

Regular article

Theoretical studies on the molecular electron densities and electrostatic potentials in azacubanes

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Abstract. Energetics and the charge distributions in azacubanes ($C_8N_\alpha H_{8-\alpha}$) have been obtained using the ab initio Hartree–Fock, second-order Møller–Plesset perturbation theory and hybrid density functional methods. For diazacubane to hexaazacubane the lowest-energy conformers have nitrogen atoms occupying the *face opposite* corners of a cube. The topography of the molecular electrostatic potential and the electron density of azacubane conformers have been investigated. The electrostatic potential studies have shown that successive substitution of nitrogen instead of CH groups of cubane engenders smaller and more localized electron-rich regions around the nitrogens of a cube. Further the bond ellipticity and the electron density at the bond critical point of the $X-N$ bonds ($X=C$ or N) in a cubanoid increase from azacubane to octaazacubane. The heats of formation of azacubanes calculated by the isodesmic reaction approach using different levels of theory correlate well with the electron density at the bond critical point of $X-N$ ($X=C$ or N) bonds in a cubanoid.

which is partly attributed to its symmetry-forbidden unimolecular dissociation to less strained fragments [3]. These azacubanes, which are isoelectronic with cubane, are expected to be quite robust structures [4]. High mass densities and the release of a large amount of energy during decomposition should facilitate their use as potential energetic materials. Engelke [4] has reported detonation and propellant performance of some such C/N cubanoids from the calculated mass densities. The complete replacement of the CH groups in the cubane structure by nitrogen atoms should produce energy-rich octaazacubane, N_8 , which has been investigated extensively by using theoretical calculations. N_8 has been predicted to be the most powerful explosive to date [5]. Further it is also known that the high energy content of nitrated cubanoids is not only due to bond strain but also to the high energy content of the N–N single bond [4]. As a pursuit of this in the present work we have undertaken systematic studies of charge distributions in azacubanes, $C_8N_\alpha H_{8-\alpha}$ ($\alpha=1-8$), using the molecular electrostatic potential (MESP) and the molecular electron density (MED) topography as a tool. The computational method is outlined in the following section.

Introduction

There has been significant progress in the synthesis and development of new energetic compounds and their use in explosives and propellants in recent years. Particularly systems containing C/N cubanoids, a class of strained hydrocarbons, have been promising in this respect. The synthesis of cubane [1], possessing nearly 6 times more strain energy than that in cyclobutane [2], has emerged as a possible route for devising newer, high-energetic materials by successive replacement of C–H groups of cubane by isoelectronic nitrogen atoms. Another interesting feature of cubane is that in spite of the high energy in a cube it is found to be thermally stable,

Computational method

Azacubane structures were generated by successive substitution of the nitrogen atoms instead of C–H groups of cubane. The atomic numbering scheme of the cubanoid in the present work is shown in Fig. 1.

Hartree–Fock (HF) geometry optimizations were carried out for possible conformers of $C_{8-\alpha}N_\alpha$ (with $\alpha=0-8$) with the internally stored 6-31G (d, p) basis set by employing the GAUSSIAN 94 program [6]. The HF geometries were subjected to subsequent optimizations using the hybrid density functional theory incorporating Beck's three-parameter exchange with Lee, Yang and Parr's (B3LYP) correlation functional [7, 8] and to the Møller–Plesset second-order perturbation theory (MP2), which includes electron correlation as well. Stationary geometries of these 22 C/N cubanoids in the HF, B3LYP and MP2 framework of theories were confirmed as the local minima on the potential-energy surface since all vibrational frequencies turn out to be real.

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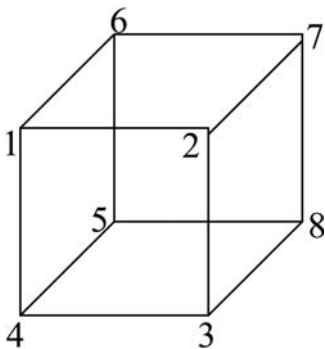


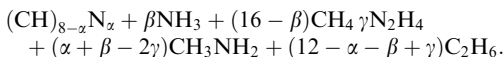
Fig. 1. Atomic numbering scheme of the cubanoid

