



**The Structure of Secondary 2-Azidoethanamines:  
A Hypergolic Fuel vs. a Nonhypergolic Fuel**

by Michael J. McQuaid

ARL-TR-3176

April 2004

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**Michael J. McQuaid**  
**Weapons and Materials Research Directorate, ARL**

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14. ABSTRACT In an attempt to find structural features of 2-azidoethanamines that correlate with their hypergolic ignition delays, density functional theory (DFT)-based quantum mechanics calculations were performed to characterize equilibrium configurations of two secondary 2-azidoethanamines: 2-azido-N-cyclopropylethanamine (CPAZ) and 2-azido-N-methylethanamine (MMAZ). The former is hypergolic with inhibited red fuming nitric acid, while the latter is not. Geometries and normal modes for 23 MMAZ conformers and 42 CPAZ conformers are presented, compared to each other, and compared to geometries and normal modes obtained previously for the hypergolic, tertiary 2-azidoethanamine 2-azido-N,N-dimethylethanamine (DMAZ). The geometries of >N-CH <sub>2</sub> -CH <sub>2</sub> -N <sub>3</sub> chains in analogous MMAZ and CPAZ conformers are found to be nearly identical, and the relative energies of MMAZ conformers as a function of this chain's orientation are mimicked in the CPAZ conformers. Some minor differences between the secondary 2-azidoethanamines and DMAZ are noted, but no structural feature is found to be unique to the hypergolic compounds.					
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## 1. Introduction

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The U.S. Army is developing a laser-guided 2.75-in rocket system for use on the AH-64 Apache, OH-58 Kiowa Warrior, and RAH-66 Comanche helicopters. Called the Advanced Precision Kill Weapon System (APKWS), the need for this system was identified in Desert Storm after-action investigations. Those investigations revealed that a large number of HELLFIRE (anti-tank missile) firings were made against soft- or lightly armored targets that could have been killed by a smaller weapon. The HELLFIRE was employed, however, because its precision guidance capability was needed to reduce the potential for collateral damage or fratricide. The APKWS is being designed to enhance the existing (unguided) Hydra-70 2.75-in rocket system and to complement the HELLFIRE. It will be the weapon of choice for operations in urban terrain or for aerial fire support missions in close proximity to friendly forces.

Among technologies being considered for insertion into the APKWS is the Impinging Stream Vortex Engine (ISVE). Under development at the U.S. Army Aviation and Missile Research Development and Engineering Center (AMRDEC), it is thought capable of yielding a hypergolic propulsion system compact enough to fit in the APKWS. So equipped, the thrust of the APKWS could be controlled, increasing the engagement stand-off distances allowed and therefore improving platform survivability.

Toward optimizing the ISVE's design, the U.S. Army Research Laboratory (ARL) is simulating ISVE performance as a function of various design parameters via a computational fluid dynamics (CFD) model of the engine (Nusca and Michaels, 2003). In support of the effort, computational chemistry is being employed to estimate various (unmeasured) properties of candidate fuels. Needed as model input, to date, the emphasis has been on characterizing potential alternatives to the best current ISVE fuel candidate—monomethylhydrazine (MMH). Acutely toxic and a suspected carcinogen (Schmidt, 2001), MMH's use requires the implementation of costly and burdensome handling procedures.

Compounds with 2-azidoethanamine chains ( $>N-CH_2-CH_2-N_3$ ) comprise a class of fuels that AMRDEC has tested in the ISVE (and has investigated for use in other propulsion applications). Collectively referred to as Competitive Impulse Non-Carcinogenic Hypergols (CINCH) (Thompson et al., 1998; Stevenson, 2002), the formulation within this class of compounds receiving the most attention is 2-azido-N,N-dimethylethanamine  $[(CH_3)_2NCH_2CH_2N_3]$ . Also referred to as DMAZ, it has been found to yield specific impulse competitive with MMH in inhibited red fuming nitric acid (IRFNA) oxidized systems, and it is much less toxic than hydrazine or its derivatives. Unfortunately, DMAZ-IRFNA systems have longer ignition delays than MMH-IRFNA systems. Increasing ignition delays result in more fuel and oxidizer accumulating in the combustion chamber during engine start up, and to avoid overpressurizing the chamber when the accumulation finally ignites, a larger chamber must be designed.

Penalizing rocket performance, this issue may negatively impact the U.S. Army's ability to field DMAZ or other CINCH fuels.

Compromised ignition delays are a common problem with hydrazine-alternative hypergols, and a mechanistic understanding of CINCH-IRFNA ignition processes is being sought in the hope of addressing the issue. Based on traditional chemical insight, and finding amine nitrate salts in the residue of DMAZ-IRFNA combustion experiments, AMRDEC has hypothesized that proton transfer from nitric acid to the fuel's amine nitrogen may be a rate-controlling step. Therefore, one of AMRDEC's approaches to addressing the ignition delay issue has been to attempt to enhance the amine's reactivity/basicity by replacing the methyl groups in DMAZ with other substituents. Two secondary amine azides synthesized on this basis were 2-azido-N-methylethanamine (MMAZ) and 2-azido-N-cyclopropylethanamine (CPAZ), and the results were mixed. MMAZ, which has a hydrogen atom in lieu of one of the methyl groups in DMAZ, is not hypergolic. CPAZ, which has a cyclopropyl group in lieu of the methyl group in MMAZ, has an ignition delay comparable to DMAZ (Stevenson, 2002). Given the hypothesized importance of base strength, the result for MMAZ is surprising because its base strength (based on measured  $pK_a$ ) is higher than DMAZ's.

In a first step toward trying to reconcile such observations via computational chemistry, ARL determined the nature of equilibrium DMAZ conformers (McQuaid et al., 2002). Twelve conformers were identified via density functional theory (DFT) calculations, and an analysis of an infrared (IR) absorption spectrum of DMAZ vapor at 298 K supported the computed differences in their energy. An interesting finding of the study was that in its lowest energy configuration, which is shown in Figure 1, the azide group shields the amine lone pair electrons from proton attack. Given the expected importance of proton transfer to the amine site, the finding suggested the possibility of molecular geometry being a factor controlling the onset of ignition.

Based on its computed electron density distribution, the energy of the "shielded" DMAZ conformer (B) appears to be lowered by an attractive interaction between a slightly positive partial charge on the middle nitrogen of the azide group (N3) and a slightly negative partial charge associated with the amine nitrogen (N1). Comparing the calculated energies of DMAZ conformers B and A, structures whose only significant difference is their C3-C4-N2-N3 dihedral angle, the attraction appears to lower B's energy by ~1 kcal/mol. Given this observation, a concern about the potential benefit of increasing the basicity of the amine nitrogen is raised. That is, should an increase in amine basicity lead to an increase in the attraction between the amine and azide groups, it might lead to a greater percentage of molecules in a population assuming a shielded configuration, offsetting the (presumed) benefit of the increased basicity.

A stereoisomer-based approach for designing molecules that preclude (or promote) a shielded configuration in amine azides has been proposed, and a theoretical study of an embodiment of the approach, namely 2-azido-N,N-dimethylcyclopropanamine (ADMCPA), suggests its promise

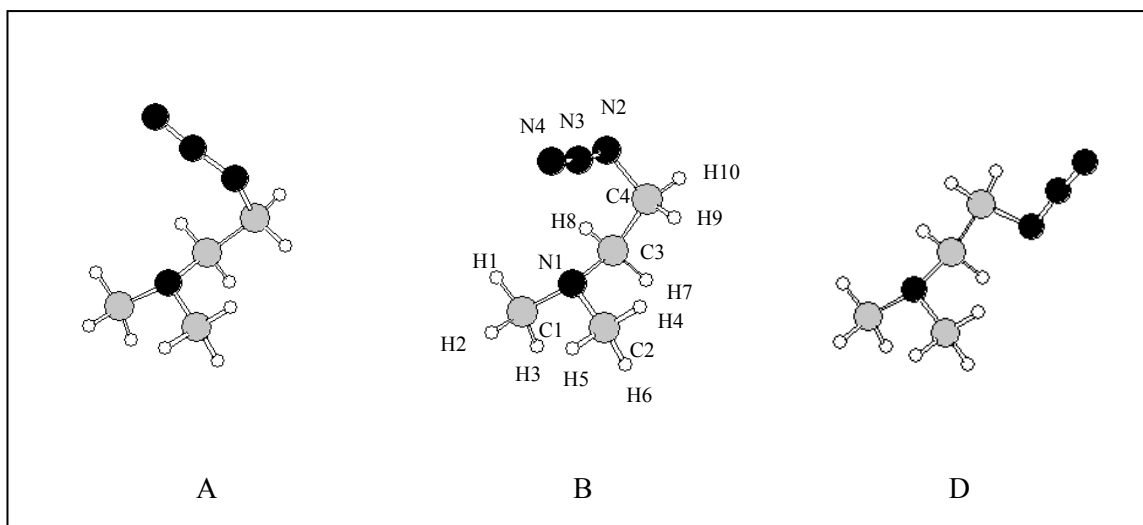


Figure 1. DMAZ conformers A, B, and D. B is the lowest energy DMAZ conformer. Labeling follows a previous reference (McQuaid et al., 2002).

(McQuaid, 2002). However, until molecules designed in this manner are synthesized and tested, the impact of shielding on the ignition process is likely to remain uncertain. In the interim, the differences (and similarities) between DMAZ, MMAZ, and CPAZ suggested that a comparison of their structures might identify differences that correlate with ignition delay. Further motivating this study was an investigation that shows that the proton affinities of azide lone pair sites are significantly higher than analogous sites in ethyl azide, and that this effect is passed from/through the ethyl chain (McQuaid, 2003). Therefore, a comprehensive survey to identify and characterize equilibrium conformers of MMAZ and CPAZ was completed. This report summarizes the findings of the study, with previously reported results for DMAZ provided for comparison.

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## 2. Computational Methods

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The Gaussian 98 (G98) suite of quantum chemistry codes (Frisch et al., 2001) was employed to identify equilibrium MMAZ and CPAZ conformers and characterize their normal modes. The choice of model—B3LYP functionals (Becke, 1993; Lee et al., 1988) and a 6-311++G(d,p) atomic orbital basis set (Miehlich et al., 1989; Clark et al., 1983; McLean and Chandler, 1980; Krishnan et al., 1980) on the G98-defined “ultrafine” integration grid—was based on its success in characterizing DMAZ (McQuaid et al., 2002). The search for equilibrium conformers did not extend much beyond finding DMAZ “analogs,” i.e., structures with the dihedral angle preferences observed in DMAZ. However, the author expects that most (if not all) of the lowest energy structures will prove to have been identified by this approach. Because the results are not compared to experimental IR data, no scaling to correct potential systematic bias in the normal mode frequency calculations was performed.

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### 3. Results

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#### 3.1 MMAZ

Figures 2 and 3 show the 23 unique MMAZ equilibrium structures identified through the study. (A total of 24 structures are given in Figures 2 and 3, but conformers I1 and I2 are mirror images of one another.) A complete description of each conformer’s geometry and normal mode frequencies is given in the appendix. The conformers are distinguished by their dihedral angles, and conformer labels were chosen to facilitate comparison with the DMAZ conformers identified and described in a previous publication (McQuaid et al., 2002). The labeling scheme for DMAZ conformers in that publication was chosen such that alphabetically adjacent conformers are nominally transformed into one another by a dihedral angle rotation about either the N(amine)-C(ethyl), C-C or C-N(azide) bond. The letter designation for an MMAZ conformer indicates the correspondence of its C-N(H)-CH<sub>2</sub>-CH<sub>2</sub>-N<sub>3</sub> orientation with that of the same-lettered DMAZ conformer.

To further facilitate comparisons with DMAZ, the structures are divided into two groups. In the first group, which is shown in Figure 2, the C1-N1-C2-C3, N1-C2-C3-N2, and C2-C3-N2-N3 dihedral angle combinations correspond to the C1-N1-C3-C4, N1-C3-C4-N2, and C3-C4-N2-N3 dihedral angle combinations of DMAZ. In this group, all but one counterpart to observed DMAZ conformers are found. Attempts to find the missing one, i.e., the analog to DMAZ conformer K, were conducted via optimizations started with geometries like the one hypothesized. But the optimizations led to either J1 or L1. In the second group, which is shown in Figure 3, the C1-N1-C2-C3, N1-C2-C3-N2, and C2-C3-N2-N3 dihedral angle combinations correspond to C2-N1-C3-C4, N1-C3-C4-N2, and C3-C4-N2-N3 dihedral angle combinations of DMAZ. In this group, analogs to all of the DMAZ conformers are found. One without a corresponding DMAZ conformer was also identified. Except for its C2-C3-N2-N3 dihedral angle, this “new” conformer is nominally the same as conformers C2 and D2 and is therefore placed between them in Figure 3. It is labeled X2 to avoid the need to change other labels.

Table 1 provides MMAZ conformer zero-point corrected energies (ZPE), the difference between their ZPE and the ZPE of the lowest energy conformer ( $\Delta E$ ), and two estimates of their probability ( $W$ ) in a gas-phase sample at  $T = 298$  K,

$$W_i = \exp(-\Delta E_i / kT) / \sum_i \exp(-\Delta E_i / kT). \quad (1)$$

The first conformer population distribution is based on  $\Delta E_i$ ’s calculated from uncorrected ZPE values. In the second distribution, the  $\Delta E_i$  are calculated assuming a C2-C3-N2-N3 dihedral angle-related bias in the energy calculations. To account for this bias, which was identified in the study of DMAZ reported previously (McQuaid et al., 2002), the ZPEs of “*anti*” conformers (i.e., those with C2-C3-N2-N3 dihedral angles near 180°) are increased 0.000637 Hartrees

