Theor Chem Acc (2005) 113: 167–177
DOI 10.1007/s00214-004-0621-0

REGULAR ARTICLE

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Molecular electrostatic potentials and electron densities in azatriprismanes and nitroazatriprismanes

Received: 29 August 2004 / Accepted: 8 November 2004 / Published online: 29 January 2005

Abstract Triprismane, a C_6H_6 isomer of benzene, belongs to a class of strained hydrocarbons. In this work, the energy and charge distributions in a series of aza ($C_6N_\alpha H_{6-\alpha}$) and nitroaza $(CNO_2)_{6-\alpha}N_\alpha$, (with $\alpha = 1 \ldots 6$) derivatives of triprismane have been analyzed using the ab initio Hartree–Fock (HF)-derived molecular electrostatic potentials and molecular electron densities. Electrostatic potential investigations have shown that the electron-rich regions around nitrogen along a series of azatriprismanes and those near oxygens of nitro group in nitroazatriprismanes become smaller on encompassing from the hexanitroaza to nitroazatriprismane. As revealed from the molecular electrostatic potential (MESP) topography for the series of azatriprismanes the MESP minimum near nitrogen become shallow with increasing nitrogen content. Heats of formation obtained from the isodesmic reaction approach in the $C_6N_6H_{6-\alpha}$ and $(CNO_2)_{6-\alpha}N_\alpha$ series correlate well with the electron density at the bond-critical point of the X—N (X = C or N) bonds of the triprismane framework.

1 Introduction

Triprismane (C_6H_6), comprised of a regular three-dimensional tetrahedrally hybridized carbon network has been of great interest since its synthesis [1]. It is an isomer of benzene and the simplest member of the highly strained [n]-prismane series. Schultz [2] has investigated the stability, face angle distortion and angular strain per carbon atom of prismanes by using the topology of the class of prismanes. Dai et al. [3] have obtained the structure, force field and vibrational frequencies of triprismane from the ab initio Hartree–Fock (HF) calculations. Energies of isomerization reactions, which involve the conversion of unsaturated systems to highly strained triprismanes, have been calculated using density functional calculations [4]. Politzer et al. [5] have investigated the bond-deviation indices and the electrostatic potentials in cyclopropane, triprismane and cubane and analyzed the extent of electron-rich regions near C—C bonds on substitution of amine group in coplanar and pyramidal orientation. Structural and spectral characteristics of N_6 triprismane have been studied from the hypersurface [6, 7], using different levels of theory. Thus, from the lowest vibrational frequency in the ab initio framework of theory the N_6 triprismane has been predicted to have a more rigidly defined structure [6, 7] compared to N_6 benzene. Murray et al. [8] have discussed the stabilities of some mono and triazatriprismane isomers and their nitro and amino derivatives and concluded that introduction of nitrogen into the strained molecular framework or N-nitro substitution enhances the stability of these molecules. This work has been extended further to obtain the relative bond strengths and stabilities of some isomeric nitroazatriprismanes [9]. Theoretical investigations of the electronic structure, bond orders and isoelectronic reaction energies of various NH_2 and NO_2 derivatives of triprismanes and some azatriprismanes have been reported earlier in the literature [10]. Thus, the influence of the push–pull mechanism on strain energies of related systems with vicinal NH_2 and NO_2 groups has been discussed. Hexaazatriprismanes, N_6 isoelectronic with the $(CH)_6$, is of recent interest owing to its potential use as receptacles for the storage of energy and theoretical calculations of Gimare et al. [11] have identified its strain energy to be comparable with that of triprismane. As a pursuit of this, we systematically investigate electronic structure, energetics and charge distributions of azatriprismanes ($C_6N_\alpha H_{6-\alpha}$) and nitroazatriprismanes, $(CNO_2)_{6-\alpha}N_\alpha$ with ($\alpha = 1 \ldots 6$) using the topography of molecular electrostatic potential and molecular electron density. In this paper, we address the following questions: How the molecular electrostatic potential (MESP) can be

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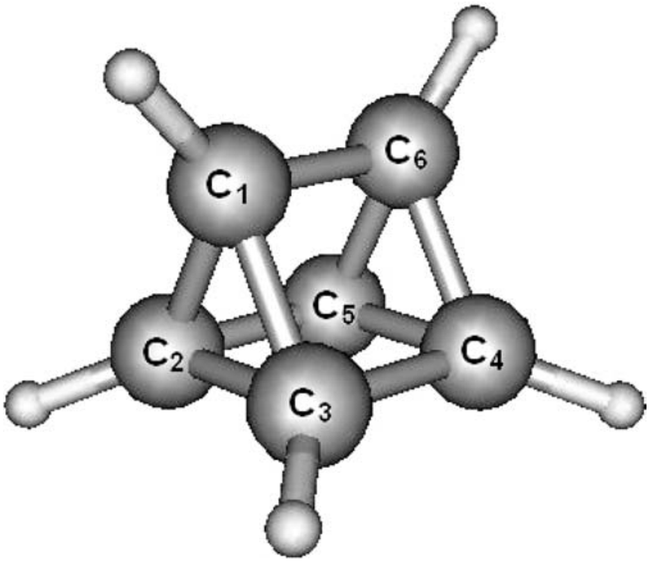
SPG is grateful to the Council of Scientific and Industrial Research (CSIR project 01(1772)/02/EMR-II), New Delhi, India. KAJ thanks CSIR for the Junior Research Fellowship. Thanks are due to C-DAC, Pune, for providing computational facilities.

used to predict azatriprismanes? How localization of electrons has been influenced by successive substitution of nitrogen instead of CH in a series of azatriprismanes? How interactions of nitro groups and nitrogen atoms within the triprismane framework influence the energetics of nitroazatriprismanes? How electron-rich regions are manifested in the electrostatic potential minima near the oxygen of nitro groups of nitroazatriprismanes? What are the implications of electron localizations pertaining to the frequency variations within the different isomers and along the series of nitroazatriprismane? Do the heats of formation show any regular trend along a series of aza and nitroazatriprismanes? The computational method used has been outlined below.

2 Computational method

The atomic numbering scheme in triprismane framework used in the present work has been shown below.