The MESP, $V(\mathbf{r})$, at a point \mathbf{r} is defined as

$$V(\mathbf{r}) = \sum_{A=1}^N \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}') d^3 \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}, \quad (1)$$

where N is the total number of nuclei in the molecule. The first term stands for the contribution due to the nuclei with charges Z_A located at \mathbf{R}_A and the second term is due to the continuous distribution of electronic charge density, $\rho(\mathbf{r})$. Thus the MESP brings about the effective localization of electron-rich regions in the molecular system. The critical points (CPs) are the points at which all three of the first partial derivatives of the function under investigation vanish, i.e. $\nabla V(\mathbf{r})=0$. The MESP CPs provides valuable information about the structure and molecular environment and are characterized as minima, maxima and saddles by knowing the rank and signature as discussed in Ref. [9]. The topography analysis was carried out by using the program UNIPROP [10] and the MESP was visualized by employing the package UNIVIS-2000 [11]. The MED topography has been studied [12].

The heats of formation, ΔH_f , of azacubanes were calculated by devising the isodesmic reaction



Here α , β and γ are the number of nitrogens in a cubanoid, the number of NH_3 groups and number of N_2H_4 groups, respectively. Thus the heat of formation of azacubane can be calculated from

$$\Delta H_f(\text{CH})_{8-x}\text{N}_x = \gamma\Delta H_f[\text{N}_2\text{H}_4] + (\alpha + \beta - 2\gamma)\Delta H_f[\text{CH}_3\text{NH}_2] \\ + (12 - \alpha - \beta + \gamma)[\text{C}_2\text{H}_6] - \beta\Delta H_f[\text{NH}_3] + (16 - \beta)\Delta H_f[\text{CH}_4] - \text{BSE},$$

where BSE, the bond separation energy, is given by

$$\text{BSE} = \text{BSE}(1) + \Delta H(T) + 0.961 \text{ ZPC}.$$

$\text{BSE}(1)$ in this equation can be calculated by subtracting the sum of the electronic energies of the reactants from those of the products and $\Delta H(T)$ refers to the heat content change resulting from the change of the number of rotational and translational degrees of freedom. The zero-point-energy correction (ZPC) is given by the difference of the sum of the zero-point energies (ZPEs) of the reactants and that of the products; thus

$$\text{BSE}(1) = \gamma E[\text{N}_2\text{H}_4] + (\alpha + \beta - 2\gamma)E[\text{CH}_3\text{NH}_2] \\ + (12 - \alpha - \beta + \gamma)E[\text{C}_2\text{H}_6] \\ - E[(\text{CH})_{8-x}\text{N}_x] - \beta E[\text{NH}_3] - (16 - \beta)E[\text{CH}_4] \Delta H(T) \\ = -5[3/2 + 3/2 + 1]RT = -20RT$$

and

$$\text{ZPC} = \gamma \text{ZPE}[\text{N}_2\text{H}_4] + (\alpha + \beta - 2\gamma)\text{ZPE}[\text{CH}_3\text{NH}_2] \\ + (12 - \alpha - \beta + \gamma)\text{ZPE}[\text{C}_2\text{H}_6] \\ - \text{ZPE}[(\text{CH})_{8-x}\text{N}_x] - \beta \text{ZPE}[\text{NH}_3] - (16 - \beta)\text{ZPE}[\text{CH}_4].$$

Thus the ΔH_f values were calculated in the HF, B3LYP and MP2 framework of theory. The isodesmic reaction approach presented here yields good estimates for the ΔH_f values.

Results and discussion

HF/6-31G(d, p) and MP2/6-31G(d, p) calculated electronic energies and the corresponding ZPE-corrected values of azacubanes, $\text{C}_8\text{N}_x\text{H}_{8-x}$ ($x=1-8$), are given in Table 1. As may be noticed readily for diazacubane to hexaazacubane, the lowest-energy conformer turns out to be the one with the most nitrogens occupying the *face opposite* corners of a cube. Thus, amongst the different conformers of tetraazacubane, the 1,3,5,7 conformer having six nitrogens on the *face opposite* corners is seen to be lower in energy than any of the remaining tetraazacubane conformers. The HF, MP2 and B3LYP ZPE-corrected relative stabilization energies of the azacubane conformer with $x=2-6$ are displayed in Table 2. Further, the MP2-calculated relative stabilization energies are overestimated by nearly 10% compared with the corresponding B3LYP values. On the other hand, the HF-predicted stabilization energies are too high, ranging from 3.3 to 44.3 kJ mol^{-1} relative to their MP2 counterparts. The averages of the MESP derived atomic charges for C and N atoms within a cubanoid obtained from the MP2 calculations are reported in Table 3. As may be noted the largest electronic charge resides on cubanoid nitrogens for the lowest-energy conformers of diazacubane to hexaazacubane.