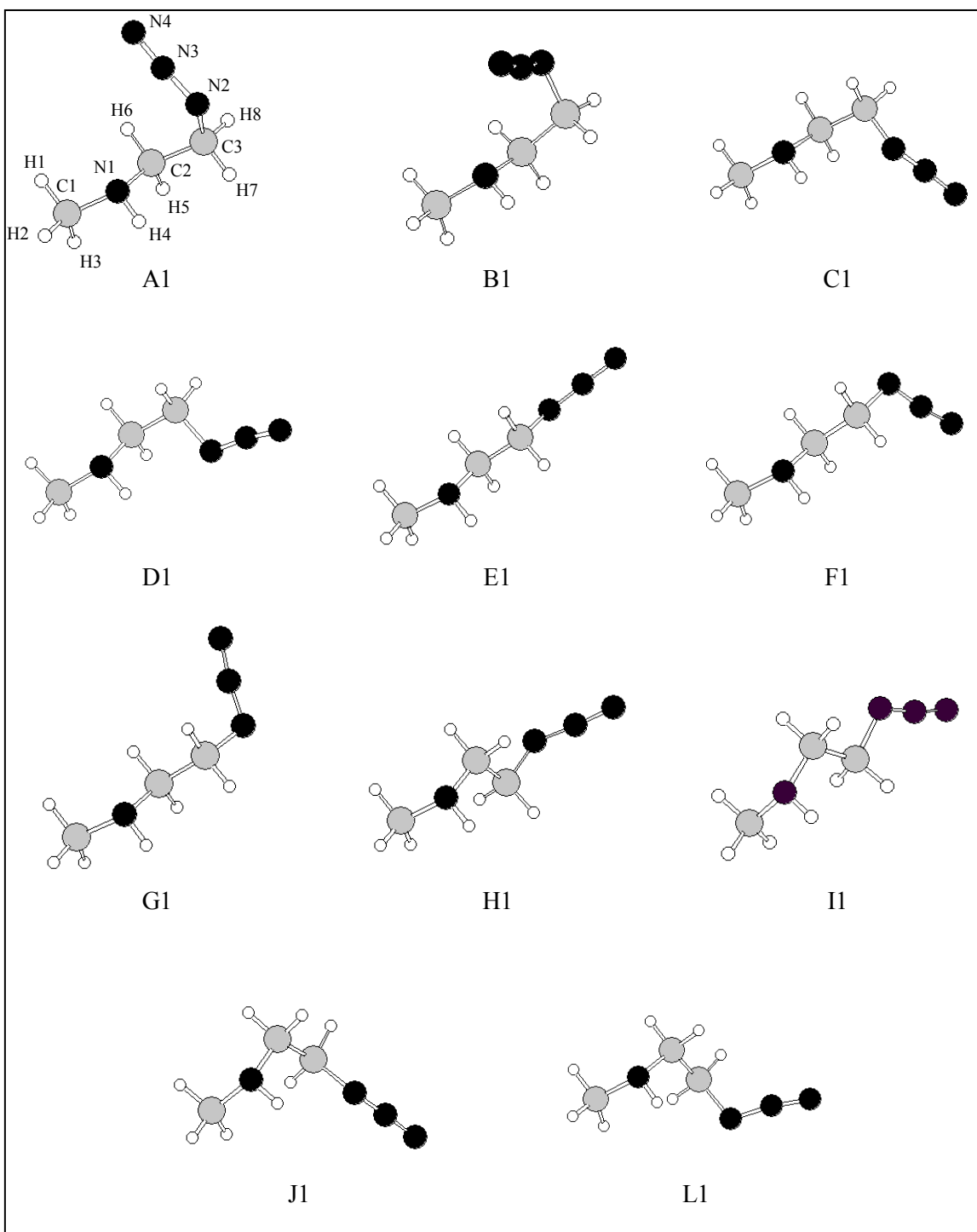


Figure 2. MMAZ group 1 conformers.

relative to “*gauche*” conformers (i.e., those with C2-C3-N2-N3 dihedral angles near  $(\pm)80^\circ$ ). It is observed that, except for A1 and A2, group 1 conformers are lower in energy than their group 2 counterparts. Somewhat surprisingly, the 2 lowest energy conformers of the entire set, i.e., D1 and C1, are not counterparts to the lowest energy DMAZ structure (B). D1 and C1 are

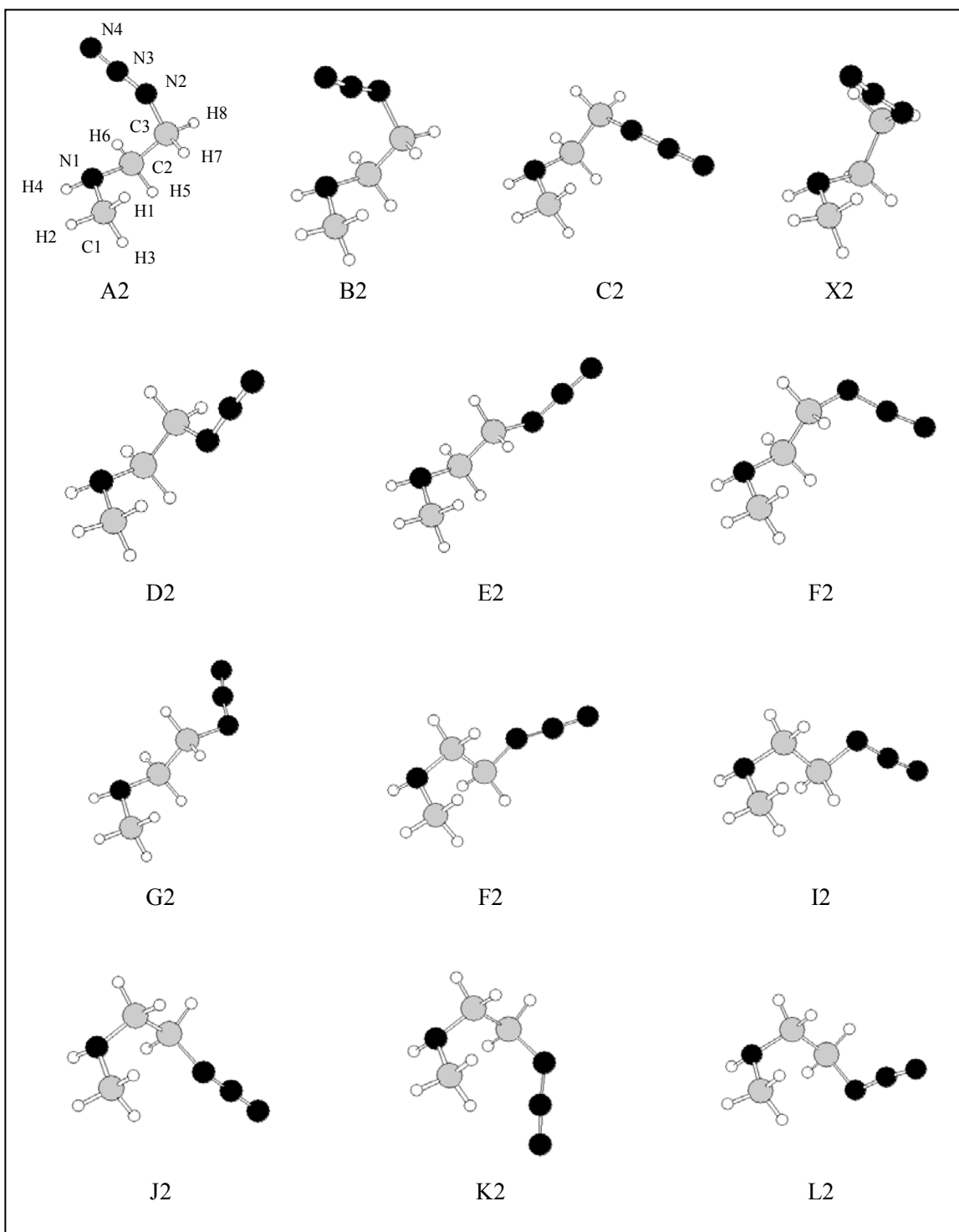


Figure 3. MMAZ group 2 conformers.

configurations in which the azide group does not shield amine site from proton attack, and they are predicted to have a combined population exceeding 50% of the total in a room temperature vapor sample. The probability of shielded MMAZ configurations (B1 and B2) in the same

Table 1. MMAZ equilibrium conformer B3LYP/6-311++G(d, p) energies and conformer probabilities in a gas-phase population at 298 K.

Conformer	ZPE (Hartrees)	$\Delta E$ (kcal/mol)	$W$	$W$ (adj.) <sup>a</sup>
D1	-338.0384	0.0	0.44	0.32
C1	-338.0373	0.7	0.13	0.19
B1	-338.0366	1.1	0.06	0.09
E1	-338.0365	1.2	0.06	0.08
F1	-338.0365	1.2	0.06	0.04
J1	-338.0365	1.2	0.06	0.04
B2	-338.0362	1.4	0.04	0.06
G1	-338.0358	1.7	0.03	0.04
E2	-338.0357	1.7	0.02	0.02
L1	-338.0353	2.0	0.02	0.02
F2	-338.0351	2.1	0.01	0.02
G2	-338.0350	2.1	0.01	0.02
D2	-338.0349	2.2	0.01	0.01
A2	-338.0348	2.3	0.01	0.01
I1/I2	-338.0346	2.4	0.01	0.01
X2	-338.0345	2.4	0.01	0.01
C2	-338.0342	2.7	0.00	0.01
H1	-338.0342	2.7	0.00	0.01
H2	-338.0341	2.7	0.00	0.01
A1	-338.0339	2.8	0.00	0.01
J2	-338.0336	3.0	0.00	0.00
L2	-338.0333	3.2	0.00	0.00
K2	-338.0329	3.5	0.00	0.00

<sup>a</sup> Population distribution obtained if the ZPEs of *anti* conformers (D, E, I, and J) are increased 0.000627 Hartrees to account for the suspected bias (vs. *gauche* conformer ZPEs) in their calculated values.

sample is predicted to be between 9% and 15%. In room temperature DMAZ vapor, the shielded conformation was observed to be present in ~45% of the total population.

Table 2 shows the ZPEs of the MMAZ conformers relative to the ZPE of the B conformer in their group and compares them to the relative energies of the DMAZ conformers. (The values are not corrected for the suspected bias in the calculation of *anti* and *gauche* conformer ZPEs.) The comparison shows that the ZPE differences between the DMAZ conformers are mimicked in MMAZ group 2, but not in MMAZ group 1. At first glance, the proximity of the amine-bonded hydrogen (H4) and the azide nitrogen (N2) in conformer D1 suggests the possibility of an intramolecular hydrogen bond, which in turn might account for the unexpectedly low energy of this conformer. However, the N1-H4-N2 angle (102°) and the lack of a significant shift in the (Mode 39) N1-H4 stretching frequency (relative to other group 1 conformers) deny the existence of a classic hydrogen bond. The table also shows that, as found for DMAZ, the proximity of the amine and azide groups in the B conformer appears to lower its energy relative to the A conformer, the difference being 1.7 kcal/mol in group 1 and 0.9 kcal/mol in group 2.

Table 2. The relative energies of MMAZ equilibrium conformers by group and in comparison to the relative energies of DMAZ equilibrium conformers.

Conformer	$\Delta E$ (kcal/mol)		
	DMAZ	MMAZ Group 1	MMAZ Group 2
A	1.2	1.7	0.9
B	0.0	0.0	0.0
C	1.3	-0.4	1.3
X	<sup>a</sup>	<sup>a</sup>	1.1
D	1.0	-1.1	0.8
E	0.4	0.1	0.3
F	0.8	0.1	0.7
G	0.9	0.5	0.8
H	1.9	1.5	1.3
I	1.6	1.3	1.0
J	2.0	0.1	1.6
K	2.4	<sup>a</sup>	2.1
L	2.2	0.8	1.9

<sup>a</sup> Searched for, but not observed.

Table 3 compares the lengths of MMAZ and DMAZ bonds. No significant differences are observed in the bond lengths of analogous conformers. If the lowest energy structures of each molecule are compared, some larger differences are observed. For example, MMAZ conformer D1 has a 0.012 Å shorter C-C bond and a 0.010 Å longer C-N(azide) bond than DMAZ conformer B. But such differences indicate that there is little difference in the bond strengths of the two conformers. (For reference, the C=C double bond in ethene is 0.22 Å shorter than the C-C single bond in ethane.) Moreover, as will be shown in the next section, the conformer dependence of MMAZ bond lengths is also found in (the hypergolic) CPAZ.

### 3.2 CPAZ

The substitution of the methyl group in MMAZ with the (rigid) cyclopropyl ring found in CPAZ introduces a 3-fold increase in the number of conformers that can be hypothesized based on observed geometric preferences. Though steric hindrance will undoubtedly (and does) reduce the number of molecular configurations to less than the 81 ( $3^4$ ) that are calculated assuming three possible dihedral angles about four different bonds, the experience with MMAZ suggested that something close to this number would be found. Coupled with the longer calculation times needed for the four extra atoms, the author decided not to attempt to establish the existence of every equilibrium conformer that can be hypothesized. Rather, a search for all of the conformers corresponding to the seven lowest energy structures of DMAZ was conducted first. It established that, as in the case of ADMCPA (McQuaid, 2002), an amine lone pair-cyclopropyl

Table 3. Comparison of bond lengths (Å) in equilibrium conformers of MMAZ and DMAZ.

<b>MMAZ Parameter</b>	<b>MMAZ B1</b>	<b>DMAZ B</b>	<b>MMAZ D1</b>	<b>DMAZ D</b>	<b>DMAZ Parameter<sup>a</sup></b>
H1-C1	1.093	1.092	1.094	1.093	H1-C1
H2-C1	1.092	1.093	1.092	1.093	H2-C1
H3-C1	1.103	1.106	1.103	1.106	H3-C1
C1-N1	1.460	1.458	1.459	1.459	C1-N1
N1-C2	1.456	1.459	1.455	1.461	C3-N1
C2-C3	1.528	1.531	1.519	1.526	C4-C3
H5-C2	1.106	1.107	1.105	1.106	H7-C3
H6-C2	1.094	1.093	1.096	1.094	H8-C3
C3-N2	1.476	1.476	1.486	1.485	N2-C4
H7-C3	1.098	1.096	1.096	1.097	H9-C4
H8-C3	1.091	1.091	1.095	1.095	H10-C4
N2-N3	1.230	1.230	1.228	1.228	N3-N2
N3-N4	1.134	1.134	1.135	1.136	N4-N3
<b>MMAZ Parameter</b>	<b>MMAZ B2</b>	<b>DMAZ B</b>	<b>MMAZ D2</b>	<b>DMAZ D</b>	<b>DMAZ Parameter<sup>a</sup></b>
H1-C1	1.093	1.092	1.089	1.088	H4-C2
H2-C1	1.092	1.092	1.092	1.093	H5-C2
H3-C1	1.103	1.106	1.103	1.106	H6-C2
C1-N1	1.459	1.458	1.464	1.462	C2-N1
N1-C2	1.457	1.459	1.461	1.461	C3-N1
C2-C3	1.532	1.531	1.525	1.526	C4-C3
H5-C2	1.105	1.107	1.103	1.106	H7-C3
H6-C2	1.093	1.093	1.094	1.094	H8-C3
C3-N2	1.475	1.476	1.485	1.485	N2-C4
H7-C3	1.096	1.096	1.097	1.097	H9-C4
H8-C3	1.091	1.091	1.095	1.095	H10-C4
N2-N3	1.230	1.230	1.227	1.228	N3-N2
N3-N4	1.135	1.134	1.136	1.136	N4-N3

<sup>a</sup> DMAZ conformer and atom labels as well as bond lengths are from a previous reference (McQuaid et al., 2002).

group orientation where the lone pair electrons point over the C1-C2 bond is energetically favored. Therefore, the search for analogs of the five remaining DMAZ structures was limited to finding conformers with this amine lone pair-cyclopropyl group orientation.

