{1g}	1141(0)	1041(0)	956(0)	923(0)	872(0)	921(0)
T_{2g}	1077(0)	960(0)	873(0)	857(0)	802(0)	851(0)
T_{1u}	1053(3)	929(5)	826(8)	792(7)	725(8)	786(9)
T_{2g}	964(0)	857(0)	755(0)	728(0)	642(0)	694(0)
E_u	727(0)	621(0)	521(0)	523(0)	463(0)	515(0)
D_{2h} (**2**)						
A_g	1539(0)	1387(0)	1274(0)	1230(0)	1131(0)	1232(0)
B_{3u}	1447(0)	1322(0)	1231(0)	1191(0)	1091(0)	1195(0)
B_{3u}	1250(2)	1154(3)	1084(3)	1071(4)	1031(6)	1070(4)
A_g	1134(0)	1034(0)	953(0)	921(0)	889(0)	919(0)
B_{1g}	1218(0)	1049(0)	914(0)	872(0)	792(0)	868(0)
B_{2u}	1284(14)	1051(11)	833(8)	771(8)	754(4)	773(9)
B_{1u}	953(0)	850(0)	775(1)	738(1)	688(5)	735(1)
B_{2u}	930(0)	836(0)	761(0)	732(1)	647(4)	728(0)
A_g	961(0)	849(0)	766(0)	728(0)	666(0)	726(0)
A_u	977(0)	849(0)	760(0)	726(0)	661(0)	717(0)
B_{2g}	900(0)	812(0)	749(0)	713(0)	674(0)	711(0)
B_{3u}	863(2)	772(1)	711(1)	669(1)	604(1)	666(1)
B_{2g}	816(0)	739(0)	675(0)	662(0)	626(0)	665(0)
B_{1g}	727(0)	685(0)	654(0)	646(0)	631(0)	647(0)
A_g	648(0)	596(0)	552(0)	533(0)	517(0)	532(0)
B_{3g}	852(0)	685(0)	542(0)	495(0)	395(0)	491(0)
B_{1u}	421(16)	382(11)	349(8)	344(8)	329(7)	348(7)
A_u	311(0)	251(0)	196(0)	189(0)	149(0)	195(0)
C_{2v} (**3**)						
A_1	1350(4)	1211(4)	1125(4)	1085(3)	1042(2)	1084(3)
B_2	1329(1)	1196(2)	1105(4)	1069(4)	990(7)	1065(4)
B_1	1200(1)	1112(2)	1038(2)	1028(1)	989(2)	1013(2)
A_1	1252(1)	1137(1)	1048(1)	1010(1)	936(1)	1006(1)
A_1	1149(1)	1053(0)	980(0)	953(0)	910(1)	951(0)
B_2	1170(2)	1029(2)	946(2)	934(2)	903(0)	930(2)
A_1	1062(1)	952(3)	866(3)	835(2)	797(3)	832(3)
A_2	1077(0)	935(0)	847(0)	820(0)	789(0)	820(0)
B_2	1028(1)	947(0)	853(0)	814(0)	733(0)	811(0)
A_2	985(0)	894(0)	821(0)	803(0)	754(0)	795(0)
B_1	1038(4)	904(2)	809(1)	779(1)	730(3)	777(1)
A_1	926(4)	858(2)	801(2)	772(2)	747(4)	767(2)
A_2	960(0)	853(0)	775(0)	747(0)	692(0)	743(0)
B_1	910(5)	802(2)	724(0)	689(0)	613(0)	678(0)
A_1	847(8)	742(12)	657(16)	620(15)	489(12)	616(18)
B_2	797(0)	684(2)	607(4)	571(4)	464(5)	558(5)
B_1	662(7)	590(6)	533(6)	519(6)	491(6)	516(7)
A_2	614(0)	528(0)	452(0)	427(0)	340(0)	426(0)