Geometry optimizations of $(CNO_2)_{6-\alpha}N_\alpha$ and $C_{6-\alpha}N_\alpha H_{6-\alpha}$ ($\alpha = 1 \ldots 6$) isomers were performed at the HF level using the GAUSSIAN-94 program [12] employing the internally stored 6-31 G(d,p) basis set. Stationary point geometries with respect to the nuclear coordinates were obtained by the simultaneous relaxation of all the geometric parameters using the analytical gradient method [17]. These geometries were further subjected to optimizations using the hybrid density functional method incorporating Becke's three-parameter exchange with Lee, Yang and Parr correlation functional (B3LYP) [14, 15]. Harmonic vibrational frequencies were calculated by the diagonalization of the force constant matrix. The stationary geometries turn out to be the local minima (since all vibrational frequencies were real) on the potential energy surface. Normal vibrations were assigned by visualizing the displacement of atoms around their equilibrium (mean) positions by using the program code UNIVIS-2000.

The MESP $V(r)$ at a point r due to a molecular system with nuclear charges $\{Z_A\}$ located at $\{R_A\}$ and the electron density $\rho(r)$ is given by

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

where N denotes the total number of nuclei in the molecule. The first term in the above equation refers to the bare nuclear potential and the second to the electronic contribution. Details of the MESP are presented in the reviews of Tomasi [16, 17] and Szabo [18]. The topography of MESP is mapped by examining the eigenvalues of the Hessian matrix at the point where the gradient $V(r)$ vanishes. The MESP critical points (CPs) were located using the fortran code UNIPROP [19]. The Fortran program UNIVIS-2000 [20, 21] was used for visualization of the MESP topography. The MESP CPs can be characterized [21, 22] in terms of an ordered pair (rank, signature), which can be grouped further into three sets viz., (3, +3), (3, +1) and (3, −1). The (3, +3) set corresponds to the set of minima and the remaining ones turn out to be the saddle points. In the molecular electron density (MED) topography, the (3, −1), (3, +1) and (3, +3) CPs refer to bond-critical point (bcp), ring CP and cage CP, respectively [21]. The computed MESP and MED CPs have been visualized using the package UNIVIS 2000 [22]. In order to calculate the heat of formation in azatriprismane isomers, the following isodesmic reaction was devised:

$$\begin{aligned} &C_6H_{6-\alpha}N_\alpha + \beta NH_3 + (12-\beta)CH_4 \rightarrow \gamma N_2H_4 \\ &\quad +(\alpha+\beta-2\gamma)CH_3NH_2 + (9-\alpha-\beta+\gamma)C_2H_6\,. \end{aligned}$$

Here α, β, and γ denote the number of nitrogen, NH_3 groups, and N_2H_4 groups, respectively. Thus, the heat of formation of azatriprismane can be calculated from

$$\begin{aligned} \Delta H_f[C_6H_{6-\alpha}N_\alpha] = {} & \gamma\Delta H_f[N_2H_4] \\ & +(\alpha+\beta-2\gamma)\Delta H_f[CH_3NH_2] \\ & +(9-\alpha-\beta+\gamma)\Delta H_f[C_2H_6] \\ & -\beta\Delta H_f[NH_3] \\ & +(12-\beta)\Delta H_f[CH_4] - \mathrm{BSE}(1) \\ & +\Delta H(\mathrm{T}) + 0.961\mathrm{ZPC}\,, \end{aligned}$$

where BSE(1) refers to the difference between the sum of electronic energy of products and that of the sum of electronic energy of reactants, ΔH(T) denotes the heat-content change due to rotational and translational degree of freedom, and ZPC represents the zero point energy correction obtained from the difference between the sum of zero point energies (ZPE) of products and that of reactants.

$$\begin{aligned} \mathrm{BSE}(1) = {} & \gamma\,E\,[N_2H_4] + (\alpha+\beta-2\gamma)E\,[CH_3NH_2] \\ & +(9-\alpha-\beta+\gamma)E\,[C_2H_6] - E\,[C_6H_{6-\alpha}N_\alpha] \\ & -\beta\,E\,[NH_3] - (12-\beta)E\,[CH_4] \end{aligned}$$

$$\Delta H(\mathrm{T}) = -4\left[\frac{3}{2} + \frac{3}{2} + 1\right] = -16RT\,.$$

Further,

$$\begin{aligned}\mathrm{ZPC} = {} & \gamma\,\mathrm{zpe}\,[\mathrm{N_2H_4}] + (\alpha+\beta-2\gamma)\mathrm{zpe}\,[\mathrm{CH_3NH_2}] \\ & +(9-\alpha-\beta+\gamma)\mathrm{zpe}\,[\mathrm{C_2H_6}] \\ & -\mathrm{zpe}\,[\mathrm{C_6H_{6-\alpha}N_\alpha}] - \beta\mathrm{zpe}\,[\mathrm{NH_3}] \\ & -(12-\beta)\mathrm{zpe}\,[\mathrm{CH_4}]\,.\end{aligned}$$

In an analogous manner, the heat of formation of nitroazatriprismane is calculated from:

$$\begin{aligned}& (\mathrm{CNO_2})_{6-\alpha}\mathrm{N_\alpha} + \beta\mathrm{NH_3} + (18-\alpha-\beta)\mathrm{CH_4} \\ & \quad \rightarrow \gamma\mathrm{N_2H_4} + (\alpha+\beta-2\gamma)\mathrm{CH_3NH_2} \\ & \qquad +(6-\alpha)\mathrm{CH_3NO_2} + (9-\alpha-\beta+\gamma)\mathrm{C_2H_6}\end{aligned}$$

$$\begin{aligned}\Delta H_\mathrm{f}[(\mathrm{CNO_2})_{6-\alpha}\mathrm{N_\alpha}] = {} & \gamma\Delta H_\mathrm{f}[\mathrm{N_2}H_4] + (\alpha+\beta-2\gamma) \\ & \times\Delta H_\mathrm{f}[\mathrm{CH_3NH_2}] \\ & + (6-\alpha)\Delta H_\mathrm{f}[\mathrm{CH_3NO_2}] \\ & + (9-\alpha-\beta+\gamma)\Delta H_\mathrm{f}[\mathrm{C_2H_6}] \\ & -\beta\Delta H_\mathrm{f}[\mathrm{NH_3}] + (18-\alpha-\beta) \\ & \times\Delta H_\mathrm{f}[\mathrm{CH_4}] - \mathrm{BSE}(1) + \Delta H(\mathrm{T}) \\ & + 0.9613\mathrm{ZPC}\,.\end{aligned}$$