Figures 4–8 show the equilibrium CPAZ structures identified by the search. The labeling follows that employed for DMAZ and MMAZ, with the letter designating a dihedral angle combination of the >NH-CH<sub>2</sub>-CH<sub>2</sub>-N<sub>3</sub> chain in common with similarly lettered MMAZ and DMAZ conformers, and the first number being a group designation associating it with one of the two groups defined for MMAZ. The second number designates which of three nominal amine

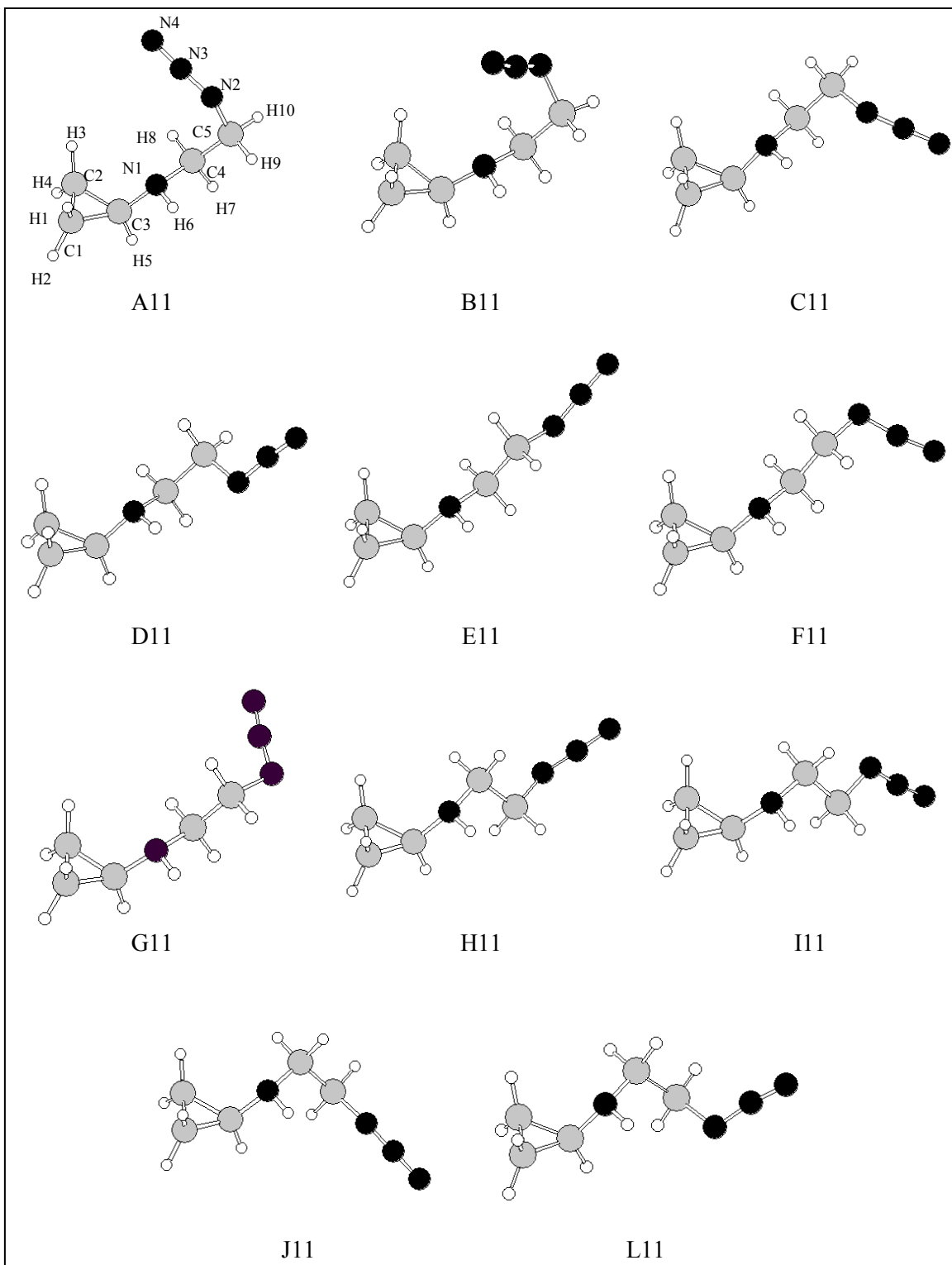


Figure 4. CPAZ group 11 conformers.

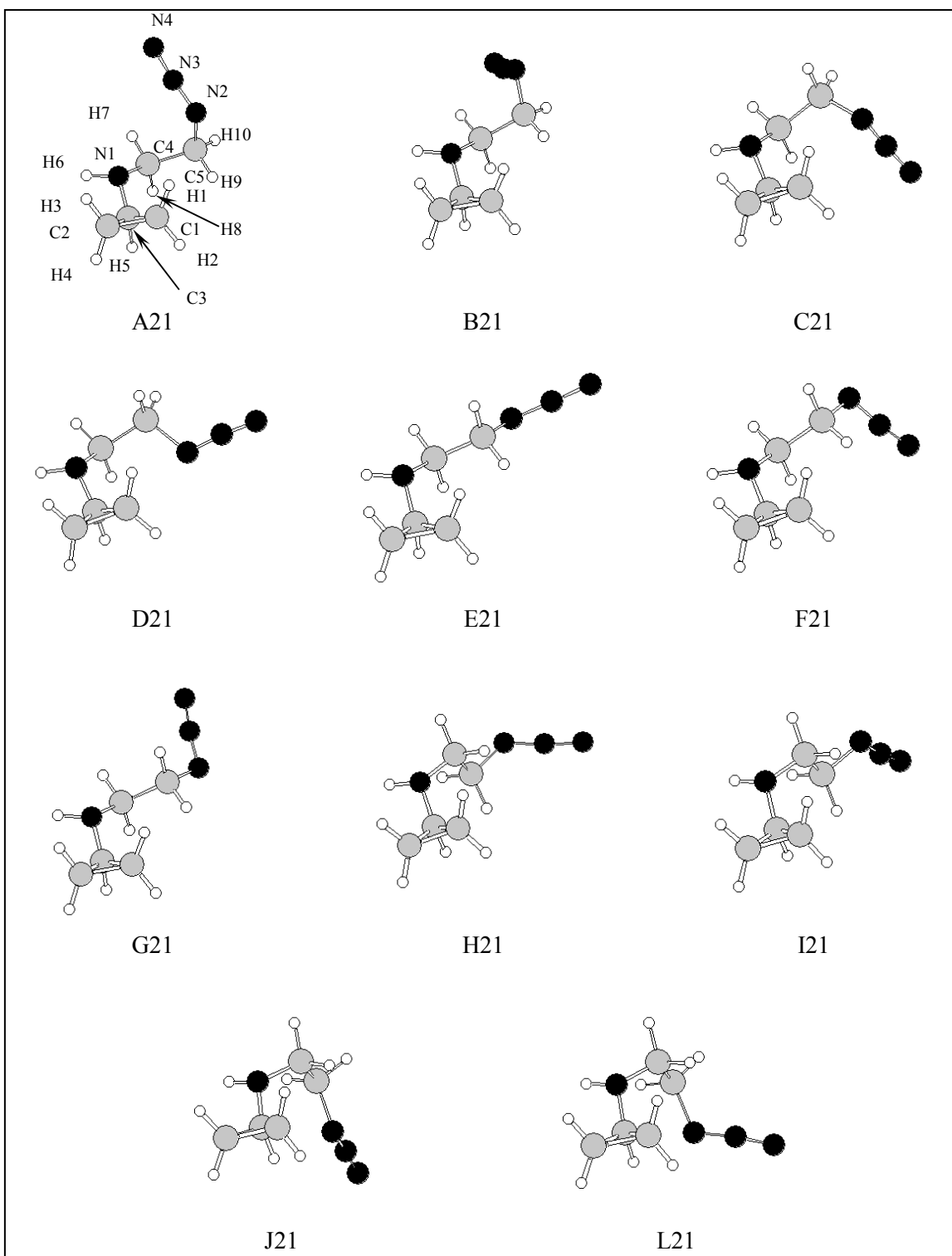


Figure 5. CPAZ group 21 conformers.

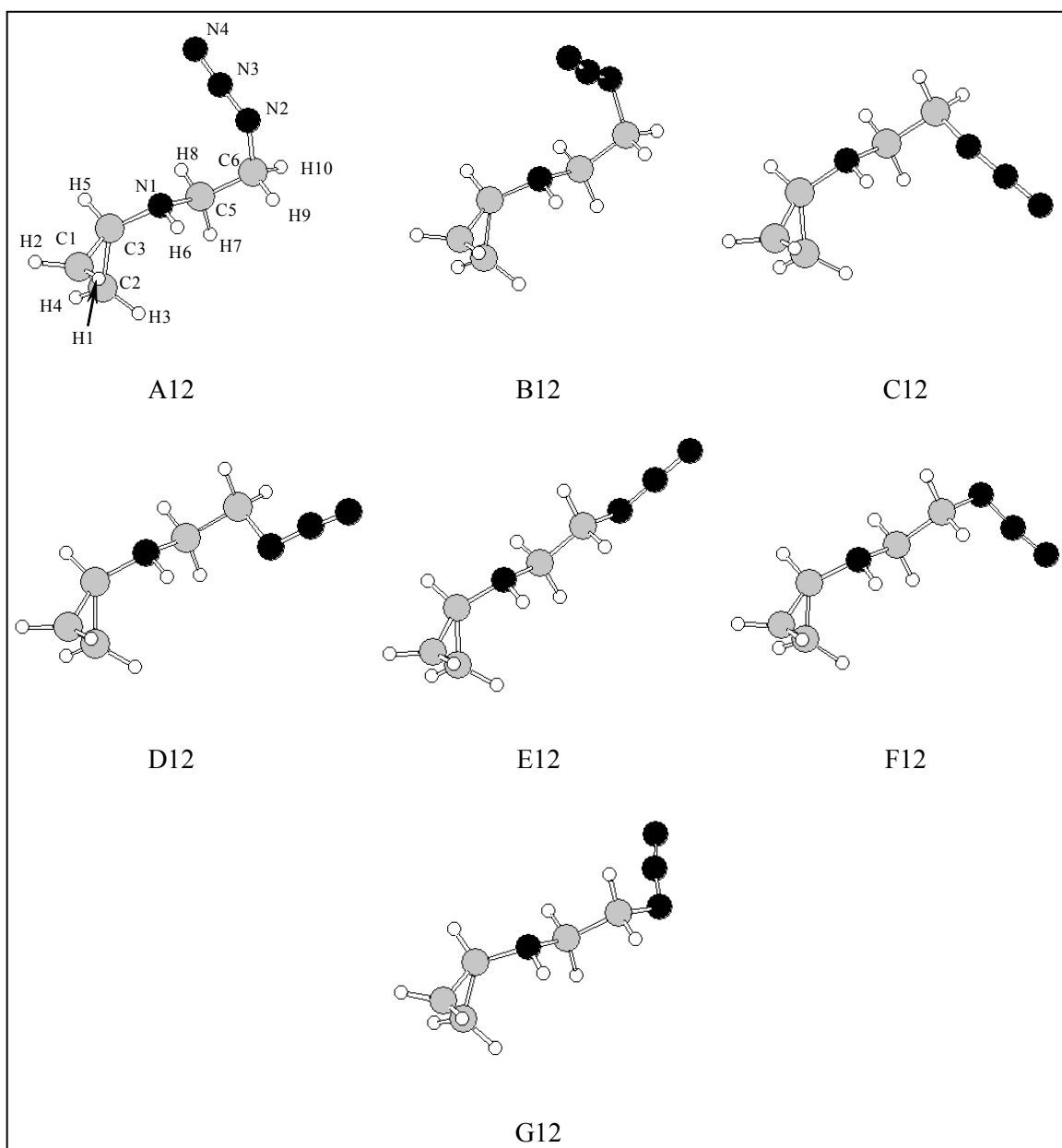


Figure 6. CPAZ group 12 conformers.

lone pair-cyclopropyl group orientations the conformer has, with “1” corresponding to the energetically preferred orientation, “2” corresponding to the orientation next lowest in energy, and “3” designating the highest energy orientation. It will be noted that there are no “23” conformers. All attempts to establish such structures through optimizations started with the hypothesized combination ended up as a structure in another group. In all, 42 unique CPAZ structures were identified. (A total of 43 conformers are shown in Figures 4–8, but I11 and I21 are mirror images of one another.) A complete description of their geometries and normal modes is provided in the appendix.

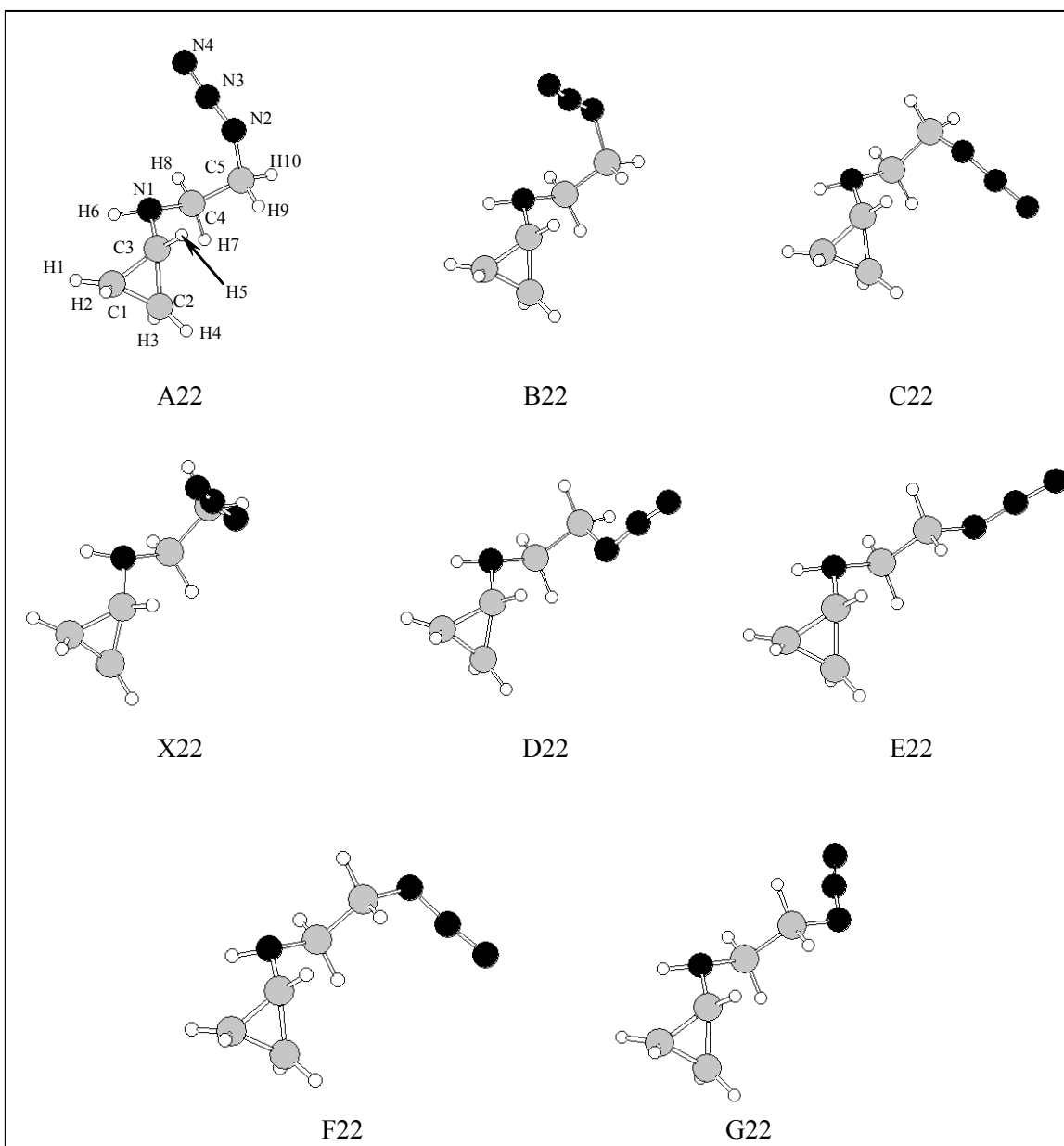


Figure 7. CPAZ group 22 conformers.