Although structures **2** and **3** lie lower energetically than structure **1** (by 40 or 70 kcal/mol), they still have high energies compared with the isomers studied in previous papers, which incorporate double bonds.[3,4] The octaazacyclooctatetraene (D_{2d} boat structure) of N_8 is about 170 kcal/mol lower than structure **1**, while the octaazapentalene (D_{2h}) structure is even lower (about −210 kcal/mol related to structure **1**).[3,4] In GJS's recent work, there are three other minima of N_8:azidopentazole (C_s), octaazasemibullvalene (C_s), and the *all-trans* open-chain structure (C_{2h}). They lie below O_h structure energetically by about 190, 140, and 220 kcal/mol, respectively.[3] The reason should be, as pointed out at the beginning of this paper, because all other isomers contain N═N double bonds, and the energy associated with a N═N double bond is more than twice that of N−N single bond.

At least one question remains. Do there exist candidates with only N−N single bonds for N_8 other than these three? Topologically, the answer is yes. According to graph theory, there are five possible graphs which have eight points connected by twelve lines with each point having a degree of three (see Figure 4).[28] However, in chemical applications, there are additional limitations of the distances between the points in the graph. In our case of N_8, the distances between two points must be in the range of a single-bond length if these points are connected by a line in the graph, while the distances must be reasonably greater than a single-bond length if they are not connected by any line. Since two of these five graphs in Figure 4 cannot satisfy the bond length requirement, there are only three isomers that are practical for the present chemical application. They are indeed the structures **1**, **2**, and **3**.

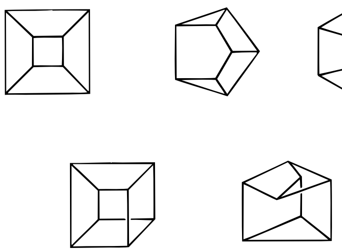


Figure 4. Possible graphs for eight points connected by twelve lines.

The energy order of the structures is structure **1** > **2** > **3**, and the symmetry order corresponds to **1** (O_h) > **2** (D_{2h}) > **3** (C_{2v}) as well. For the N_8 isomers with the same bonding characteristics, it appears that the ones with higher symmetry have the higher energy. The N−N bond lengths in structures **2** and **3** are shorter than those in structure **1** except in a few instances. It is interesting that the energy of structure **3** is lower than that of **2** but that the average bond length of **3** is longer than that of **2**. It is thus demonstrated that the decrease of bond length is not necessarily in concert with the decrease of the energy.

The theoretical harmonic vibrational frequencies and IR intensities for the three structures **1**, **2**, and **3** at different levels of theory are given in Table 2. Since they have no imaginary vibrational frequencies, they are all minima on the N_8 potential energy hypersurface. Electron correlation has a large effect on the vibrational frequencies. Most frequencies decrease from SCF to DFT methods. But the MP2 frequencies decrease too much relative to the SCF results. The lowest predicted frequency at the highest level (B3LYP/6-311+G*) for structure **3** is 426 cm^{-1}, which is larger than that of structure **2** (195 cm^{-1}, at the same level of theory), indicating that the potential surface of structure **3** in the vicinity of the minimum point on the potential energy hypersurface is steeper than that for structure **2**.

Structures **1**, **2**, and **3** (Figures 1−3) consist only of single bonds, so they can interconvert from one structure to another by breaking two old bonds and forming two new ones. For instance, in **1**, the breaking of bonds 1−5 and 4−8 and the formation of new bonds 1−4 and 5−8 will turn structure **1** into structure **2**. Similarly, in **2**, the breaking of bonds 4−7 and 5−8 and the formation of new bonds 5−7 and 4−8 will transform it into **3**.

4. Conclusions

In addition to octaazacubane (structure **1**), we have reported geometries, energies, and harmonic vibrational frequencies for two new isomers of N_8 containing only N−N single bonds, structures **2** and **3** (octaazacuneane), using both *ab initio* and DFT methods. Vibrational frequency analyses show that the two new structures are minima on the potential energy hypersurface of N_8. Each structure is found to be high-lying in energy compared with the isomers reported previously, which contain N═N double bonds. The energetical ordering of the three structures is **1** (O_h) > **2** (D_{2h}) > **3** (C_{2v}).

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