For nitroazatriprismanes, one writes

$$\Delta H(\mathrm{T}) = -4\left[\frac{3}{2}+\frac{3}{2}+1\right] = -16RT$$

$$\begin{aligned}\mathrm{BSE}(1) = {} & \gamma E\,[\mathrm{N_2H_4}] + (\alpha+\beta-2\gamma)E\,[\mathrm{CH_3NH_2}] \\ & + (6-\alpha)E\,[\mathrm{CH_3NO_2}] \\ & + (9-\alpha-\beta+\gamma)E\,[\mathrm{C_2H_6}] - E\,[(\mathrm{CNO_2})_{6-\alpha}\mathrm{N_\alpha}] \\ & -\beta\,E\,[\mathrm{NH_3}] - (18-\alpha-\beta)\,E\,[\mathrm{CH_4}]\end{aligned}$$

in the above equation. ZPC is further given by:

$$\begin{aligned}\mathrm{ZPC} = {} & \gamma\,\mathrm{zpe}\,[\mathrm{N_2H_4}] + (\alpha+\beta-2\gamma)\,\mathrm{zpe}\,[\mathrm{CH_3NH_2}] \\ & + (6-\alpha)\mathrm{zpe}\,[\mathrm{CH_3NO_2}] \\ & + (9-\alpha-\beta+\gamma)E\,[\mathrm{C_2H_6}] - \mathrm{zpe}\,[(\mathrm{CNO_2})_{6-\alpha}\mathrm{N_\alpha}] \\ & -\beta\mathrm{zpe}[\mathrm{NH_3}] - (18-\alpha-\beta)\mathrm{zpe}[\mathrm{CH_4}]\,.\end{aligned}$$

It may be noted that the isodesmic reaction approach provides an economical yet very good estimate of heats of formation.

3 Results and discussion

3.1 Azatriprismanes

Zpe corrected B3LYP/6-31G(d,p) electronic energies of azatriprismanes, $C_6N_\alpha H_{6-\alpha}$ ($\alpha = 1\ldots6$), are given in Table 1. For di- to tetraazatriprismanes the lowest energy isomer possesses nitrogen atoms, which occupy the diagonally opposite corners of a rectangular face of triprismane skeleton. Thus, in azatriprismanes the 1,4,5-isomer, with all the nitrogen atoms on the diagonally opposite sites of the rectangular faces of triprismane, turns out to be 106.8 kJ mol^{-1} lower in energy than the 1,2,3-azatriprismane isomer. In the latter, nitrogen atoms are on the same face of the triprismane skeleton, which causes large destabilization owing to large electron repulsion in the molecule. Similar inference may be drawn for other isomers in azatriprismane series.

Table 1 B3LYP electronic and relative stabilization energies (ΔE) of azatriprisamanes (in a.u. and kJ mol^{-1}, respectively)

	Electronic energy	ΔE
Triprismane	−231.967713	–
Nitroazatriprismanes	−248.009381	–
1,4-Dinitroazatriprismanes	−264.052162	0.0
1,6-Dianitrozatriprismanes	−264.033993	47.7
1,2-Dianitrozatriprismanes	−264.033849	48.1
1,4,5-Trinitroazatriprismanes	−280.078703	0.0
1,2,5-Trinitroazatriprismanes	−280.060063	48.9
1,2,3-Trinitroazatriprismanes	−280.038010	106.8
1,3,4,5-Tetranitroazatriprismanes	−296.089113	0.0
1,2,5,6-Tetranitroazatriprismanes	−296.068471	75.9
1,2,3,4-Tetranitroazatriprismanes	−296.066262	60.0
1,2,3,4,5-Pentanitroazatriprismanes	−312.078091	–
Hexaazatriprismane	−326.201478	–

Table 2 B3LYP frequencies (in cm^{-1}) of the lowest vibration of azatriprismanes

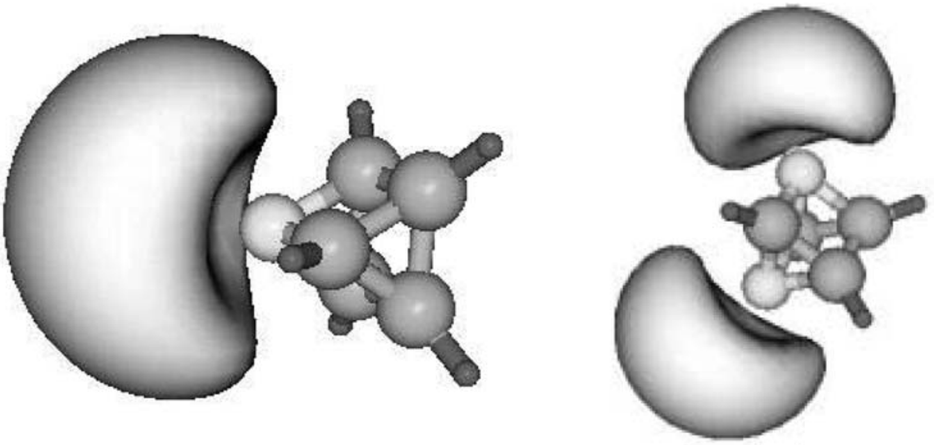
	B3LYP
Triprismanes	649
Azatriprismanes	645
1,4-Diazatriprismanes	640
1,2-Diazatriprismanes	639
1,6-Diazatriprismanes	635
1,4,5-Triazatriprismanes	632
1,2,5-Triazatriprismanes	629
1,2,3-Triazatriprismanes	638
1,3,4,5-Tetraazatriprismanes	617
1,2,5,6-Tetraazatriprismanes	618
1,2,3,4-Tetraazatriprismanes	625
1,2,3,4,5-Pentaazatriprismanes	609
Hexaazatriprismane	595

B3LYP frequencies (in cm^{-1}) of the lowest vibration of azatriprismanes are given in Table 2. As may be seen, the lowest vibrations of azatriprismanes are predicted to be ~500 cm^{-1} or more, which suggest a rigid structure for aza derivative of triprismane.