CPAZ conformer ZPEs, their ZPEs relative to that of the lowest energy conformer (D11), and their predicted statistical weight in a gas-phase sample at 298 K are shown in Table 4. Like MMAZ, the group 1 conformers are lower in energy than their group 2 counterparts. The two lowest energy conformers correspond to group 11 configurations (D11 and C11), and over 95% of the conformers will have the energetically preferred H5-C3-N1-C4 dihedral angle found in groups 11 and 21. Less than 12% of all CPAZ conformers in a gas-phase sample at 298 K are expected to be in shielded configurations (B11 and B21).

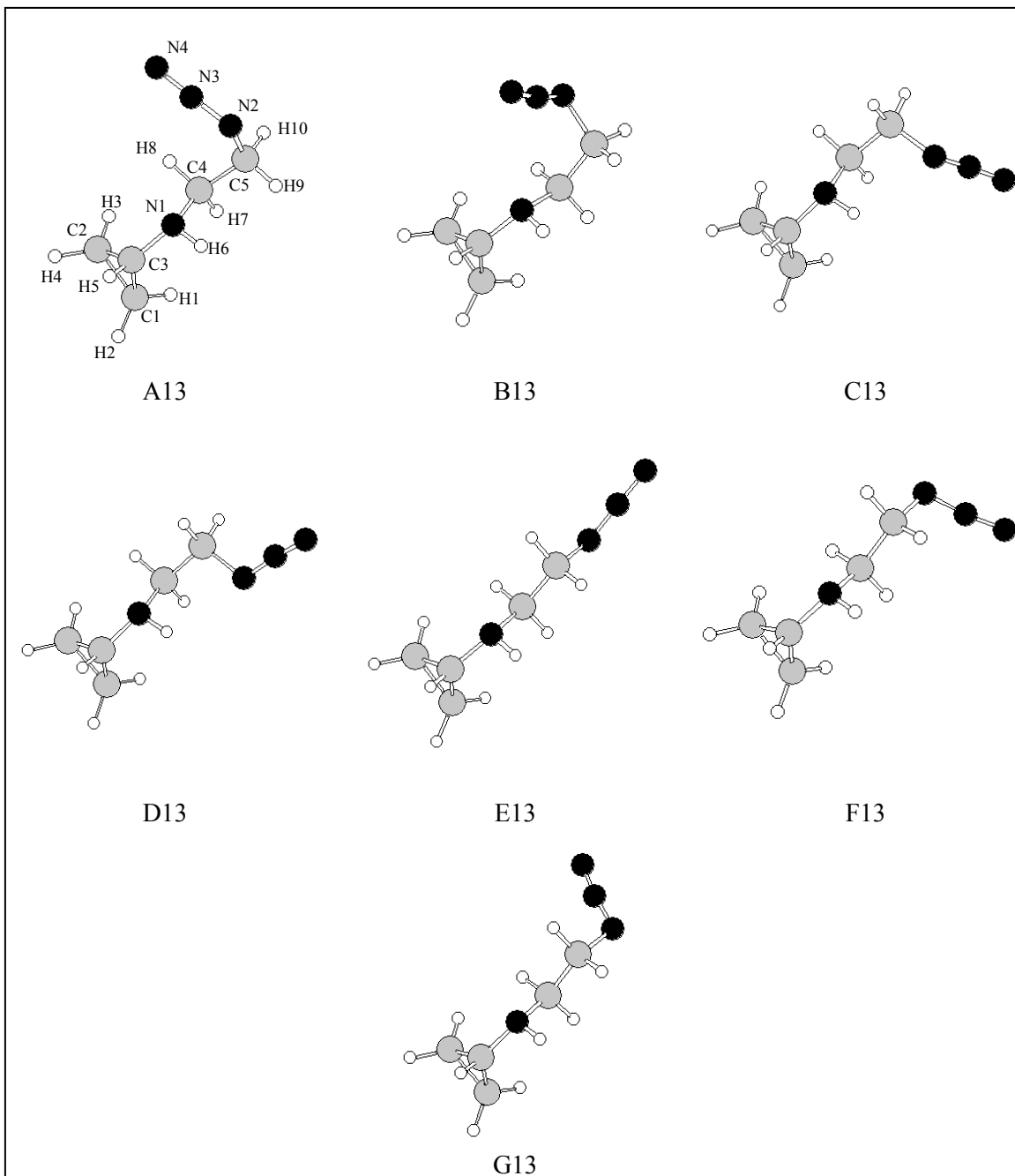


Figure 8. CPAZ group 13 conformers.

Table 5 shows CPAZ group 11 and group 21 conformer ZPEs by group relative to the group's B conformer. It also compares them to DMAZ and MMAZ (intragroup)  $\Delta E$ s. The similarities between CPAZ group 11 and MMAZ group 1 conformer  $\Delta E$ s are striking. Only the A-analog  $\Delta E$ s (CPAZ A11 vs. MMAZ A1) differ by more than 0.2 kcal/mol. Like MMAZ group 2 conformers, the relative energies of the conformers found in group 21 follow those of their DMAZ analogs.

Table 4. The relative energies of CPAZ equilibrium conformers and conformer probabilities for a gas-phase population at 298 K.

Conformer	ZPE (Hartrees)	$\Delta E$ (kcal/mol)	$W$	$W$ (adj.) <sup>a</sup>	Conformer	ZPE (Hartrees)	$\Delta E$ (kcal/mol)	$W$	$W$ (adj.) <sup>a</sup>
D11	-415.4099	0.0	0.42	0.26	B12	-415.4050	3.1	0.00	0.01
C11	-415.4088	0.7	0.13	0.17	B22	-415.4049	3.1	0.00	0.00
J11	-415.4084	1.0	0.08	0.07	E12	-415.4049	3.1	0.00	0.00
B11	-415.4082	1.1	0.07	0.10	D21	-415.4048	3.2	0.00	0.00
E11	-415.4080	1.2	0.06	0.05	E22	-415.4045	3.4	0.00	0.00
G11	-415.4073	1.6	0.03	0.04	C21	-415.4043	3.5	0.00	0.00
F11	-415.4073	1.6	0.03	0.04	F12	-415.4042	3.6	0.00	0.00
L11	-415.4072	1.7	0.02	0.04	G12	-415.4042	3.6	0.00	0.00
B21	-415.4071	1.7	0.02	0.02	F22	-415.4039	3.7	0.00	0.00
E21	-415.4070	1.8	0.02	0.03	G22	-415.4038	3.8	0.00	0.00
I11/I21	-415.4066	2.1	0.01	0.01	D22	-415.4037	3.9	0.00	0.00
F21	-415.4065	2.1	0.01	0.02	X22	-415.4035	4.0	0.00	0.00
A11	-415.4064	2.2	0.01	0.02	C22	-415.4032	4.2	0.00	0.00
G21	-415.4064	2.2	0.01	0.02	A12	-415.4032	4.2	0.00	0.00
H21	-415.4062	2.3	0.01	0.02	D13	-415.4026	4.6	0.00	0.00
H11	-415.4062	2.3	0.01	0.02	A22	-415.4018	5.1	0.00	0.00
D12	-415.4059	2.5	0.01	0.01	C13	-415.4015	5.3	0.00	0.00
C12	-415.4058	2.6	0.01	0.01	B13	-415.4008	5.7	0.00	0.00
J21	-415.4057	2.6	0.01	0.01	E13	-415.4008	5.7	0.00	0.00
A21	-415.4056	2.7	0.00	0.01	G13	-415.4000	6.2	0.00	0.00
L21	-415.4054	2.8	0.00	0.01	F13	-415.4001	6.2	0.00	0.00
—	—	—	—	—	A13	-415.3989	6.9	0.00	0.00

<sup>a</sup> Population distribution obtained if the ZPEs of *anti* conformers (D, E, I, and J) are increased 0.000627 Hartrees to account for the suspected bias (vs. *gauche* conformer ZPEs) in their calculated values.

Table 5. The relative energies of CPAZ equilibrium conformers by group and in comparison to DMAZ and MMAZ equilibrium conformers.

Conformer	DMAZ	CPAZ Group 11	MMAZ Group 1	CPAZ Group 21	MMAZ Group 2
A	1.2	1.1	1.7	0.9	0.9
B	0.0	0.0	0.0	0.0	0.0
C	1.3	-0.4	-0.4	1.8	1.3
X	a	a	a	a	1.1
D	1.0	-1.1	-1.1	1.5	0.8
E	0.4	0.1	0.1	0.0	0.3
F	0.8	0.6	0.1	0.4	0.7
G	0.9	0.6	0.5	0.5	0.8
H	1.9	1.3	1.5	0.6	1.3
I	1.6	1.0	1.3	0.3	1.0
J	2.0	-0.1	0.1	0.9	1.6
K	2.4	a	a	a	2.1
L	2.2	0.7	0.8	1.1	1.9

<sup>a</sup> Searched for, but not observed.

Table 6 compares the geometric parameters of CPAZ conformers B11 and D11 with those of MMAZ conformers B1 and D1. It is observed that except for parameters that include atoms of the methyl and cyclopropyl substituents, the differences between CPAZ B11 and MMAZ B1 and between CPAZ D11 and MMAZ D1 are negligible. Even the N(amine)-C(substituent) bond lengths are not that different, the C3-N1 bond in CPAZ conformers being only 0.02 Å shorter than the C1-N1 bond of their MMAZ analogs.

Table 6. Comparison of MMAZ and CPAZ equilibrium conformer geometries.

<b>MMAZ Parameter</b>	<b>MMAZ B1</b>	<b>CPAZ B11</b>	<b>MMAZ D1</b>	<b>CPAZ D11</b>	<b>CPAZ Parameter</b>
<b>Bond Length (Å)</b>					
H3-C1	1.103	1.093	1.103	1.093	H5-C3
C1-N1	1.460	1.441	1.459	1.440	C3-N1
N1-C2	1.456	1.459	1.455	1.459	N1-C4
H4-N1	1.015	1.016	1.015	1.016	H6-N1
C2-C3	1.528	1.528	1.519	1.519	C4-C5
H5-C2	1.106	1.105	1.105	1.103	H7-C4
H6-C2	1.094	1.093	1.096	1.095	H8-C4
C3-N2	1.476	1.476	1.486	1.486	C5-N2
H7-C3	1.098	1.098	1.096	1.096	H9-C5
H8-C3	1.091	1.091	1.095	1.095	H10-C5
N2-N3	1.230	1.230	1.228	1.228	N2-N3
N3-N4	1.134	1.135	1.135	1.135	N3-N4
<b>Simple Angle (degrees)</b>					
H3-C1-N1	114.0	116.9	113.9	116.9	H5-C3-N1
C1-N1-C2	114.2	114.8	113.5	114.1	C3-N1-C4
N1-C2-C3	111.3	111.2	111.1	111.0	N1-C4-C5
H4-N1-C2	110.0	110.5	108.9	109.4	H6-N1-C4
C2-C3-N2	113.2	113.2	108.4	108.5	C4-C5-N2
H5-C2-C3	108.3	108.2	109.0	108.9	H7-C4-C5
H6-C2-C3	108.6	108.9	108.0	108.2	H8-C4-C5
C3-N2-N3	117.2	117.2	116.2	116.2	C5-N2-N3
H7-C3-N2	110.5	110.4	109.6	109.6	H9-C5-N2
H8-C3-N2	105.4	105.4	109.9	109.9	H10-C5-N2
N2-N3-N4	171.8	171.9	173.9	173.9	N2-N3-N4
<b>Dihedral Angle (degrees)</b>					
H3-C1-N1-C2	56.0	57.2	55.5	56.4	H5-C3-N1-C4
C1-N1-C2-C3	170.0	168.8	-179.4	179.5	C3-N1-C4-C5
N1-C2-C3-N2	-68.1	-68.0	64.8	64.6	N1-C4-C5-N2
H4-N1-C2-C3	-66.0	-66.0	-56.3	-56.5	H6-N1-C4-C5
C2-C3-N2-N3	80.3	81.3	-172.1	-172.0	C4-C5-N2-N3
H5-C2-C3-N2	166.5	166.9	-60.4	-60.4	H7-C4-C5-N2
H6-C2-C3-N2	50.8	50.9	-176.3	-176.5	H8-C4-C5-N3
C3-N2-N3-N4	169.4	168.8	-178.8	-179.2	C5-N2-N3-N4
H7-C3-N2-N3	-44.1	-43.1	67.8	67.9	H9-C5-N2-N3
H8-C3-N2-N3	-160.0	-159.1	-52.0	-51.9	H10-C5-N2-N3

Table 7 compares the normal modes of CPAZ conformer D11 with analogous modes in MMAZ conformer D1. (The comparability of modes was established by visual inspection of mode animations rendered by the graphical user interface GaussView.) For modes involving primarily the >N-CH<sub>2</sub>-CH<sub>2</sub>-N<sub>3</sub> chain in each molecule, mode motions are similar, and their frequency differences tend to be less than 20 cm<sup>-1</sup>. One relatively large discrepancy is observed; namely, CPAZ mode 30 (1414 cm<sup>-1</sup>) vs. MMAZ mode 30 (1518 cm<sup>-1</sup>). But these modes involve motions that span the amine site. Moreover, they are only nominally similar, their equivalence in the table partly a consequence of specifying a 1-to-1 correspondence between MMAZ and CPAZ modes. Nominally a N1-H4 wag/C1-N1-C2 asymmetric stretch in MMAZ and a N1-H6 wag/C3-N2-C4 asymmetric stretch in CPAZ, given the complexity and overlap of the modes in the frequency range from 1400 to 1520 cm<sup>-1</sup> and the number of CPAZ modes that do not have a corresponding MMAZ mode, it is hard to imagine that this difference is a significant factor in the difference in ignition delay of these two compounds.

Table 7. Comparison of MMAZ and CPAZ normal modes (cm<sup>-1</sup>).