It has already been pointed out in Sect. 2 that the MESP brings about effective localization of electron-rich regions in the molecular systems. The MP2/6-31G(d,p)-derived MESP isosurfaces ($-78.8 \text{ kJ mol}^{-1}$) of 22 C/N azacubanes are displayed in Fig. 2. It should as well be remarked here that the electron-rich regions derived from the HF calculations qualitatively agree well with those obtained from the MP2 calculations. The isopotential surfaces, however, become more localized with shallow MESP minima when the electron correlation is present, consistent with the conclusions drawn earlier in Ref. [13]. As is transparent from Fig. 2, the electron-rich regions around nitrogen become more localized with increasing number of nitrogen atoms as in azacubane to octaazacubane. The MESP minima and their corresponding distances from the nearest nitrogens obtained from the HF/6-31G(d, p) and MP2/6-31G(d, p) calculations are given in Table 4. A decreasing trend of the MESP value at the minimum was noted in a series encompassing azacubane to octaazacubane.

Figure 2 shows that amongst the different conformers of diazacubane to hexaazacubane the electron-rich regions get localized to a larger extent in the lowest-energy conformer. In this azacubane series the most destabilized conformer yields a deeper MESP minimum relative to conformers which are preferred energetically. As seen earlier amongst the different conformers of diazacubane to hexaazacubane, in the lowest-energy conformer nitrogens occupy the *face opposite* and not the alternate

Table 1. Hartree–Fock (HF) and Møller–Plesset second-order perturbation theory (MP2) electronic energies (au) of azacubanes. The corresponding zero-point-energy (ZPE) corrected values are given in parentheses

| | HF | MP2 |
|---------------------------|----------------------------|---------------------------|
| Azacubane | −323.3892529 (−323.256594) | −323.387265 (−324.362612) |
| 1,3-Diazacubane | −339.3737148 (−339.252708) | −339.370174 (−340.384248) |
| 1,8-Diazacubane | −339.3673299 (−339.246454) | −339.363722 (−340.371971) |
| 1,2-Diazacubane | −339.3434590 (−339.223079) | −339.338194 (−340.359178) |
| 1,3,5-Triazacubane | −355.3605029 (−355.251244) | −355.355492 (−356.407854) |
| 1,2,5-Triazacubane | −355.3246965 (−355.216136) | −355.317665 (−356.378555) |
| 1,2,3-Triazacubane | −355.3010657 (−355.192928) | −355.292558 (−356.358553) |
| 1,3,5,7-Tetraazacubane | −371.3489486 (−371.251564) | −371.342142 (−372.433064) |
| 1,2,3,5-Tetraazacubane | −371.2847109 (−371.188484) | −371.274220 (−372.380364) |
| 1,2,5,8-Tetraazacubane | −371.2788443 (−371.182769) | −371.267960 (−372.375831) |
| 1,2,3,7-Tetraazacubane | −371.2613342 (−371.165435) | −371.249472 (−372.360451) |
| 1,2,3,6-Tetraazacubane | −371.2553885 (−371.159674) | −371.243407 (−372.355589) |
| 1,2,3,4-Tetraazacubane | −371.2302432 (−371.134960) | −371.218191 (−372.333366) |
| 1,2,3,5,7-Pentaazacubane | −387.2466845 (−387.162841) | −387.232413 (−388.384417) |
| 1,2,3,5,6-Pentaazacubane | −387.2121602 (−387.128943) | −387.196442 (−388.355393) |
| 1,2,3,4,5-Pentaazacubane | −387.1873767 (−387.104484) | −387.171491 (−388.333187) |
| 1,2,3,5,6,8-Hexaazacubane | −403.1462804 (−403.075919) | −403.126098 (−404.335856) |
| 1,2,3,4,6,8-Hexaazacubane | −403.1422216 (−403.072009) | −403.120489 (−404.333204) |
| 1,2,3,4,5,6-Hexaazacubane | −403.1161817 (−403.046276) | −403.096038 (−404.308644) |
| Heptaazacubane | −419.0472345 (−418.990302) | −419.021872 (−420.287560) |
| N ₈ | −434.9491622 (−434.905638) | −434.919264 (−436.240129) |