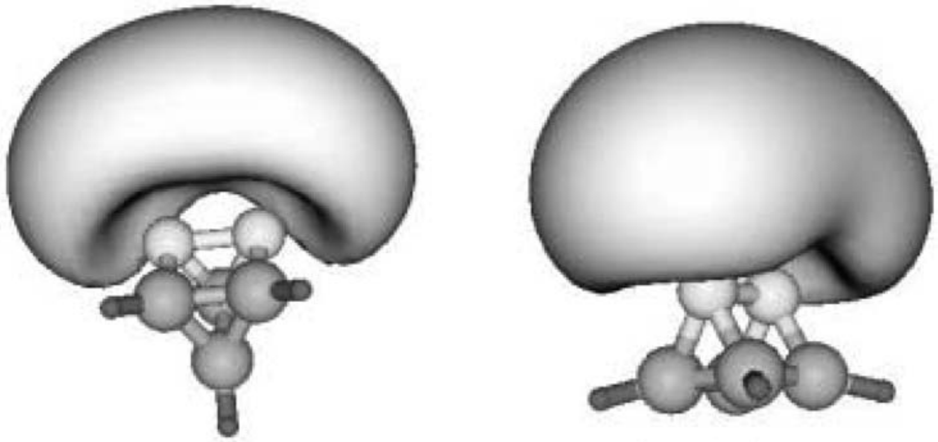
It was pointed out earlier in the preceeding section that the MESP brings about the effective localization of electron-rich

Table 3 Molecular electrostatic potential minima (kJ mol^{-1}) for azatriprismanes

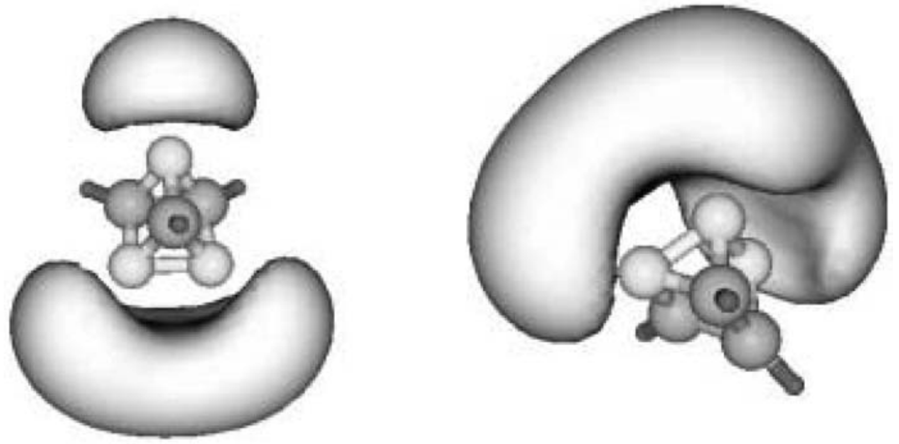
	MESP
Azatriprismanes	−322.7
1,4-Diazatriprismanes	−281.2
1,2-Diazatriprismanes	−288.5
1,6-Diazatriprismanes	−289.0
1,4,5-Triazatriprismanes	−238.9
1,2,5-Triazatriprismanes	−243.3
1,2,3-Triazatriprismanes	−249.3
1,3,4,5-Tetraazatriprismanes	−191.6
1,2,5,6-Tetraazatriprismanes	−198.2
1,2,3,4-Tetraazatriprismanes	−196.2
1,2,3,4,5-Pentaazatriprismanes	−141.9
Hexaazatriprismane	−84.5



azatriprismane 1,4-diazatriprismane



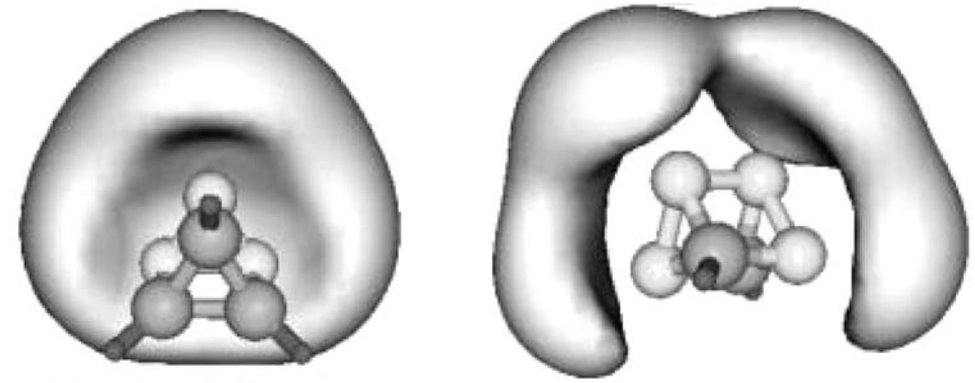
1,2-diazatriprismane 1,6-diazatriprismane



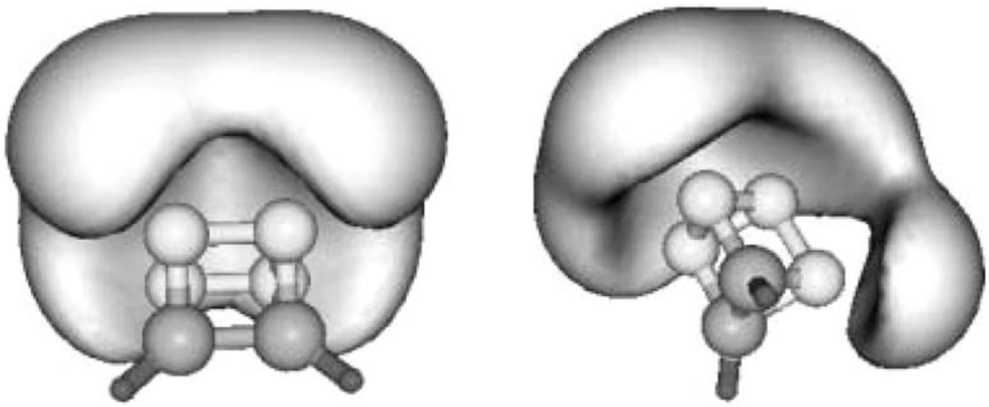
1,4,5-triazatriprismane 1,2,5-triazatriprismane