CPAZ Mode	CPAZ D11	MMAZ D1	MMAZ Mode	MMAZ (CPAZ) Mode Description <sup>a</sup>
10	507	520	8	N1-C2-C3 bend
11	558	556	9	N2-N3-N4 bend
12	638	639	10	N2-N3-N4 bend
14	785	781	11	N1-H4 rock
15	821	839	12	CH <sub>2</sub> rocks
18	895	882	13	N1-H rock/C3-N2 stretch
19	947	1005	14	—
20	1004	1033	15	C1-N1 stretch/C2-C3 stretch
24	1094	1081	16	—
25	1131	1142	17	C1-N1 stretch/N1-C2-C3 asym. stretch
26	1144	1161	18	C1-N1-C2 asym stretch
27	1188	1195	19	N1-C2 stretch (C3-N1 stretch)
29	1239	1245	20	CH <sub>2</sub> wags
31	1285	1305	21	CH <sub>2</sub> wags
32	1337	1338	22	C3-N2-N3 asym stretch
33	1373	1376	23	CH <sub>2</sub> wags
34	1390	1402	24	CH <sub>2</sub> wags
36	1454	1458	25	C1H <sub>3</sub> bend (C1H <sub>2</sub> + C2H <sub>2</sub> bends)
37	1481	1481	26	C3H <sub>2</sub> bend/N1-H4 wag
38	1484	1487	27	C1H <sub>3</sub> asym bend/N1-H4 wag
39	1501	1495	28	—
40	1511	1506	29	—
30	1414	1518	30	N1-H4 wag/C1-N1-C2 asym stretch
41	2238	2239	31	N2-N3-N4 asym stretch
42	2940	2924	32	C2-H5 stretch (C4-H7 stretch)
44	3038	2936	33	C1-H3 stretch (C3-H5 stretch)
43	3010	3010	34	C3H <sub>2</sub> sym stretch
45	3054	3039	35	C2-H8 stretch (C4H <sub>2</sub> asym stretch)
—	—	3047	36	C1-H stretches
46	3058	3059	37	C3H <sub>2</sub> asym stretch (C5H <sub>2</sub> asym stretch)
—	—	3096	38	C1-H stretches
51	3509	3522	39	N1-H4 stretch

<sup>a</sup> Modes not described are relatively complex, defying convenient description.

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## 4. Discussion

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One of the original reasons for undertaking this study was to assess the possibility that an increase in the basicity of the amine lone pair site in an amine azide fuel would lead to a concomitant increase in the fraction of a fuel sample that assumed a configuration in which the azide group shields the amine lone pair from proton attack. Such an effect would compromise the (presumed) benefit of substituent-mediated increases in the basicity of the site. In parallel with the effort summarized in this report, the author employed computational methods to quantify the differences in the basicity of amine azide lone pair sites. Based on gas-phase proton affinities, the basicities of MMAZ and CPAZ amine lone pair sites are nearly identical to each other, and they are less than that of the amine site in DMAZ. Thus, the finding that shielded configurations in MMAZ and CPAZ are, like DMAZ,  $\sim 1$  kcal/mol (or more) lower in energy than otherwise similar conformers (i.e., B conformers vs. A conformers) does not support the suspicion that the strength of the interaction is related to the basicity of the amine site. Indeed, it is observed that other steric effects are more effective in reducing the energy of these molecules, two nonshielding configurations being found to be lower in energy than the shielded configurations. Clearly, amine basicity alone is not a good predictor of an amine azide's propensity for assuming a shielded configuration.

The possibility that substituent-mediated differences in the  $>N-CH_2-CH_2-N_3$  chain might be observed and indicate an ignition-enabling reaction mechanism was also considered. However, the energy differences of the eight lowest energy structures of MMAZ and CPAZ have the same  $>N-CH_2-CH_2-N_3$  chain orientation dependence and the geometric parameters of this chain in MMAZ and CPAZ analogs are essentially identical. Thus, it does not appear that the difference in MMAZ and CPAZ ignition delays is due to differences in their  $>NH-CH_2-CH_2-N_3$  chains. Rather, the results indicate that the cyclopropyl group is involved in the mechanism that enables ignition.

Considering the ignition delays of MMAZ and DMAZ, the prediction that shielded configurations have a much smaller probability in a MMAZ sample than they do in a DMAZ sample is at odds with the hypothesis that shielding acts as a barrier to the ignition process. And though differences in the basicities of MMAZ and DMAZ lone pair sites are observed and may be a mitigating factor, coupled with the lack of differences observed between MMAZ and CPAZ, the potential of simple structural analyses for predicting the hypergolic ignition delays of 2-azidothalamines appears to be negligible. The focus of future ARL computational studies will therefore shift to investigating the possible importance of reaction mechanisms.

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## 5. Conclusions

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In an attempt to identify structural differences between DMAZ, MMAZ, and CPAZ that correlate with their ignition delays, equilibrium geometries and normal modes for MMAZ and CPAZ have been determined via B3LYP/6-311++G(d, p) calculations and compared to each other and to results obtained previously for DMAZ. It is observed that MMAZ and CPAZ conformer energy orderings have the same  $>\text{NH-CH}_2\text{-CH}_2\text{-N}_3$  chain orientation dependence, and that bond lengths, simple bond angles and dihedral angles in this chain are essentially the same for MMAZ and CPAZ analogs. Coupled with a prior finding that the site-specific basicities of the lone pair sites in these two molecules are nearly identical, the results imply that the difference in MMAZ and CPAZ hypergolicities is not associated with differences in their  $>\text{N-CH}_2\text{-CH}_2\text{-N}_3$  chains. Based on the results, it is also predicted that less than 15% of the molecules in 298 K gas-phase samples of either MMAZ or CPAZ will be in configurations where the amine lone pair site is shielded from proton attack by the azide group. This is in contrast to DMAZ, where approximately 45% of the molecules in a gas-phase sample at 298 K are in such a configuration. Taken together, the results indicate that structural characterizations (alone) will not predict a 2-azidothalamine's ignition delay.

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## 6. References

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## **Appendix. Geometric Parameters and Normal Mode Frequencies for 2-Azido-N-Methylethanamine (MMAZ) and 2-Azido-N- Cyclopropylethanamine (CPAZ)**

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This appendix provides complete descriptions of the geometric parameters and normal mode frequencies of equilibrium 2-azido-N-methylethanamine (MMAZ) and 2-azido-N-cyclopropylethanamine (CPAZ) structures. Atom labels in the tables of geometric parameters refer to those of the figures in the main body of this report.

Table A-1. Geometric parameters for MMAZ group 1 conformers.

MMAZ Parameter	Conformer										
	A1	B1	C1	D1	E1	F1	G1	H1	I1	J1	L1
<b>Bond Length (Å)</b>											
H1-C1	1.093	1.093	1.094	1.094	1.094	1.094	1.094	1.094	1.094	1.094	1.094
H2-C1	1.092	1.092	1.092	1.092	1.092	1.092	1.092	1.092	1.092	1.092	1.092
H3-C1	1.104	1.103	1.103	1.103	1.103	1.103	1.103	1.101	1.102	1.102	1.101
C1-N1	1.458	1.460	1.458	1.459	1.460	1.461	1.461	1.460	1.459	1.459	1.460
N1-C2	1.453	1.456	1.454	1.455	1.458	1.457	1.458	1.454	1.454	1.454	1.454
H4-N1	1.015	1.015	1.015	1.015	1.015	1.015	1.015	1.013	1.013	1.014	1.014
C2-C3	1.528	1.528	1.526	1.519	1.524	1.531	1.531	1.544	1.536	1.534	1.541
H5-C2	1.107	1.106	1.107	1.105	1.103	1.105	1.103	1.095	1.095	1.096	1.097
H6-C2	1.097	1.094	1.097	1.096	1.094	1.094	1.096	1.095	1.094	1.094	1.096
C3-N2	1.479	1.476	1.486	1.486	1.481	1.479	1.480	1.480	1.483	1.484	1.484
H7-C3	1.092	1.098	1.095	1.096	1.095	1.089	1.095	1.097	1.096	1.096	1.090
H8-C3	1.097	1.091	1.090	1.095	1.098	1.097	1.091	1.089	1.098	1.097	1.097
N2-N3	1.227	1.230	1.229	1.228	1.228	1.229	1.229	1.229	1.228	1.228	1.229
N3-N4	1.136	1.134	1.136	1.135	1.136	1.136	1.136	1.136	1.136	1.136	1.136
<b>Simple Angle (degrees)</b>											
H1-C1-N1	109.4	109.4	109.6	109.6	109.4	109.4	109.4	109.0	109.0	109.3	109.2
H2-C1-N1	109.5	109.4	109.5	109.5	109.4	109.4	109.4	109.1	109.1	109.1	109.1
H3-C1-N1	114.0	114.0	113.9	113.9	113.9	113.9	113.9	115.3	115.4	115.2	115.1
C1-N1-C2	113.8	114.2	113.8	113.5	113.7	113.8	113.7	116.4	116.6	115.9	115.7
N1-C2-C3	112.5	111.3	111.1	111.1	110.0	110.1	110.0	115.7	115.7	116.7	116.9
C2-C3-N2	115.6	113.2	112.2	108.4	108.3	112.4	112.4	112.2	107.9	108.1	112.3
H4-N1-C2	110.4	110.0	109.4	108.9	109.9	110.0	109.8	111.5	111.5	109.9	110.1
H5-C2-C3	107.0	108.3	109.3	109.0	109.2	109.7	109.2	108.6	108.7	107.8	107.7
H6-C2-C3	109.7	108.6	108.0	108.0	108.8	108.6	109.2	108.9	108.3	108.3	108.8
C3-N2-N3	116.9	117.2	116.2	116.2	116.2	116.5	116.4	116.5	116.1	116.2	116.4
H7-C3-N2	104.6	110.5	110.3	109.6	110.8	106.0	111.1	110.4	109.8	109.8	105.2
H8-C3-N2	109.6	105.4	105.4	109.9	109.7	110.2	105.1	105.1	109.9	110.0	110.4
N2-N3-N4	173.1	171.8	173.3	173.9	173.6	173.0	173.1	173.0	173.8	173.9	173.3
<b>Dihedral Angle (degrees)</b>											
H1-C1-N1-C2	-64.5	-64.8	-65.0	-65.3	-65.3	-65.1	-65.3	-58.2	-57.9	-60.5	-60.0
H2-C1-N1-C2	177.8	177.5	177.2	176.9	177.0	177.2	176.9	-175.3	-174.9	-177.7	-177.2
H3-C1-N1-C2	56.2	56.0	55.7	55.5	55.5	55.7	55.4	63.2	63.5	61.1	61.6
C1-N1-C2-C3	-178.7	170.0	-177.4	-179.4	172.8	172.9	173.7	-66.9	-66.1	-65.1	-65.4
N1-C2-C3-N2	-56.4	-68.1	63.7	64.8	178.3	-178.0	176.4	177.4	-178.9	-60.8	-59.9
H4-N1-C2-C3	-53.9	-66.0	-53.3	-56.3	-63.9	-63.5	-63.1	62.4	63.5	61.5	60.9
C2-C3-N2-N3	-47.0	80.3	84.3	-172.1	176.6	-78.4	79.1	77.1	-178.1	176.1	-83.0
H5-C2-C3-N2	178.4	166.5	-61.9	-60.4	53.1	56.8	51.2	55.3	58.8	176.8	177.9
H6-C2-C3-N2	63.8	50.8	-177.4	-176.3	-63.1	-59.5	-65.3	-60.6	-56.7	61.4	62.8
C3-N2-N3-N4	179.3	169.4	173.9	-178.8	180.0	-174.4	175.8	173.8	-179.7	179.4	-174.0
H7-C3-N2-N3	-168.8	-44.1	-39.1	67.8	56.2	161.9	-44.5	-46.3	-56.9	54.6	156.1
H8-C3-N2-N3	76.6	-160.0	-156.4	-52.0	-63.1	45.4	-161.0	-162.4	62.0	-64.2	40.0

Table A-2. Geometric parameters for MMAZ group 2 conformers.

MMAZ Parameter	Conformer												
	A2	B2	C2	D2	E2	F2	G2	H2	I2	J2	K2	L2	X2
<b>Bond Length (Å)</b>													
H1-C1	1.093	1.093	1.091	1.089	1.093	1.093	1.093	1.094	1.094	1.093	1.093	1.094	1.092
H2-C1	1.092	1.092	1.092	1.092	1.092	1.092	1.092	1.092	1.092	1.093	1.093	1.093	1.092
H3-C1	1.104	1.103	1.103	1.103	1.103	1.103	1.103	1.101	1.102	1.097	1.104	1.104	1.104
C1-N1	1.459	1.459	1.463	1.464	1.461	1.461	1.461	1.459	1.459	1.462	1.460	1.462	1.462
N1-C2	1.455	1.457	1.458	1.461	1.459	1.459	1.460	1.454	1.454	1.453	1.452	1.452	1.453
H4-N1	1.012	1.011	1.013	1.012	1.012	1.012	1.012	1.013	1.013	1.014	1.013	1.014	1.011
C2-C3	1.532	1.532	1.534	1.525	1.528	1.536	1.536	1.543	1.536	1.534	1.541	1.543	1.532
H5-C2	1.107	1.105	1.106	1.103	1.102	1.104	1.102	1.094	1.095	1.096	1.097	1.097	1.099
H6-C2	1.095	1.093	1.095	1.094	1.092	1.093	1.094	1.096	1.094	1.095	1.095	1.096	1.097
C3-N2	1.478	1.475	1.484	1.485	1.482	1.481	1.481	1.481	1.483	1.484	1.483	1.482	1.479
H7-C3	1.090	1.096	1.097	1.097	1.095	1.089	1.095	1.095	1.096	1.098	1.096	1.091	1.093
H8-C3	1.097	1.091	1.089	1.095	1.096	1.095	1.089	1.091	1.098	1.098	1.094	1.098	1.095
N2-N3	1.227	1.230	1.228	1.227	1.227	1.229	1.229	1.229	1.228	1.228	1.225	1.228	1.229
N3-N4	1.136	1.135	1.136	1.136	1.136	1.136	1.136	1.136	1.136	1.136	1.137	1.136	1.135
<b>Simple Angle (degrees)</b>													
H1-C1-N1	110.2	110.3	110.0	109.9	110.3	110.3	110.5	110.1	109.0	108.9	109.0	109.0	110.0
H2-C1-N1	109.2	109.2	109.2	109.2	109.2	109.2	109.2	109.2	109.1	109.3	109.3	109.3	109.2
H3-C1-N1	113.7	113.6	113.4	113.3	113.6	113.6	113.6	115.4	115.4	115.1	115.7	114.9	113.6
C1N1-C2	115.3	115.2	115.7	115.5	115.0	115.0	114.9	116.6	116.6	117.7	118.5	117.4	115.6
N1-C2-C3	113.3	112.0	113.6	113.5	110.8	110.9	110.7	115.7	115.7	118.5	118.7	118.4	112.3
H4-N1-C2	109.5	110.6	109.2	109.4	109.9	110.1	110.1	111.4	107.9	111.3	111.8	111.0	110.7
C2-C3-N2	115.4	112.7	114.4	110.3	108.0	111.9	112.2	112.0	111.5	110.6	112.9	115.0	112.4
H5-C2-C3	106.4	108.0	109.0	108.7	108.8	109.3	108.8	108.2	108.7	106.5	106.3	106.4	109.0
H6-C2-C3	109.1	108.0	106.5	106.5	108.3	108.1	108.7	109.1	108.3	108.6	108.4	109.2	107.1
C3-N2-N3	117.2	117.1	116.3	116.0	116.2	116.6	116.5	116.5	116.1	116.0	117.3	116.3	116.8
H7-C3-N2	104.8	110.5	105.5	108.9	110.6	106.1	111.0	110.2	109.8	109.9	110.6	105.0	105.9
H8-C3-N2	109.6	105.5	105.4	110.1	109.7	110.2	105.1	105.4	109.9	109.3	106.2	109.7	110.4
N2-N3-N4	173.0	173.7	173.2	173.8	173.7	173.1	173.1	173.1	173.8	173.8	173.6	173.3	173.5
<b>Dihedral Angle (degrees)</b>													
H1-C1-N1-C2	69.9	65.5	68.2	65.5	66.8	66.6	66.5	58.1	-57.9	56.1	51.4	56.9	62.5
H2-C1-N1-C2	-172.6	-177.0	-173.6	-176.1	-175.6	-175.8	-175.9	175.1	-174.9	172.9	168.4	173.6	-179.5
H3-C1-N1-C2	-51.5	-55.6	-57.8	-55.1	-54.3	-54.5	-54.6	-63.4	63.5	-64.8	-70.1	-64.3	-58.3
C1-N1-C2-C3	-72.7	-84.7	-81.7	-88.9	-84.8	-85.0	-84.6	66.5	-66.1	72.8	74.1	69.8	-106.1
N1-C2-C3-N2	-53.9	-66.9	73.1	72.3	178.5	-178.3	176.0	176.7	-178.9	-71.8	-73.6	-69.4	62.2
H4-N1-C2-C3	162.4	149.2	154.0	147.1	150.4	150.0	150.6	-63.0	63.5	-57.3	-58.2	-59.5	127.9
C2-C3-N2-N3	-44.8	81.2	77.2	-170.9	178.2	-80.9	78.7	80.5	-178.1	177.4	111.3	-72.5	-94.0
H5-C2-C3-N2	-178.3	168.6	-53.7	-53.9	53.9	57.3	51.5	54.5	58.8	106.7	164.7	169.1	-61.8
H6-C2-C3-N2	66.2	52.7	-168.5	-169.0	-62.2	-59.0	-65.0	-61.3	-56.7	52.2	50.4	54.9	-177.1
C3-N2-N3-N4	-179.9	168.0	175.8	180.0	-179.7	-174.2	175.3	174.8	-179.7	-179.2	-176.7	-177.2	-172.0
H7-C3-N2-N3	-167.3	-43.4	-46.1	69.2	58.2	159.9	-44.5	-43.9	-56.9	55.6	-13.1	166.4	146.3
H8-C3-N2-N3	78.2	-159.5	-167.8	-50.2	-61.1	43.2	-161.1	-160.1	62.0	-62.6	-130.0	51.0	28.9