Table 2. ZPE-corrected relative stabilization energies (kJ mol^{−1}) of diazacubane to hexaaza-cubane conformers

| | HF | MP2 | B3LYP |
|---------------------------|-------|-------|-------|
| 1,3-Diazacubane | 0.0 | 0.0 | 0.0 |
| 1,8-Diazacubane | 16.4 | 32.2 | 10.5 |
| 1,2-Diazacubane | 77.8 | 65.8 | 61.4 |
| 1,3,5-Triazacubane | 00.0 | 00.0 | 00.0 |
| 1,2,5-Triazacubane | 92.2 | 76.9 | 70.3 |
| 1,2,3-Triazacubane | 153.1 | 129.4 | 120.5 |
| 1,3,5,7-Tetraazacubane | 0.0 | 0.0 | 0.0 |
| 1,2,3,5-Tetraazacubane | 165.6 | 138.4 | 127.8 |
| 1,2,5,8-Tetraazacubane | 180.6 | 150.3 | 138.1 |
| 1,2,3,7-Tetraazacubane | 226.1 | 190.7 | 177.7 |
| 1,2,3,6-Tetraazacubane | 241.3 | 203.4 | 188.1 |
| 1,2,3,4-Tetraazacubane | 306.1 | 261.8 | 242.4 |
| 1,2,3,5,7-Pentaazacubane | 0.0 | 0.0 | 0.0 |
| 1,2,3,5,6-Pentaazacubane | 89.0 | 76.2 | 69.9 |
| 1,2,3,4,5-Pentaazacubane | 153.2 | 134.5 | 123.6 |
| 1,2,3,5,6,8-Hexaazacubane | 0.0 | 0.0 | 0.0 |
| 1,2,3,4,6,8-Hexaazacubane | 10.3 | 7.0 | 7.1 |
| 1,2,3,4,5,6-Hexaazacubane | 77.8 | 71.5 | 64.8 |

Table 3. MP2/6-31G (d, p) derived net atomic charges of C and N atoms in azacubanes

| Molecule | C | N |
|---------------------------|-------|--------|
| Azacubane | 0.116 | −0.824 |
| 1,3-Diazacubane | 0.330 | −0.956 |
| 1,8-Diazacubane | 0.179 | −0.544 |
| 1,2-Diazacubane | 0.116 | −0.386 |
| 1,3,5-Triazacubane | 0.647 | −1.013 |
| 1,2,5-Triazacubane | 0.310 | −0.511 |
| 1,2,3-Triazacubane | 0.228 | −0.397 |
| 1,3,5,7-Tetraazacubane | 1.126 | −1.041 |
| 1,2,3,5-Tetraazacubane | 0.572 | −0.545 |
| 1,2,5,8-Tetraazacubane | 0.457 | −0.441 |
| 1,2,3,7-Tetraazacubane | 0.494 | −0.477 |
| 1,2,3,6-Tetraazacubane | 0.319 | −0.322 |
| 1,2,3,4-Tetraazacubane | 0.122 | −0.164 |
| 1,2,3,5,7-Pentaazacubane | 1.082 | −0.598 |
| 1,2,3,5,6-Pentaazacubane | 0.664 | −0.370 |
| 1,2,3,4,5-Pentaazacubane | 0.365 | −0.226 |
| 1,2,3,4,5,7-Hexaazacubane | 1.020 | −0.313 |
| 1,2,3,5,6,8-Hexaazacubane | 1.090 | −0.320 |
| 1,2,3,4,5,6-Hexaazacubane | 0.375 | −0.133 |
| Heptaazacubane | 1.006 | −0.130 |
| N ₈ | − | 0.0 |

corners of a cube, which is partly attributed to the nitrogen lone pair...H interactions. This is evident from the MESP value at the minimum near the nitrogen atom of the lowest-energy conformer.

Electron density topography of strained molecules has been studied in detail in the literature [14, 15]. The electron density at the bond CP (ρ_{bcp}) of the X–N bonds (X = C or N) of azacubane conformers calculated from the HF/6-31G(d, p) wavefunction is presented in Table 5. On successive substitution of nitrogen atoms from monoazacubane to octaazacubane ρ_{bcp} of the X–N bonds increase regularly, indicating greater bond strengths of the bonds within a C/N cubanoid.