Fig. 1 MESP isosurface ($V = -57.8\,\mathrm{kJ\,mol^{-1}}$) in azatriprismanes

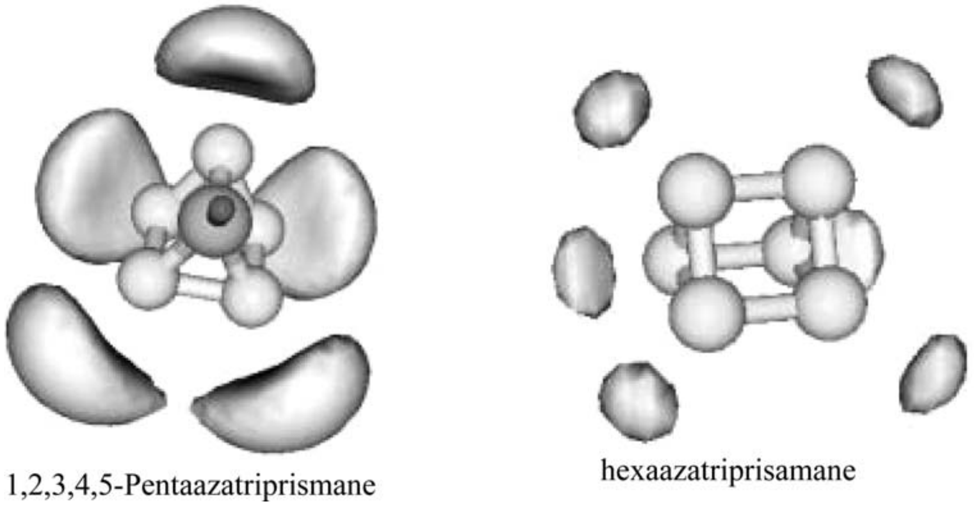
regions in the molecular system. The MESP isosurfaces ($V = -57.8\,\mathrm{kJ\,mol^{-1}}$) of different $C_6N_\alpha H_{6-\alpha}$ ($\alpha = 1\ldots6$) isomers are depicted in Fig. 1. Amongst $C_6N_\alpha H_{6-\alpha}$ isomers, the smaller electron-rich regions around the nitrogen atoms are observed for the lowest energy isomer (cf. Table 3), whereas the destabilized isomer exhibits a deeper MESP minimum. As seen from Fig. 1 the electron-rich region around nitrogen becomes smaller and thus localized to a greater extent with successive substitution of nitrogen atoms in the series. The MESP minimum and its distance from hydrogen on the



1,2,3-triazatriprismane 1,3,4,5-tetraazatriprismane



1,2,5,6-tetraazatriprismane 1,2,3,4-tetraazatriprismane



1,2,3,4,5-Pentaazatriprismane hexaazatriprisamane

Fig. 1 (Contd.)

adjacent carbon atom is given in Table 4. For the lowest energy isomer, the MESP minimum near nitrogen decreases on encompassing from the azatriprismane to hexaazatriprismane, whereas the separation of corresponding minima and the hydrogen on the adjacent carbon atom increases steadily.

The HF-calcaluted dipole moments of azatriprismane isomers are displayed in Table 5. Thus, for di- to pentaazatriprismanes the spatial configuration with nitrogen atoms occupying diagonally opposite corners of a rectangular face of the triprismane framework engenders lower dipole

Table 4 Molecular electrostatic potential minima (kJ mol^{-1}) and their corresponding distances (Å) from the hydrogen atom on the adjacent carbon atoms for the lowest energy conformers of azatriprismanes

	MESP	*H* in triangular plane	*H* in rectangular plane
Azatriprismanes	−322.7	2.80	2.958
1,4-Diazatriprismanes	−281.2	2.921	2.994
1,4,5-Triazatriprismanes	−238.9	2.983	3.031
1,3,4,5-Tetraazatriprismanes	−191.6	3.077	3.106
1,2,3,4,5-Pentaazatriprismanes	−141.9	3.130	3.193
Hexaazatriprismane	−84.5	–	–

Table 5 Dipole moments (in D) of azatriprismanes

	HF
Triprisamanes	0.0
Azatriprismanes	2.25
1,4-Diazatriprismanes	1.78
1,2-Diazatriprismanes	3.71
1,6-Diazatriprismanes	3.71
1,4,5-Triazatriprismanes	1.72
1,2,5-Triazatriprismanes	3.93
1,2,3-Triazatriprismanes	4.98
1,3,4,5-Tetraazatriprismanes	2.34
1,2,5,6-Tetraazatriprismanes	4.60
1,2,3,4-Tetraazatriprismanes	4.08
1,2,3,4,5-Pentaazatriprismanes	3.08
Hexaazatriprismane	0.0

moment relative to other isomers, partly attributed to a large cancellation of the C—N bond moments. Thus 1,4,5-azatriprismane has dipole moment 1.7 D (cf. Table 5). A large dipole moment of 1,2,3-triazatriprismane with all nitrogens occupying the sites of a triangular face of triprismane skeleton has also been explained similarly and corresponds to a electron-rich nitrogen.

The topography of molecular electron density in strained molecules has been of considerable interest in the literature [23,24]. Bader has shown that the interaction of two bonded atoms can be characterized from the electron density at the bond CP. The electron density at the bond CP (ρ_{bcp}) of the X—N bonds (X = C or N) of azatriprismane conformers was thus calculated from the HF wavefunction (cf. Table 6). On successive substitution of nitrogens in C_6H_6 triprismane, the calculated mean ρ_{bcp} of the X—N bonds increases on compassing from aza- to pentaazatriprismane, implying increased bond strengths in a triprismane skeleton. Thus, the use of azatriprismanes as high-energy molecules stems from large X—N bond strengths in azatriprismanes.