Table A-3. Normal mode frequencies (cm<sup>-1</sup>) for MMAZ group 1 conformers.

Mode	Conformer										
	A1	B1	C1	D1	E1	F1	G1	H1	I1	J1	L1
1	31	58	35	39	34	45	41	46	34	35	35
2	89	94	108	89	102	85	83	60	90	81	58
3	147	111	118	142	112	109	106	124	114	133	134
4	177	221	205	192	123	187	191	191	139	196	188
5	245	258	242	238	230	231	237	231	218	238	245
6	273	283	293	283	257	266	255	293	319	261	300
7	346	344	354	327	368	394	394	349	322	400	410
8	522	517	517	520	430	421	423	469	462	520	515
9	561	558	554	556	549	556	557	556	549	553	554
10	686	652	658	639	662	677	677	677	656	626	658
11	731	751	768	781	770	767	768	684	684	723	713
12	842	832	825	839	813	812	817	785	786	818	817
13	865	900	879	882	936	922	919	922	933	869	850
14	990	990	989	1005	995	984	984	956	964	988	960
15	1023	1024	1022	1033	1052	1031	1033	1000	1031	1000	999
16	1061	1047	1088	1081	1082	1082	1079	1048	1049	1048	1053
17	1137	1133	1146	1142	1139	1136	1136	1139	1140	1142	1145
18	1168	1165	1155	1161	1161	1171	1169	1169	1158	1156	1157
19	1188	1188	1191	1195	1186	1190	1194	1192	1188	1197	1189
20	1272	1281	1245	1245	1256	1260	1258	1272	1269	1246	1255
21	1289	1283	1300	1305	1313	1307	1306	1308	1327	1318	1310
22	1333	1344	1336	1338	1332	1328	1323	1342	1337	1337	1336
23	1388	1386	1376	1376	1345	1357	1362	1356	1341	1372	1374
24	1405	1393	1395	1402	1416	1407	1409	1402	1405	1395	1394
25	1459	1458	1459	1458	1459	1459	1459	1456	1456	1454	1455
26	1485	1481	1487	1481	1487	1487	1488	1483	1484	1474	1475
27	1491	1491	1487	1487	1494	1493	1494	1492	1492	1482	1485
28	1500	1494	1495	1495	1499	1501	1501	1494	1495	1496	1497
29	1513	1507	1509	1506	1516	1516	1516	1503	1501	1502	1503
30	1520	1519	1519	1518	1522	1520	1521	1524	1524	1525	1526
31	2234	2239	2229	2239	2238	2228	2230	2226	2235	2237	2229
32	2900	2909	2901	2924	2940	2918	2940	2953	2948	2945	2952
33	2933	2940	2935	2936	2943	2942	2943	3005	2994	3001	3009
34	3012	3002	3022	3010	2995	3006	3035	3024	3033	3024	3022
35	3022	3054	3035	3039	3045	3054	3038	3049	3038	3042	3046
36	3051	3055	3047	3047	3053	3056	3053	3065	3048	3045	3050
37	3091	3100	3097	3059	3063	3098	3098	3093	3078	3071	3093
38	3099	3103	3118	3096	3098	3125	3099	3118	3092	3092	3112
39	3522	3512	3524	3522	3514	3515	3515	3540	3541	3538	3536

Table A-4. Normal mode frequencies (cm<sup>-1</sup>) for MMAZ group 2 conformers.

Mode	Conformer												
	A2	B2	C2	X2	D2	E2	F2	G2	H2	I2	J2	K2	L2
1	33	60	40	38	35	35	51	40	50	34	36	27	38
2	64	73	74	72	80	90	56	58	54	90	62	51	69
3	162	126	135	96	130	108	114	109	126	114	120	128	141
4	176	201	213	189	185	134	192	189	197	139	186	210	209
5	250	267	229	258	208	213	242	233	239	218	211	244	225
6	296	283	342	285	313	320	307	306	294	319	307	306	337
7	398	405	370	388	378	354	357	363	339	322	354	354	351
8	509	496	487	489	485	445	454	455	467	462	496	495	502
9	561	556	555	548	553	550	555	557	553	549	552	542	556
10	685	651	656	640	628	650	675	677	675	656	629	642	655
11	721	720	729	694	732	737	727	727	681	684	676	653	686
12	827	828	813	810	820	796	799	796	789	786	819	789	811
13	855	872	872	896	880	930	922	924	917	933	867	887	862
14	970	982	969	946	967	959	937	939	955	964	978	957	962
15	997	999	1000	1007	1024	1050	1023	1023	1001	1031	1014	995	989
16	1064	1048	1080	1073	1073	1074	1081	1077	1048	1049	1037	1040	1044
17	1133	1138	1147	1145	1149	1144	1144	1143	1139	1140	1146	1144	1149
18	1168	1159	1162	1161	1164	1157	1160	1161	1166	1158	1164	1161	1156
19	1195	1191	1180	1180	1183	1181	1189	1188	1197	1188	1182	1191	1189
20	1270	1267	1257	1262	1253	1259	1263	1263	1271	1269	1267	1267	1271
21	1288	1299	1319	1312	1322	1328	1319	1310	1315	1327	1321	1316	1311
22	1336	1345	1334	1355	1342	1334	1331	1335	1337	1337	1338	1366	1338
23	1394	1380	1382	1379	1384	1343	1358	1360	1360	1341	1382	1376	1382
24	1405	1398	1398	1394	1403	1413	1406	1409	1399	1405	1391	1392	1389
25	1458	1458	1458	1456	1456	1459	1459	1459	1456	1456	1456	1456	1456
26	1484	1481	1481	1479	1477	1485	1485	1485	1483	1484	1471	1471	1472
27	1492	1486	1486	1483	1479	1492	1491	1491	1492	1492	1479	1480	1484
28	1499	1493	1487	1487	1486	1496	1496	1496	1495	1495	1490	1494	1492
29	1506	1498	1502	1496	1501	1507	1507	1508	1504	1501	1501	1502	1503
30	1520	1520	1526	1523	1525	1520	1519	1519	1524	1524	1524	1527	1526
31	2233	2236	2226	2236	2235	2237	2228	2228	2227	2235	2234	2234	2227
32	2902	2918	2913	2944	2941	2942	2929	2943	2952	2948	2983	2976	2986
33	2931	2939	2937	2986	2945	2950	2942	2949	3021	2994	2992	3008	2996
34	3010	3019	3013	3026	2998	3012	3029	3039	3029	3033	3015	3015	3012
35	3051	3056	3053	3045	3054	3051	3058	3056	3048	3038	3027	3053	3045
36	3060	3072	3071	3066	3060	3058	3074	3059	3067	3048	3055	3060	3052
37	3102	3100	3113	3088	3071	3078	3100	3100	3093	3078	3063	3071	3087
38	3110	3101	3121	3106	3119	3099	3125	3119	3100	3092	3088	3091	3098
39	3555	3564	3546	3568	3550	3561	3558	3558	3541	3541	3537	3545	3536

Table A-5. Geometric parameters for CPAZ group 11 conformers.

CPAZ Parameter	Conformer										
	A11	B11	C11	D11	E11	F11	G11	H11	I11	J11	L11
<b>Bond Length (Å)</b>											
H5-C3	1.093	1.093	1.093	1.093	1.093	1.093	1.093	1.091	1.092	1.092	1.091
C3-N1	1.439	1.441	1.439	1.440	1.441	1.441	1.441	1.440	1.439	1.439	1.440
N1-C4	1.457	1.459	1.458	1.459	1.461	1.460	1.461	1.457	1.457	1.457	1.457
H6-N1	1.016	1.016	1.016	1.016	1.016	1.016	1.016	1.014	1.014	1.015	1.015
C4-C5	1.528	1.528	1.526	1.519	1.524	1.531	1.531	1.542	1.534	1.532	1.539
H7-C4	1.105	1.105	1.105	1.103	1.102	1.104	1.102	1.093	1.094	1.095	1.096
H8-C4	1.096	1.093	1.096	1.095	1.093	1.093	1.094	1.095	1.094	1.094	1.096
C5-N2	1.480	1.476	1.487	1.486	1.481	1.480	1.480	1.481	1.483	1.484	1.484
H9-C5	1.091	1.098	1.095	1.096	1.095	1.089	1.095	1.097	1.098	1.096	1.090
H10-C5	1.097	1.091	1.090	1.095	1.098	1.097	1.091	1.089	1.096	1.097	1.097
N2-N3	1.227	1.230	1.229	1.228	1.228	1.229	1.229	1.229	1.228	1.228	1.229
N3-N4	1.136	1.135	1.136	1.135	1.136	1.136	1.136	1.136	1.136	1.136	1.136
<b>Simple Angle (degrees)</b>											
H5-C3-N1	116.9	116.9	116.9	116.9	116.9	116.9	116.9	118.1	118.2	118.0	117.9
C3-N1-C4	114.4	114.8	114.3	114.1	114.2	114.4	114.3	116.9	117.1	116.2	116.1
N1-C4-C5	112.3	111.2	111.0	111.0	109.9	110.0	109.8	115.2	115.3	116.4	116.6
H6-N1-C4	110.8	110.5	109.9	109.4	110.4	110.5	110.3	111.9	111.9	110.3	110.6
C4-C5-N2	115.5	113.2	112.3	108.5	108.2	112.3	112.4	112.3	108.0	108.3	112.4
H7-C4-C5	107.0	108.2	109.3	108.9	109.1	109.6	109.1	108.7	108.8	108.0	107.8
H8-C4-C5	109.9	108.9	108.2	108.2	109.1	108.9	109.5	109.0	108.5	108.4	108.9
C5-N2-N3	116.9	117.2	116.2	116.2	116.2	116.5	116.4	116.5	116.1	116.2	116.3
H9-C5-N2	104.6	110.4	110.2	109.6	110.7	106.0	111.0	110.3	109.9	109.9	105.3
H10-C5-N2	109.5	105.4	105.3	109.9	109.7	110.2	105.1	105.1	109.9	109.9	110.4
N2-N3-N4	173.1	171.9	173.3	173.9	173.6	173.0	173.0	173.0	173.8	173.9	173.3
<b>Dihedral Angle (degrees)</b>											
H5-C3-N1-C4	56.8	57.2	56.6	56.4	56.3	56.7	56.4	62.7	62.9	61.7	61.9
C3-N1-C4-C5	179.7	168.8	-178.2	179.5	171.5	171.4	172.0	-67.6	-66.9	-65.7	-66.2
N1-C4-C5-N2	-56.6	-68.0	63.5	64.6	177.9	-178.3	176.1	177.9	-178.5	-60.8	-60.0
H6-N1-C4-C5	-53.8	-66.0	-53.2	-56.5	-64.3	-64.0	-63.7	62.8	63.8	61.8	61.0
C4-C5-N2-N3	-47.4	81.3	83.9	-172.0	176.7	-78.3	78.7	77.1	-177.5	175.3	-82.6
H7-C4-C5-N2	178.4	166.9	-61.8	-60.4	52.9	56.8	51.1	55.9	59.4	177.0	178.1
H8-C4-C5-N3	63.5	50.9	-177.6	-176.5	-63.6	-59.8	-65.7	-60.4	-56.6	61.1	62.6
C5-N2-N3-N4	178.9	168.8	174.0	-179.2	-179.8	-174.3	175.5	174.1	-179.7	179.5	-174.2
H9-C5-N2-N3	-169.2	-43.1	-39.6	67.9	56.3	162.0	-45.0	-46.4	62.4	53.9	156.7
H10-C5-N2-N3	76.2	-159.1	-156.8	-51.9	-62.9	45.5	-161.4	-162.6	-56.5	-65.0	40.5

Table A-6. Geometric parameters for CPAZ group 21 conformers.