Earlier using the Hückel molecular orbital theory Martensson [16] concluded the presence of bent bonds in

cubane, wherein the maximum electron density was found to lie outside the vectors joining contiguous carbon atoms. Now, the increased strain in the series from azacubane to octaazacubane is expected to yield cubanoid bonds which are more bent. Thus we analyze the curvature of bonds within a cubanoid using the bond ellipticity, ϵ , [12] given by $\epsilon = (\lambda_1/\lambda_2) - 1$, where λ_1 and λ_2 are the eigenvalues (both less than zero) at the bond CP. The calculated bond ellipticity of azacubane conformers (taken as an average of all the bonds in a cubanoid) is presented in Table 5. ϵ increases steadily from monoazacubane to octaazacubane.

From the knowledge of ΔH_f values the explosive or ballistic parameters of high-energy materials can be

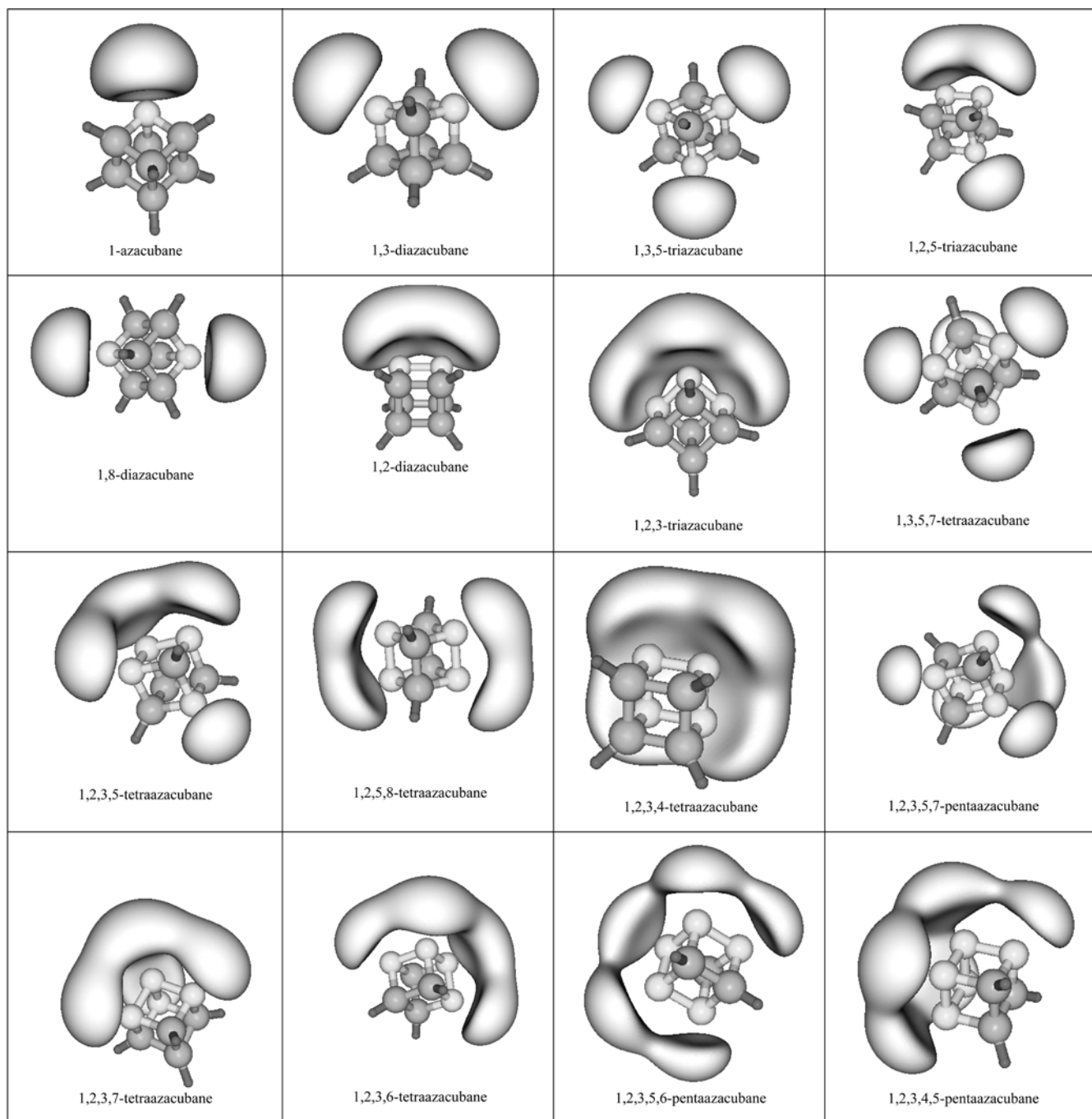


Fig. 2. Molecular electrostatic potential isosurface ($V = -78.8 \text{ kJ mol}^{-1}$) in nitroazacubanes