Table 6 Bond CP (ρ_{bcp}) of the X—N bonds (X = C or N) in azatriprismanes

	ρ_{bcp}
Azatriprismanes	0.269
1,4-Diazatriprismanes	0.278
1,2-Diazatriprismanes	0.280
1,6-Diazatriprismanes	0.278
1,4,5-Triazatriprismanes	0.283
1,2,5-Triazatriprismanes	0.286
1,2,3-Triazatriprismanes	0.294
1,3,4,5-Tetraazatriprismanes	0.290
1,2,5,6-Tetraazatriprismanes	0.297
1,2,3,4-Tetraazatriprismanes	0.298
1,2,3,4,5-Pentaazatriprismanes	0.309
Hexaazatriprismane	0.326

Table 7 ΔH_{f} values (in kJ mol^{-1}) of azatriprismanes

	HF	B3LYP
Triprisamanes	639.7	603.8
Azatriprismanes	692.0	652.0
1,4-Diazatriprismanes	738.5	697.9
1,2-Diazatriprismanes	803.3	760.0
1,6-Diazatriprismanes	803.3	760.0
1,4,5-Triazatriprismanes	842.2	800.0
1,2,5-Triazatriprismanes	911.3	923.0
1,2,3-Triazatriprismanes	980.3	933.9
1,3,4,5-Tetraazatriprismanes	1006.7	957.7
1,2,5,6-Tetraazatriprismanes	1082.0	1025.1
1,2,3,4-Tetraazatriprismanes	1082.4	1030.9
1,2,3,4,5-Pentaazatriprismanes	1242.6	1245.2
Hexaazatriprismane	1470.3	1442.6

The ΔH_{f} values of $C_6N_\alpha H_{6-\alpha}$ isomers, calculated by using the isodesmic reaction approach described in Sect. 2, from the HF/6-31G(d,p) theory, are reported in Table 7. For the azatriprismane series, the ΔH_{f} increases from the azatriprismane to hexaazatriprismane. On encompassing from di- to pentaazatriprismanes, the lowest energy isomer has lower ΔH_{f} as a function of mean ρ_{bcp} of X—N bonds (X = C or N) in azatriprismane as shown in Fig. 2. As shown, the plot turns out be a straight line with a correlation coefficient of 0.992. A liner correlation has also been derived from the B3LYP calculations.

3.2 Nitroazatriprismanes

Successive replacement of C—NO_2 of hexanitrotriprismane by nitrogens yields nitroazatriprismane $(CNO_2)_{6-\alpha}$ N_α (with $\alpha = 1 \ldots 6$) series. Zpe corrected B3LYP electronic and relative stabilization energies of nitroazatriprismane isomers are given in Table 8. In the lowest energy isomers of di-, tri- and tetranitroazatriprismane isomers, more nitrogens occupy diagonally opposite sites of a rectangular face of triprismane framework. Thus, 1,4,5-nitroazatriprismane isomer with nitrogens occupying diagonally opposite corners of a rectangular face of triprismane turns out to be lower in energy relative to the one where nitrogen atoms occupy adjacent corners.

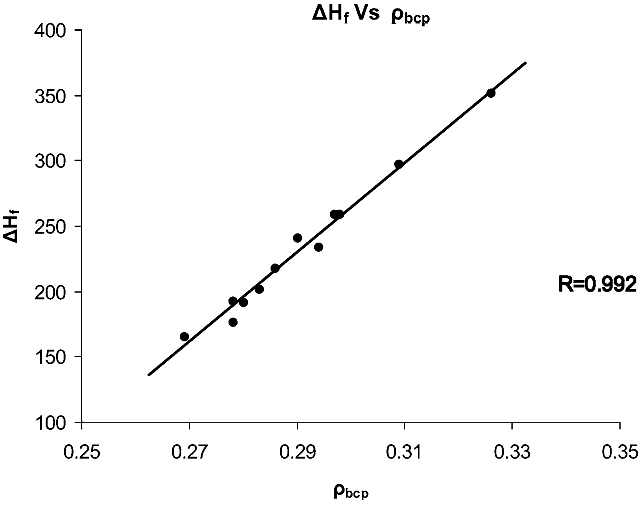


Fig. 2 The heat of formation (in kJ mol^{-1}) versus the ρ_{bcp} of X—N bonds in azatriprismanes

Table 8 B3LYP electronic and relative stabilization energies (ΔE) of nitroazatriprisamanes (in a.u. and kJ mol^{-1}, respectively)

	Electronic energy	ΔE
Hexanitrotriprisamanes	−1458.835257	–
1-Nitroazatriprismanes	−1270.399697	–
1,4-Dinitroazatriprismanes	−1081.943430	0.0
1,6-Dianitrozatriprismanes	−1081.943859	−1.3
1,2-Dianitrozatriprismanes	−1081.943036	1.0
1,4,5-Trinitroazatriprismanes	−893.510226	0.0
1,2,5-Trinitroazatriprismanes	−893.490752	51.1
1,2,3-Trinitroazatriprismanes	−893.464782	119.3
1,3,4,5-Tetranitroazatriprismanes	−705.042513	0.0
1,2,5,6-Tetranitroazatriprismanes	−705.020498	57.8
1,2,3,4-Tetranitroazatriprismanes	−705.016781	67.6
1,2,3,4,5-Pentanitroazatriprismanes	−516.553017	–
Hexaazatriprismane	−328.069198	–

Table 9 B3LYP frequencies (in cm^{-1}) of the lowest vibration of nitroazatriprismanes

	B3LYP
Hexanitrotriprisamanes	32
Nitroazatriprismanes	32
1,4-Dinitroazatriprismanes	31
1,6-Dianitrozatriprismanes	40
1,2-Dianitrozatriprismanes	35
1,4,5-Trinitroazatriprismanes	11
1,2,5-Trinitroazatriprismanes	36
1,2,3-Trinitroazatriprismanes	41
1,3,4,5-Tetranitroazatriprismanes	47
1,2,5,6-Tetranitroazatriprismanes	26
1,2,3,4-Tetranitroazatriprismanes	30
1,2,3,4,5-Pentanitroazatriprismanes	61
Hexaazatriprismane	595

B3LYP frequencies of the lowest vibration of nitroazatriprismanes displayed in Table 9 range from 11 cm^{-1} (for 1,2,5-trinitroazatriprismane) to 61 cm^{-1} (for 1,2,3,4,5-pentanitroazatriprimane), which predict less rigid structures for these molecules relative to azatriprismanes.