CPAZ Parameter	Conformer										
	A21	B21	C21	D21	E21	F21	G21	H21	I21	J21	L21
<b>Bond Length (Å)</b>											
H5- C3	1.094	1.093	1.093	1.092	1.093	1.093	1.093	1.091	1.092	1.088	1.089
C3-N1	1.440	1.441	1.444	1.444	1.442	1.442	1.442	1.440	1.439	1.442	1.442
N1-C4	1.458	1.460	1.463	1.464	1.462	1.462	1.463	1.457	1.457	1.457	1.455
H6-N1	1.014	1.013	1.013	1.014	1.013	1.013	1.013	1.014	1.014	1.014	1.015
C4-C5	1.532	1.531	1.533	1.526	1.527	1.535	1.535	1.542	1.534	1.532	1.541
H7-C4	1.105	1.104	1.104	1.102	1.101	1.103	1.101	1.094	1.094	1.097	1.097
H8-C4	1.095	1.093	1.095	1.094	1.093	1.093	1.094	1.095	1.094	1.093	1.095
C5-N2	1.479	1.477	1.481	1.483	1.483	1.481	1.481	1.481	1.483	1.483	1.482
H9-C5	1.089	1.095	1.098	1.097	1.095	1.089	1.095	1.095	1.096	1.098	1.091
H10-C5	1.097	1.091	1.089	1.095	1.095	1.094	1.088	1.091	1.098	1.098	1.098
N2-N3	1.227	1.229	1.227	1.226	1.227	1.229	1.229	1.229	1.228	1.228	1.228
N3-N4	1.136	1.135	1.137	1.137	1.136	1.136	1.136	1.136	1.136	1.136	1.136
<b>Simple Angle (degrees)</b>											
H5-C3-N1	116.5	116.0	116.1	116.2	116.3	116.3	116.3	118.1	118.1	117.8	117.7
C3-N1-C4	115.7	115.5	116.4	116.4	115.4	115.5	115.3	117.0	117.1	117.6	117.6
N1-C4-C5	113.5	112.6	114.4	114.3	111.4	111.5	111.3	115.3	115.3	117.6	117.9
H6-N1-C4	110.1	110.6	109.5	109.1	109.9	110.0	110.0	111.8	111.9	111.7	111.5
C4-C5-N2	115.2	112.6	115.2	110.4	107.8	111.6	112.0	112.0	108.0	110.6	114.8
H7-C4-C5	106.5	107.9	109.2	108.2	108.7	109.1	108.6	108.4	108.5	106.4	106.5
H8-C4-C5	109.3	108.1	106.2	106.9	108.3	108.1	108.8	109.3	108.8	109.2	109.5
C5-N2-N3	117.0	117.4	116.5	116.2	116.2	116.6	116.5	116.5	116.1	116.0	116.3
H9-C5-N2	104.8	110.7	109.2	108.5	110.5	106.0	110.9	110.2	109.9	109.7	105.0
H10-C5-N2	109.6	105.3	105.3	110.7	109.9	110.4	105.3	105.3	109.9	109.6	109.8
N2-N3-N4	173.1	171.9	173.1	173.7	173.7	173.1	173.1	173.1	173.8	173.8	173.3
<b>Dihedral Angle (degrees)</b>											
H5-C3-N1-C4	-51.5	-49.2	-48.9	-45.1	-49.1	-49.6	-49.4	-62.9	-62.9	-60.4	-62.3
C3-N1-C4-C5	-72.5	-87.4	-88.3	-80.9	-82.2	-82.8	-82.1	67.1	66.8	79.7	72.7
N1-C4-C5-N2	-55.0	-68.1	72.4	80.3	-178.6	-176.1	178.4	176.5	178.5	-67.7	-67.6
H6-N1-C4-C5	161.3	146.6	147.0	154.8	152.9	151.9	152.8	-63.5	-63.8	-51.0	-57.5
C4-C5-N2-N3	-48.1	83.1	68.1	-163.9	-178.5	-82.2	78.0	80.3	177.5	177.8	-73.4
H7-C4-C5-N2	180.0	167.5	-54.6	-46.3	56.7	59.3	53.7	54.6	56.6	170.7	171.1
H8-C4-C5-N3	65.2	51.7	-169.1	-161.5	-59.4	-57.0	-62.8	-61.6	-59.3	55.7	56.4
C5-N2-N3-N4	179.9	168.7	178.0	178.5	-179.6	-174.4	175.2	174.9	179.7	-179.8	-176.7
H9-C5-N2-N3	-170.1	-41.4	-55.0	76.8	61.8	158.7	-45.1	-43.9	56.5	56.3	165.6
H10-C5-N2-N3	74.8	-157.9	-171.3	-42.4	-57.8	41.7	-162.0	-160.2	-62.5	-61.9	50.2

Table A-7. Geometric parameters for CPAZ group 12 conformers.

CPAZ Parameter	Conformer						
	A12	B12	C12	D12	E12	F12	G12
<b>Bond Length (Å)</b>							
H5-C3	1.086	1.086	1.087	1.087	1.086	1.086	1.086
C3-N1	1.440	1.441	1.440	1.441	1.442	1.442	1.442
N1-C4	1.456	1.459	1.458	1.459	1.460	1.460	1.461
H6-N1	1.014	1.015	1.015	1.015	1.015	1.015	1.015
C4-C5	1.528	1.528	1.526	1.519	1.524	1.531	1.531
H7-C4	1.104	1.104	1.104	1.102	1.101	1.103	1.101
H8-C4	1.096	1.094	1.096	1.095	1.094	1.094	1.095
C5-N2	1.479	1.476	1.487	1.486	1.481	1.480	1.480
H9-C5	1.092	1.098	1.095	1.096	1.095	1.089	1.095
H10-C5	1.097	1.091	1.090	1.095	1.098	1.098	1.091
N2-N3	1.227	1.230	1.229	1.228	1.228	1.229	1.229
N3-N4	1.136	1.134	1.136	1.135	1.136	1.136	1.136
<b>Simple Angle (degrees)</b>							
H5-C3-N1	112.4	112.3	112.5	112.5	112.3	112.3	112.3
C3-N1-C4	114.6	114.9	114.6	114.4	114.4	114.5	114.5
N1-C4-C5	112.3	111.2	110.9	110.8	109.8	109.9	109.8
H6-N1-C4	111.3	110.9	110.2	109.7	110.8	110.9	110.7
C4-C5-N2	115.6	113.2	112.2	108.4	108.2	112.3	112.4
H7-C4-C5	107.2	108.5	109.6	109.2	109.4	109.9	109.3
H8-C4-C5	109.7	108.7	108.0	108.0	108.9	108.7	109.3
C5-N2-N3	116.9	117.2	116.2	116.2	116.2	116.5	116.4
H9-C5-N2	104.6	110.5	110.2	109.6	110.8	106.0	111.0
H10-C5-N2	109.6	105.4	105.3	109.9	109.7	110.2	105.1
N2-N3-N4	173.1	171.9	173.3	173.9	173.6	173.0	173.1
<b>Dihedral Angle (degrees)</b>							
H5-C3-N1-C4	-72.4	-72.0	-72.1	-72.2	-72.3	-72.2	-72.6
C3-N1-C4-C5	179.5	167.2	-178.9	178.8	170.0	170.3	170.8
N1-C4-C5-N2	-56.7	-68.1	63.6	64.5	178.3	-178.1	176.2
H6-N1-C4-C5	-53.1	-66.4	-52.5	-55.9	-64.3	-63.9	-63.5
C4-C5-N2-N3	-48.4	81.1	83.9	-172.7	176.9	-78.3	78.7
H7-C4-C5-N2	178.1	166.6	-61.9	-60.6	53.1	56.8	51.0
H8-C4-C5-N3	63.3	50.7	-177.7	-176.7	-63.3	-59.7	-65.7
C5-N2-N3-N4	179.3	168.8	173.9	-179.1	179.9	-174.5	175.6
H9-C5-N2-N3	-170.2	-43.3	-39.5	67.3	56.4	161.9	-45.1
H10-C5-N2-N3	75.2	-159.2	-156.8	-52.5	-62.8	45.4	-161.5

Table A-8. Geometric parameters for CPAZ group 22 conformers.

CPAZ Parameter	Conformer						
	A22	B22	C22	D22	E22	F22	G22
<b>Bond Length (Å)</b>							
H5-C3	1.086	1.086	1.084	1.083	1.086	1.086	1.086
C3-N1	1.440	1.440	1.444	1.444	1.442	1.442	1.442
N1-C4	1.456	1.458	1.461	1.463	1.461	1.460	1.461
H6-N1	1.012	1.011	1.012	1.012	1.011	1.011	1.011
C4-C5	1.532	1.532	1.533	1.525	1.527	1.535	1.535
H7-C4	1.104	1.103	1.103	1.100	1.100	1.102	1.100
H8-C4	1.095	1.093	1.095	1.094	1.093	1.093	1.094
C5-N2	1.479	1.476	1.484	1.484	1.482	1.480	1.481
H9-C5	1.090	1.096	1.097	1.098	1.095	1.089	1.095
H10-C5	1.097	1.091	1.089	1.095	1.096	1.095	1.090
N2-N3	1.227	1.230	1.228	1.227	1.227	1.229	1.229
N3-N4	1.136	1.135	1.136	1.136	1.136	1.136	1.136
<b>Simple Angle (degrees)</b>							
H5-C3-N1	113.2	113.6	113.0	112.9	113.4	113.4	113.4
C3-N1-C4	116.4	116.6	116.6	116.3	116.3	116.3	116.2
N1-C4-C5	113.1	112.1	113.3	113.2	110.8	110.9	110.7
H6-N1-C4	111.3	112.0	110.5	110.6	111.1	111.3	111.3
C4-C5-N2	115.4	112.8	114.2	110.0	108.0	111.9	112.2
H7-C4-C5	106.4	107.9	109.2	109.0	108.8	109.2	108.8
H8-C4-C5	109.4	108.2	106.6	106.6	108.3	108.2	108.9
C5-N2-N3	117.1	117.1	116.3	116.1	116.2	116.6	116.5
H9-C5-N2	104.8	110.5	109.5	109.1	110.6	106.1	111.0
H10-C5-N2	109.6	105.5	105.3	110.0	109.8	110.2	105.1
N2-N3-N4	173.0	171.9	173.2	173.8	173.7	173.0	173.1
<b>Dihedral Angle (degrees)</b>							
H5-C3-N1-C4	79.4	78.2	75.8	72.6	78.6	78.6	78.3
C3-N1-C4-C5	-68.6	-81.5	-81.7	-89.5	-81.1	-81.1	-80.9
N1-C4-C5-N2	-54.2	-66.2	70.4	70.4	-179.9	-177.4	177.3
H6-N1-C4-C5	161.8	148.0	151.0	143.6	150.4	150.2	150.6
C4-C5-N2-N3	-46.7	82.0	75.5	-171.2	-179.7	-80.8	77.9
H7-C4-C5-N2	-179.1	169.5	-56.0	-55.3	55.6	58.3	52.8
H8-C4-C5-N3	65.7	53.3	-171.3	-170.9	-60.9	-58.4	-64.1
C5-N2-N3-N4	-180.0	167.9	175.5	-180.0	-179.7	-174.2	175.3
H9-C5-N2-N3	-168.8	-42.5	-47.8	68.9	60.3	159.8	-45.4
H10-C5-N2-N3	76.5	-158.7	-164.5	-50.6	-59.1	43.0	-162.0

Table A-9. Geometric parameters for CPAZ group 13 conformers.

CPAZ Parameter	Conformer						
	A13	B13	C13	D13	E13	F13	G13
<b>Bond Length (Å)</b>							
H5-C3	1.085	1.085	1.085	1.085	1.085	1.085	1.085
C3-N1	1.447	1.450	1.448	1.448	1.450	1.450	1.450
N1-C4	1.453	1.456	1.454	1.456	1.458	1.457	1.458
H6-N1	1.015	1.016	1.016	1.016	1.016	1.016	1.016
C4-C5	1.529	1.530	1.527	1.520	1.525	1.533	1.533
H7-C4	1.105	1.104	1.105	1.103	1.101	1.103	1.101
H8-C4	1.095	1.092	1.094	1.093	1.092	1.092	1.093
C5-N2	1.479	1.475	1.486	1.486	1.481	1.479	1.480
H9-C5	1.091	1.098	1.095	1.096	1.095	1.089	1.094
H10-C5	1.097	1.091	1.090	1.095	1.098	1.097	1.091
N2-N3	1.228	1.231	1.229	1.228	1.228	1.229	1.229
N3-N4	1.136	1.134	1.135	1.135	1.136	1.136	1.136
<b>Simple Angle (degrees)</b>							
H5-C3-N1	110.5	109.9	110.4	110.2	109.9	109.9	109.9
C3-N1-C4	118.9	119.0	118.7	118.5	118.5	118.6	118.6
N1-C4-C5	111.5	110.4	110.1	110.1	109.1	109.2	109.0
H6-N1-C4	110.3	109.5	109.2	108.7	109.4	109.5	109.3
C4-C5-N2	115.5	113.2	112.4	108.5	108.1	112.2	112.3
H7-C4-C5	106.3	108.0	108.7	108.4	108.8	109.3	108.7
H8-C4-C5	109.3	108.0	107.5	107.4	108.3	108.1	108.7
C5-N2-N3	116.8	117.2	116.2	116.2	116.1	116.5	116.4
H9-C5-N2	104.6	110.5	110.2	109.6	110.8	106.1	111.1
H10-C5-N2	109.7	105.4	105.4	109.9	109.7	110.2	105.2
N2-N3-N4	173.0	171.7	173.3	173.9	173.6	173.0	173.0
<b>Dihedral Angle (degrees)</b>							
H5-C3-N1-C4	-167.1	178.7	-169.2	-171.6	179.5	-180.0	-178.8
C3-N1-C4-C5	-175.6	167.0	-176.5	-179.2	170.4	170.1	172.1
N1-C4-C5-N2	-55.9	-68.6	63.4	64.6	-182.1	-178.5	175.8
H6-N1-C4-C5	-48.1	-67.6	-50.4	-54.2	-65.0	-64.9	-63.2
C4-C5-N2-N3	-49.5	80.3	83.5	-172.6	177.1	-79.0	79.6
H7-C4-C5-N2	178.8	179.7	-62.3	-60.7	52.9	56.6	50.8
H8-C4-C5-N3	64.2	50.7	-177.8	-176.5	-63.3	-59.7	-65.8
C5-N2-N3-N4	179.7	168.3	173.9	-179.2	-180.0	-174.0	175.5
H9-C5-N2-N3	-171.3	-44.1	-39.8	67.4	56.8	161.4	-44.0
H10-C5-N2-N3	74.0	-160.1	-157.2	-52.5	-62.5	44.8	-160.6

Table A-10. Normal mode frequencies (cm<sup>-1</sup>) for CPAZ group 11 conformers.