calculated, which enables one to assess the performance of energy-rich materials. The HF-, MP2- and B3LYP-calculated ΔH_f values of azacubane conformers, using the isodesmic reaction approach as described in Sect. 2, are given in Table 6. The ΔH_f values increase from azacubane to octaazacubane. As seen from Table 6 the HF-calculated values are in better agreement with the corresponding MP2 ones. ΔH_f values from the B3LYP theory are consistently lower than their HF or MP2 counterparts. For diazacubane to hexaazacubane the

ΔH_f value is predicted to be lower for the conformers wherein nitrogens occupy the *face-opposite* corners of a cube. A plot of ΔH_f predicted from the HF theory as a function of ρ_{bcp} of the $X\text{-N}$ bonds in azacubane conformers is depicted in Fig. 3, which shows increased strain from monoazacubane to octaazacubane. The plot is linear, with the correlation coefficient being 0.96 for all theoretical methods employed. The B3LYP and MP2 results are also in very good agreement with this result.

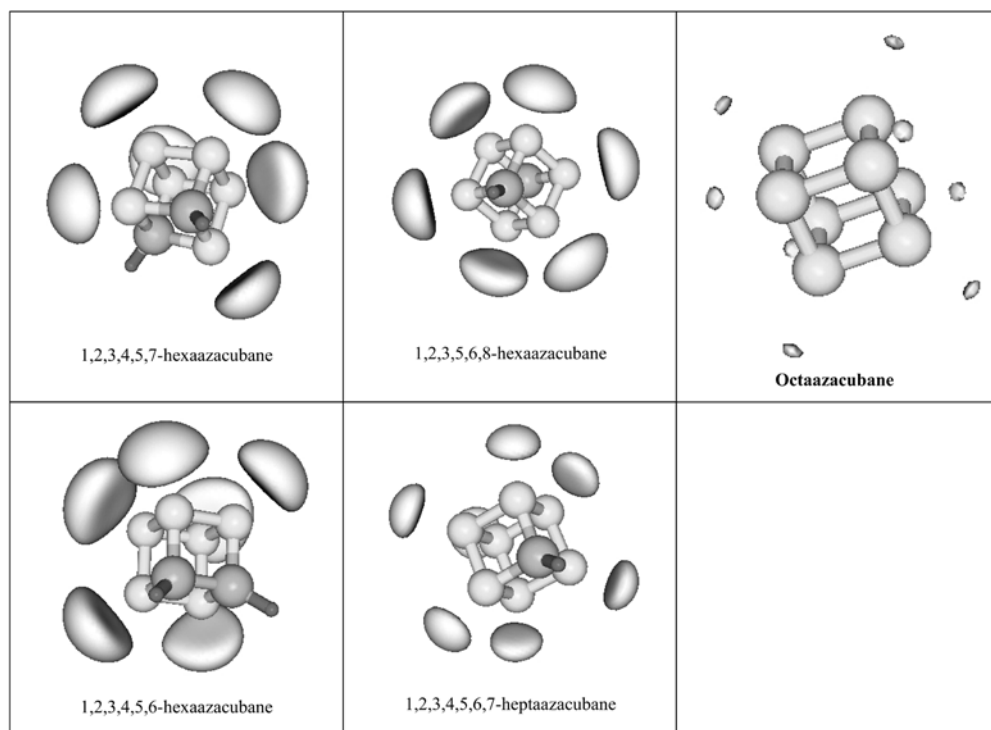


Fig. 2. (Contd.)

Conclusions

The following conclusions may be drawn from the MESP and MED analysis presented in this work.