Table 10 MESP at the (3, +3) CP (kJ mol^{-1}) near nitro oxygen

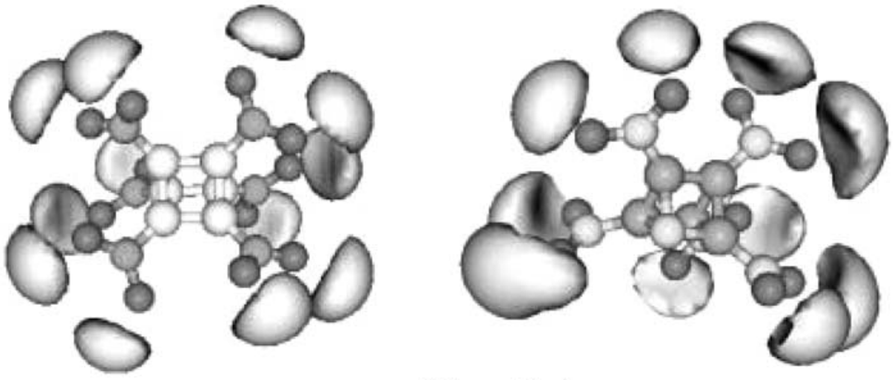
	MESP
Hexanitrotriprismanes	−67.3
Nitroazatriprismanes	−66.7
1,4-Dinitroazatriprismanes	−63.7
1,6-Dianitrozatriprismanes	−72.4
1,2-Dianitrozatriprismanes	−64.4
1,4,5-Trinitroazatriprismanes	−67.2
1,2,5-Trinitroazatriprismanes	−69.5
1,2,3-Trinitroazatriprismanes	−62.0
1,3,4,5-Tetranitroazatriprismanes	−71.7
1,2,5,6-Tetranitroazatriprismanes	−79.3
1,2,3,4-Tetranitroazatriprismanes	−74.2
1,2,3,4,5-Pentanitroazatriprismanes	−75.8

Table 11 Dipole moments (in D) of nitroazatriprismanes

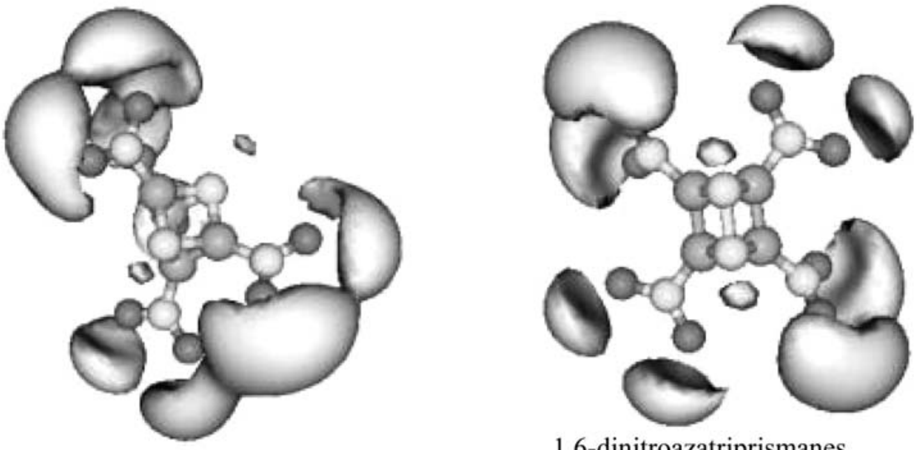
	HF
Hexanitrotriprisamanes	0.0
Nitroazatriprismanes	0.62
1,4-Dinitroazatriprismanes	0.12
1,6-Dianitrozatriprismanes	0.64
1,2-Dianitrozatriprismanes	1.03
1,4,5-Trinitroazatriprismanes	0.35
1,2,5-Trinitroazatriprismanes	0.65
1,2,3-Trinitroazatriprismanes	1.35
1,3,4,5-Tetranitroazatriprismanes	0.45
1,2,5,6-Tetranitroazatriprismanes	0.58
1,2,3,4-Tetranitroazatriprismanes	1.01
1,2,3,4,5-Pentanitroazatriprismanes	0.75
Hexaazatriprismane	0.0

The MESP isosurface ($V = -26.3\,\mathrm{kJ\,mol^{-1}}$) derived from the HF wave function of $(\mathrm{CNO_2})_{6-\alpha}\mathrm{N}_\alpha$ ($\alpha = 1\ldots6$) isomers are depicted in Fig. 3. As may be inferred, the successive substitution by nitrogen atoms instead of C—NO$_2$ engenders more electron-rich regions around oxygen of nitro group. This has also been evident from the MESP minimum near oxygen for hexanitroazatriprismane to pentanitroazatriprismane reported in Table 10, which ranges from −67.3 to −75.8 kJ mol^{-1}. It may as well be remarked here that amongst nitroazatriprismanes isomers (with $\alpha = 2$–4) the electron-rich regions of nitro groups are more delocalized for the lowest energy isomer.

The HF dipole moments of the different nitroazatriprismane isomers are shown in Table 11. Thus, it may be seen that the dipole moments of nitroazatriprismanes are dependent on nitrogen sites in triprismane, as a result of addition of C—N bond moments. Consequently, the isomer with nitrogen atoms occupying diagonally opposite corners of the rectangular face of triprismane has the least dipole moment. In 1,4,5-trinitroazatriprismane, N-O and C—N bond moments in triprismane engender dipole moment of 0.35 D. As may be noted, the largely destabilized di-, tri- and tetra nitroazatriprismane isomers exhibit high dipole moment (predominantly resulting from only one of the components). Since the MESP is governed by NO$_2$ groups, a direct correlation between electrostatic potential and the dipole moment was found to be difficult. Thus, the expectation that more localized electron-rich regions in the MESP should lead to a larger



Hexanitrotriprisamanes Nitroazatriprismanes



1,4-dinitroazatriprismanes 1,6-dinitroazatriprismanes

Fig. 3 MESP isosurface ($V = -26.3\,\mathrm{kJ\,mol^{-1}}$) in nitroazatriprismanes

Table 12 Bond CP (ρ_{bcp}) of the X—N bonds (X = C or N) in nitroazatriprismanes

	ρ_{bcp}
Nitroazatriprismanes	0.285
1,4-Dinitroazatriprismanes	0.285
1,6-Dianitrozatriprismanes	0.291
1,2-Dianitrozatriprismanes	0.292
1,4,5-Trinitroazatriprismanes	0.294
1,2,5-Trinitroazatriprismanes	0.295
1,2,3-Trinitroazatriprismanes	0.301
1,3,4,5-Tetranitroazatriprismanes	0.300
1,2,5,6-Tetranitroazatriprismanes	0.304
1,3,4,51-Tetranitroazatriprismanes	0.305
1,2,3,4,5-Pentanitroazatriprismanes	0.312
Hexaazatriprismane	0.326