Mode	Conformer										
	A11	B11	C11	D11	E11	F11	G11	H11	I11	J11	L11
1	24	39	30	32	28	34	36	37	27	29	32
2	49	62	57	60	67	50	47	51	62	52	41
3	95	74	80	88	82	80	77	65	84	80	66
4	138	148	139	131	98	131	134	111	93	149	138
5	185	173	171	185	153	145	147	210	161	179	178
6	209	267	225	202	191	245	238	244	232	214	249
7	302	302	328	292	294	320	318	298	302	304	328
8	401	394	411	411	346	329	332	333	326	401	401
9	426	429	433	432	439	441	441	438	437	457	458
10	519	515	506	507	482	482	482	525	523	533	528
11	562	557	553	558	549	555	557	557	550	556	556
12	684	652	658	638	658	677	677	680	656	628	660
13	723	741	755	760	756	754	756	682	684	723	714
14	778	779	778	785	777	775	776	755	756	760	761
15	821	824	816	821	812	812	815	790	790	807	807
16	841	838	840	842	830	830	829	828	827	841	837
17	845	843	842	849	843	843	843	842	842	847	841
18	888	912	892	895	939	927	923	921	937	884	872
19	952	959	948	947	950	940	941	944	948	946	939
20	997	986	989	1004	999	991	996	971	971	981	963
21	1005	1003	1041	1042	1043	1043	1043	1010	1043	1022	1021
22	1045	1045	1050	1060	1070	1059	1056	1044	1049	1043	1044
23	1073	1073	1070	1070	1086	1071	1071	1071	1071	1071	1071
24	1101	1093	1100	1094	1099	1102	1098	1094	1091	1091	1099
25	1131	1130	1131	1131	1128	1128	1129	1127	1126	1128	1125
26	1147	1147	1140	1144	1142	1151	1155	1150	1142	1144	1139
27	1188	1187	1190	1188	1188	1186	1186	1186	1186	1183	1185
28	1195	1195	1194	1194	1194	1194	1194	1195	1195	1195	1195
29	1241	1240	1235	1239	1224	1236	1234	1240	1235	1232	1234
30	1250	1253	1242	1241	1241	1241	1241	1252	1247	1251	1256
31	1281	1279	1282	1285	1310	1300	1305	1306	1327	1297	1289
32	1331	1344	1334	1337	1328	1327	1316	1335	1332	1337	1333
33	1378	1380	1371	1373	1344	1354	1359	1356	1339	1372	1374
34	1400	1386	1387	1390	1396	1391	1394	1397	1399	1390	1391
35	1412	1412	1412	1414	1421	1417	1417	1409	1410	1409	1408
36	1455	1455	1454	1454	1454	1454	1454	1454	1454	1454	1454
37	1479	1476	1483	1481	1482	1482	1483	1479	1480	1470	1472
38	1499	1495	1488	1484	1497	1498	1498	1487	1487	1487	1489
39	1506	1497	1504	1501	1508	1507	1508	1503	1501	1494	1496
40	1515	1513	1512	1511	1521	1519	1519	1507	1507	1510	1510
41	2233	2236	2229	2238	2238	2228	2230	2226	2235	2237	2229
42	2916	2922	2917	2940	2955	2932	2954	3006	2994	3001	3013
43	3014	3003	3029	3010	2995	3007	3036	3028	3035	3030	3023
44	3033	3040	3036	3038	3042	3042	3042	3050	3041	3044	3053
45	3038	3070	3043	3054	3047	3071	3051	3076	3050	3048	3058
46	3092	3103	3118	3058	3074	3124	3100	3118	3085	3076	3113
47	3125	3125	3124	3123	3124	3125	3125	3125	3125	3124	3124
48	3129	3129	3129	3129	3129	3129	3129	3130	3130	3129	3129
49	3207	3207	3206	3205	3206	3207	3207	3208	3207	3206	3206
50	3220	3220	3219	3219	3219	3220	3220	3221	3220	3220	3220
51	3507	3499	3511	3509	3501	3502	3502	3526	3528	3527	3525

Table A-11. Normal mode frequencies (cm<sup>-1</sup>) for CPAZ group 21 conformers.

Mode	Conformer										
	A21	B21	C21	D21	E21	F21	G21	H21	I21	J21	L21
1	27	48	25	23	30	38	34	39	28	33	32
2	56	54	40	38	71	47	53	44	63	43	47
3	88	76	103	92	78	79	74	71	85	96	92
4	141	115	107	113	90	94	90	113	93	103	120
5	199	236	202	184	154	232	224	220	162	178	211
6	256	259	249	240	260	258	266	244	232	244	238
7	300	300	339	317	310	292	279	293	302	278	313
8	408	401	407	403	327	347	354	330	326	389	394
9	435	445	413	411	419	418	418	437	437	445	444
10	530	514	505	506	517	517	519	523	523	510	516
11	559	555	559	551	551	556	558	555	550	554	557
12	683	649	660	630	650	675	678	677	656	628	655
13	716	719	716	726	735	728	729	680	684	680	688
14	774	766	753	762	764	761	762	758	756	763	764
15	816	813	799	801	797	799	797	791	789	806	803
16	834	831	837	835	826	827	827	827	827	842	837
17	838	841	841	848	838	839	838	843	842	847	845
18	880	902	887	896	937	924	923	919	937	883	876
19	955	949	952	962	960	946	946	943	948	949	940
20	972	982	966	967	968	960	966	973	971	973	964
21	995	990	1043	1041	1043	1040	1040	1009	1044	1020	1009
22	1048	1044	1053	1057	1068	1052	1050	1044	1049	1041	1042
23	1075	1075	1069	1068	1073	1072	1072	1072	1071	1068	1070
24	1096	1091	1088	1087	1092	1092	1093	1091	1091	1095	1085
25	1130	1132	1116	1121	1131	1132	1131	1128	1126	1127	1132
26	1145	1139	1130	1128	1137	1145	1141	1155	1142	1141	1145
27	1187	1185	1189	1189	1183	1189	1189	1186	1186	1187	1187
28	1197	1196	1193	1194	1195	1196	1195	1195	1195	1195	1196
29	1236	1239	1241	1241	1234	1237	1237	1240	1235	1240	1240
30	1266	1264	1262	1246	1257	1262	1261	1252	1247	1248	1254
31	1291	1303	1314	1319	1327	1315	1309	1313	1327	1311	1303
32	1335	1347	1338	1349	1331	1331	1332	1330	1332	1335	1332
33	1377	1377	1376	1379	1343	1356	1355	1359	1339	1379	1378
34	1399	1386	1388	1383	1390	1386	1390	1395	1399	1386	1390
35	1415	1415	1417	1416	1420	1417	1417	1408	1410	1407	1406
36	1456	1455	1456	1454	1455	1455	1455	1454	1454	1454	1454
37	1488	1481	1480	1479	1485	1482	1482	1479	1480	1472	1470
38	1492	1482	1485	1480	1493	1491	1492	1487	1487	1479	1483
39	1496	1493	1489	1492	1504	1505	1505	1504	1501	1492	1495
40	1507	1505	1507	1506	1509	1509	1510	1507	1507	1508	1509
41	2231	2234	2226	2234	2237	2228	2228	2227	2235	2234	2228
42	2918	2936	2937	2952	2959	2940	2959	3024	2994	2984	2997
43	3011	3035	3005	3001	3018	3039	3036	3033	3036	3014	3015
44	3030	3036	3039	3051	3040	3042	3041	3052	3041	3025	3055
45	3050	3071	3053	3056	3057	3074	3056	3070	3050	3077	3086
46	3123	3101	3123	3064	3080	3123	3124	3101	3085	3098	3098
47	3124	3125	3124	3123	3123	3124	3129	3125	3125	3123	3124
48	3128	3130	3133	3129	3128	3129	3130	3130	3130	3128	3129
49	3207	3208	3206	3204	3206	3206	3206	3208	3207	3205	3206
50	3221	3222	3225	3219	3219	3219	3219	3221	3220	3218	3219
51	3534	3544	3531	3526	3538	3536	3535	3528	3528	3523	3523

Table A-12. Normal mode frequencies (cm<sup>-1</sup>) for CPAZ group 12 conformers.

Mode	Conformer						
	A12	B12	C12	D12	E12	F12	G12
1	25	44	28	37	28	35	32
2	45	53	61	48	65	50	51
3	90	73	76	85	85	84	77
4	136	129	141	132	90	113	115
5	178	175	173	197	143	151	150
6	200	252	228	202	193	241	243
7	296	290	321	284	296	299	299
8	400	409	391	389	329	334	333
9	441	439	436	435	433	436	436
10	507	502	516	518	491	490	491
11	562	557	554	556	548	556	557
12	664	651	657	638	658	675	672
13	682	694	709	723	711	710	715
14	763	763	765	767	764	763	763
15	807	808	808	808	805	803	809
16	840	828	814	823	809	809	810
17	846	853	860	868	850	852	848
18	885	913	893	894	938	921	920
19	940	940	942	939	943	939	940
20	988	990	988	992	985	977	978
21	1004	998	1006	1031	1035	1035	1035
22	1034	1034	1035	1035	1065	1053	1053
23	1066	1064	1067	1066	1073	1066	1066
24	1081	1068	1106	1094	1095	1091	1087
25	1125	1125	1125	1124	1123	1123	1124
26	1133	1129	1134	1136	1125	1126	1129
27	1189	1189	1188	1189	1182	1189	1189
28	1196	1194	1191	1196	1189	1194	1195
29	1241	1238	1234	1234	1232	1236	1235
30	1271	1275	1255	1252	1263	1263	1263
31	1282	1284	1290	1296	1313	1303	1306
32	1332	1343	1334	1336	1324	1325	1316
33	1357	1362	1357	1361	1344	1352	1353
34	1397	1386	1382	1381	1376	1375	1381
35	1415	1407	1411	1416	1423	1415	1416
36	1461	1462	1461	1461	1462	1462	1462
37	1489	1485	1488	1482	1494	1493	1494
38	1500	1495	1495	1495	1497	1499	1499
39	1511	1501	1508	1503	1514	1514	1514
40	1516	1517	1512	1512	1519	1517	1518
41	2233	2237	2229	2239	2237	2229	2230
42	2926	2931	2928	2950	2964	2942	2963
43	3013	3001	3026	3010	2994	3006	3036
44	3027	3063	3037	3045	3046	3063	3043
45	3091	3102	3113	3059	3068	3113	3099
46	3112	3113	3117	3113	3113	3118	3113
47	3118	3118	3118	3117	3118	3125	3118
48	3123	3126	3120	3120	3125	3126	3125
49	3191	3191	3191	3191	3191	3191	3192
50	3206	3206	3206	3206	3206	3206	3206
51	3529	3519	3528	3525	3521	3522	3521

Table A-13. Normal mode frequencies (cm<sup>-1</sup>) for CPAZ group 22 conformers.

Mode	Conformer							
	A22	B22	C22	X22	D22	E22	F22	G22
1	27	39	31	20	32	27	36	33
2	41	52	52	39	45	55	47	50
3	78	73	88	54	85	82	66	55
4	137	116	109	92	113	90	99	96
5	190	208	214	225	175	154	227	213
6	234	249	235	242	242	239	251	257
7	310	309	319	289	289	307	281	282
8	398	393	393	371	383	319	335	336
9	470	478	457	468	462	439	442	442
10	503	490	500	482	496	509	508	510
11	560	555	556	550	553	550	555	558
12	631	631	649	594	623	625	634	637
13	691	651	665	648	666	680	690	690
14	760	756	751	753	750	754	753	753
15	812	809	802	804	805	793	794	793
16	825	830	815	813	816	816	818	816
17	848	843	857	851	859	841	840	840
18	879	898	890	906	899	940	925	922
19	942	941	933	937	938	947	943	949
20	968	978	968	970	970	961	952	952
21	985	986	1016	993	1018	1034	1022	1022
22	1034	1035	1035	1035	1033	1049	1037	1037
23	1069	1068	1066	1066	1064	1067	1068	1067
24	1085	1079	1096	1087	1095	1097	1096	1095
25	1133	1128	1112	1119	1118	1127	1127	1125
26	1138	1130	1133	1129	1131	1131	1139	1136
27	1191	1189	1188	1188	1188	1184	1189	1189
28	1193	1191	1191	1190	1192	1191	1191	1193
29	1241	1242	1245	1246	1243	1238	1243	1242
30	1275	1270	1256	1262	1251	1259	1262	1261
31	1285	1297	1312	1307	1317	1330	1317	1311
32	1335	1346	1334	1353	1341	1334	1334	1332
33	1375	1371	1377	1376	1373	1343	1356	1361
34	1395	1388	1384	1381	1387	1375	1376	1375
35	1404	1399	1401	1397	1405	1414	1407	1410
36	1462	1462	1462	1461	1461	1462	1462	1462
37	1489	1479	1479	1475	1475	1487	1486	1487
38	1495	1492	1487	1484	1478	1496	1495	1495
39	1501	1494	1496	1493	1495	1504	1505	1505
40	1512	1510	1513	1510	1515	1511	1510	1510
41	2232	2235	2227	2234	2235	2237	2228	2228
42	2927	2942	2940	3004	2971	2972	2952	2971
43	3011	3020	3012	3025	2998	3010	3028	3036
44	3051	3073	3054	3050	3053	3051	3074	3057
45	3110	3100	3112	3090	3062	3079	3114	3114
46	3114	3114	3117	3113	3111	3114	3119	3115
47	3119	3118	3122	3118	3116	3119	3122	3119
48	3127	3121	3153	3131	3161	3123	3125	3126
49	3192	3193	3191	3193	3190	3193	3193	3193
50	3207	3208	3206	3207	3205	3208	3208	3208
51	3567	3578	3556	3584	3558	3571	3570	3568

Table A-14. Normal mode frequencies (cm<sup>-1</sup>) for CPAZ group 13 conformers.

Mode	Conformer						
	A13	B13	C13	D13	E13	F13	G13
1	26	28	26	23	27	26	23
2	31	56	41	40	49	46	43
3	88	81	91	83	82	81	80
4	142	126	135	139	91	107	101
5	176	208	188	180	143	154	159
6	206	254	219	218	189	255	246
7	293	289	320	281	319	289	290
8	377	398	385	385	368	390	389
9	454	438	440	439	395	399	399
10	547	548	550	548	522	522	523
11	562	559	557	559	548	555	557
12	682	652	658	641	661	674	673
13	694	719	729	734	737	736	739
14	757	757	762	767	757	755	756
15	797	793	798	797	799	799	799
16	829	815	818	821	806	805	811
17	845	844	843	854	828	831	829
18	873	894	880	880	911	909	913
19	929	943	927	928	946	930	923
20	994	991	984	999	995	985	990
21	1006	995	1029	1033	1034	1034	1034
22	1034	1036	1052	1061	1060	1051	1050
23	1069	1065	1068	1067	1067	1066	1066
24	1087	1077	1090	1077	1094	1072	1070
25	1114	1106	1108	1112	1111	1124	1124
26	1135	1130	1134	1134	1130	1132	1134
27	1189	1188	1188	1189	1186	1189	1189
28	1195	1191	1196	1196	1191	1193	1195
29	1247	1251	1236	1238	1226	1237	1235
30	1270	1262	1267	1269	1267	1265	1266
31	1287	1285	1284	1285	1314	1302	1309
32	1330	1345	1332	1338	1331	1331	1317
33	1387	1383	1377	1377	1344	1354	1360
34	1401	1392	1395	1399	1411	1406	1408
35	1410	1415	1410	1412	1415	1412	1412
36	1463	1463	1464	1463	1463	1463	1463
37	1491	1485	1488	1482	1495	1496	1497
38	1503	1496	1499	1499	1499	1500	1501
39	1513	1505	1509	1505	1519	1516	1518
40	1524	1526	1522	1522	1525	1525	1525
41	2234	2237	2230	2239	2238	2228	2230
42	2913	2927	2917	2941	2960	2937	2957
43	3014	3003	3031	3011	2996	3009	3039
44	3043	3085	3050	3059	3052	3085	3064
45	3092	3102	3119	3063	3087	3120	3102
46	3118	3119	3120	3120	3120	3127	3120
47	3129	3128	3127	3127	3128	3129	3129
48	3134	3142	3134	3134	3139	3139	3138
49	3196	3196	3197	3197	3197	3197	3198
50	3213	3211	3212	3212	3212	3212	3213
51	3511	3503	3510	3508	3504	3505	3503

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