1. Electron-rich regions near the nitrogen atoms become more localized with increasing number of nitrogen atoms in a C/N cubanoid of azacubanes.
2. In a series of diazacubane to hexaazacubane conformers having more nitrogen atoms at the *face opposite* the corners of a cube is preferred

energetically, which is partly attributed to the cubyl hydrogen and the nitrogen lone pair interactions. This is manifested in the MESP minima near nitrogen.

3. Amongst the different conformers of diazacubane to hexaazacubane the electron-rich regions are more localized for the lowest-energy structure in contrast to the most destabilized conformer.
4. The ρ_{bcp} of X–N (X=C or N) bonds in a cube increase steadily from azacubane to octaazacubane, indicating stronger bonds.

Table 4. Molecular electrostatic potential minima (kJ mol^{-1}) in azacubanes and their corresponding distances (Å) from the nearest atom

| | HF | | MP2 | |
|---------------------------|----------------|----------|----------------|----------|
| | Critical point | Distance | Critical point | Distance |
| Azacubane | –351.9 | 1.212 | –314.3 | 1.241 |
| 1,3-Diazacubane | –318.3 | 1.222 | –282.8 | 1.252 |
| 1,8-Diazacubane | –321.9 | 1.218 | –285.0 | 1.248 |
| 1,2-Diazacubane | –335.7 | 1.225 | –295.6 | 1.259 |
| 1,3,5-Triazacubane | –281.9 | 1.235 | –249.0 | 1.266 |
| 1,2,5-Triazacubane | –295.4 | 1.233 | –258.4 | 1.267 |
| 1,2,3-Triazacubane | –301.6 | 1.238 | –262.8 | 1.276 |
| 1,3,5,7-Tetraazacubane | –242.1 | 1.250 | –212.0 | 1.283 |
| 1,2,3,5-Tetraazacubane | –258.9 | 1.250 | –223.8 | 1.288 |
| 1,2,5,8-Tetraazacubane | –262.4 | 1.246 | –226.5 | 1.284 |
| 1,2,3,7-Tetraazacubane | –261.0 | 1.255 | –224.4 | 1.296 |
| 1,2,3,6-Tetraazacubane | –265.3 | 1.251 | –228.7 | 1.291 |
| 1,2,3,4-Tetraazacubane | –272.6 | 1.257 | –237.5 | 1.297 |
| 1,2,3,5,6-Pentaazacubane | –216.3 | 1.270 | –183.6 | 1.313 |
| 1,2,3,5,7-Pentaazacubane | –225.2 | 1.267 | –191.4 | 1.310 |
| 1,2,3,4,5-Pentaazacubane | –229.0 | 1.273 | –196.2 | 1.316 |
| 1,2,3,5,6,8-Hexaazacubane | –182.7 | 1.293 | –153.1 | 1.341 |
| 1,2,3,4,6,8-Hexaazacubane | –184.9 | 1.288 | –154.5 | 1.336 |
| 1,2,3,4,5,6-Hexaazacubane | –189.4 | 1.294 | –161.4 | 1.339 |
| Heptaazacubane | –143.3 | 1.321 | –120.3 | 1.370 |
| N ₈ | –98.5 | 1.357 | –84.1 | 1.406 |

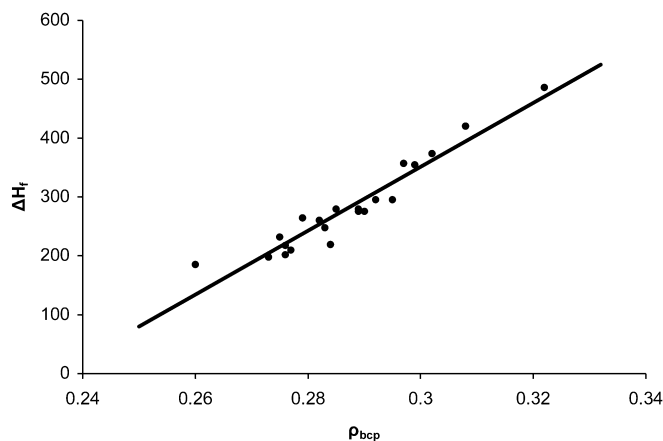
Table 5. The bond critical point, ρ_{bcp} , of the X–N bonds ($X = \text{C}$ or N) from molecular electron density and ellipticity, ϵ , of azacubanes

| | ρ_{bcp} | ϵ |
|---------------------------|---------------------|------------|
| Azacubane | 0.260 | 0.014 |
| 1,3-Diazacubane | 0.273 | 0.037 |
| 1,8-Diazacubane | 0.276 | 0.024 |
| 1,2-Diazacubane | 0.276 | 0.035 |
| 1,3,5-Triazacubane | 0.277 | 0.042 |
| 1,2,5-Triazacubane | 0.275 | 0.043 |
| 1,2,3-Triazacubane | 0.283 | 0.036 |
| 1,3,5,7-Tetraazacubane | 0.284 | 0.046 |
| 1,2,3,5-Tetraazacubane | 0.282 | 0.045 |
| 1,2,5,8-Tetraazacubane | 0.279 | 0.045 |
| 1,2,3,7-Tetraazacubane | 0.289 | 0.065 |
| 1,2,3,6-Tetraazacubane | 0.285 | 0.057 |
| 1,2,3,4-Tetraazacubane | 0.292 | 0.063 |
| 1,2,3,5,7-Pentaazacubane | 0.290 | 0.057 |
| 1,2,3,5,6-Pentaazacubane | 0.289 | 0.060 |
| 1,2,3,4,5-Pentaazacubane | 0.295 | 0.072 |
| 1,2,3,4,5,7-Hexaazacubane | 0.299 | 0.072 |
| 1,2,3,5,6,8-Hexaazacubane | 0.297 | 0.066 |
| 1,2,3,4,5,6-Hexaazacubane | 0.302 | 0.076 |
| Heptaazacubane | 0.308 | 0.087 |
| N_8 | 0.322 | 0.102 |

Table 6. ΔH_f values of azacubanes. The ΔH_f values of CH_4 , N_2H_4 , CH_3NH_2 , C_2H_6 and NH_3 used are -17.8 , -9.3 , 26.2 , -20.0 and -19.3 kcal mol $^{-1}$, respectively

| | HF | MP2 | B3LYP |
|---------------------------|-------|-------|-------|
| Azacubane | 185.5 | 183.7 | 174.7 |
| 1,3-Diazacubane | 198.2 | 197.6 | 187.4 |
| 1,8-Diazacubane | 202.2 | 201.4 | 190.0 |
| 1,2-Diazacubane | 217.5 | 217.2 | 205.3 |
| 1,3,5-Triazacubane | 209.4 | 209.7 | 199.4 |
| 1,2,5-Triazacubane | 232.1 | 233.1 | 219.4 |
| 1,2,3-Triazacubane | 247.4 | 248.7 | 234.6 |
| 1,3,5,7-Tetraazacubane | 219.3 | 221.0 | 210.7 |
| 1,2,3,5-Tetraazacubane | 260.1 | 263.0 | 247.6 |
| 1,2,5,8-Tetraazacubane | 264.0 | 266.8 | 250.0 |
| 1,2,3,7-Tetraazacubane | 275.6 | 278.5 | 262.7 |
| 1,2,3,6-Tetraazacubane | 279.2 | 282.2 | 265.3 |
| 1,2,3,4-Tetraazacubane | 295.4 | 297.8 | 281.4 |
| 1,2,3,5,7-Pentaazacubane | 287.4 | 292.0 | 274.9 |
| 1,2,3,5,6-Pentaazacubane | 309.4 | 314.2 | 294.8 |
| 1,2,3,4,5-Pentaazacubane | 325.4 | 329.8 | 310.8 |
| 1,2,3,4,5,7-Hexaazacubane | 354.4 | 360.9 | 339.1 |
| 1,2,3,5,6,8-Hexaazacubane | 356.9 | 364.3 | 340.8 |
| 1,2,3,4,5,6-Hexaazacubane | 373.7 | 379.6 | 357.3 |
| Heptaazacubane | 420.5 | 428.5 | 403.3 |
| N_8 | 486.0 | 494.9 | 467.1 |

5. The increased strain from azacubane to octaazacubane engenders increased bond ellipticity for the cubanoid bonds in this series of azacubanes. The calculated heat of formation varies linearly with the electron density at the bond CP.

**Fig. 3.** The heat of formation (kcal mol $^{-1}$) versus the electron density at the bond critical point of X–N bonds in a cubanoid of nitroazacubanes

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