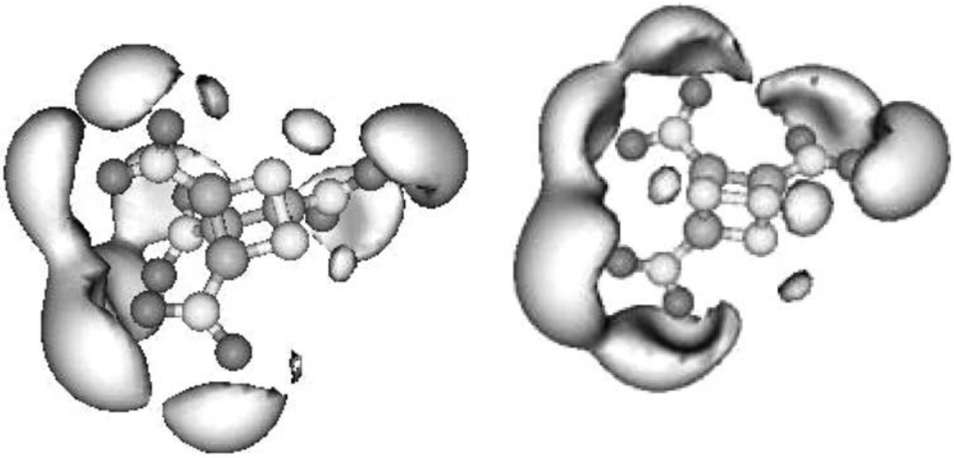
Table 13 ΔH_{f} values (in $\mathrm{kJ\,mol^{-1}}$) of nitroazatriprismanes

	HF	B3LYP
Hexanitrotriprisamanes	858.6	670.3
Nitroazatriprismanes	875.7	706.3
1,4-Dinitroazatriprismanes	892.7	743.5
1,6-Dianitrozatriprismanes	964.4	808.3
1,2-Dianitrozatriprismanes	965.3	810.4
1,4,5-Trinitroazatriprismanes	970.0	839.3
1,2,5-Trinitroazatriprismanes	1040.6	903.7
1,2,3-Trinitroazatriprismanes	1124.7	985.3
1,3,4,5-Tetranitroazatriprismanes	1099.1	986.6
1,2,5,6-Tetranitroazatriprismanes	1178.2	1063.6
1,2,3,4-Tetranitroazatriprismanes	1182.8	1067.3
1,2,3,4,5-Pentanitroazatriprismanes	1296.2	1203.7
Hexaazatriprismane	1470.3	1442.2

dipole moment in nitroazatriprismane isomers has not been borne out by the present calculations.

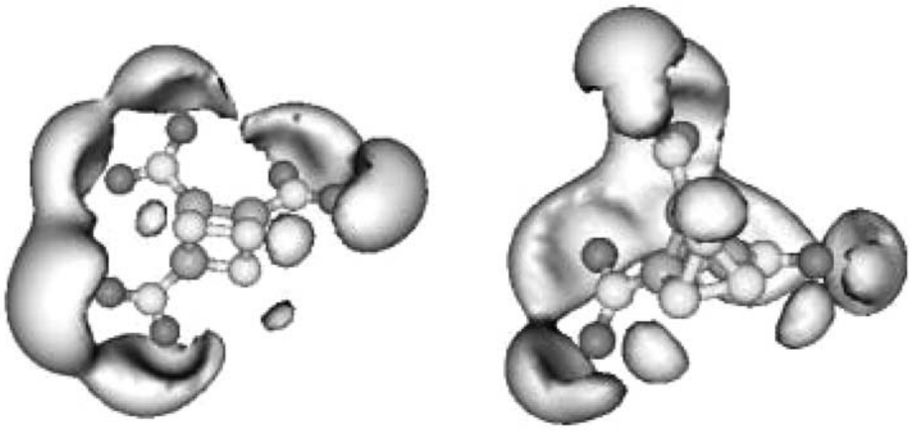
In the following paragraphs, we represent the MED topographical analysis in nitroazatriprismane series. The bond-critical points, discussed earlier in the section on computational method, were obtained using the HF/6-31G (d,p) wave function. The electron densities at the bond CP of X—N bonds (X = C or N) in the triprismane framework are reported in Table 12. Thus, successive substitution of nitrogen atoms instead of C—NO_2 of hexanitrotriprismane leads to increase in the ρ_{bcp} value (average of X—N bonds). For di- to tetranitroazatriprismanes, a smaller ρ_{bcp} value was found when more nitrogens occupy diagonally opposite corners of the rectangular face of triprismane framework.

The ΔH_{f} values of the $(CNO_2)_{6-\alpha}N_\alpha$ ($\alpha = 1\ldots6$) isomers are presented in Table 13. These are useful in modeling



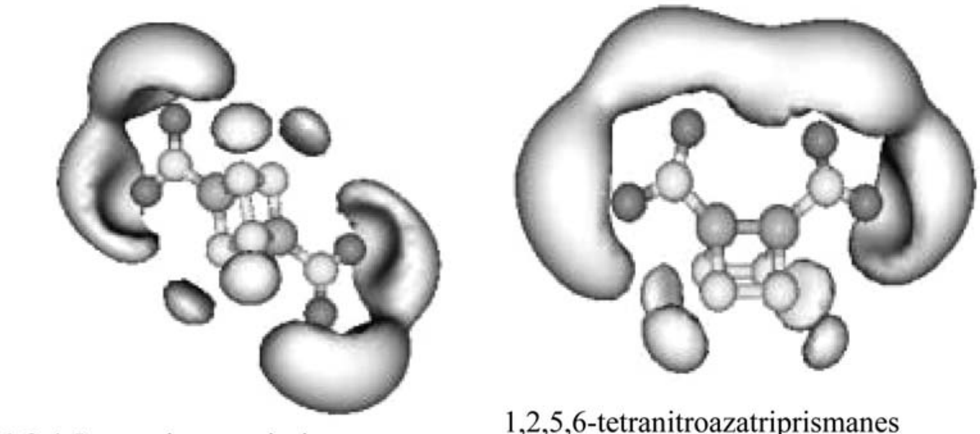
1,2-dinitroazatriprismanes

1,4,5-trinitroazatriprismanes



1,2,5-trinitroazatriprismanes

1,2,3-trinitroazatriprismanes

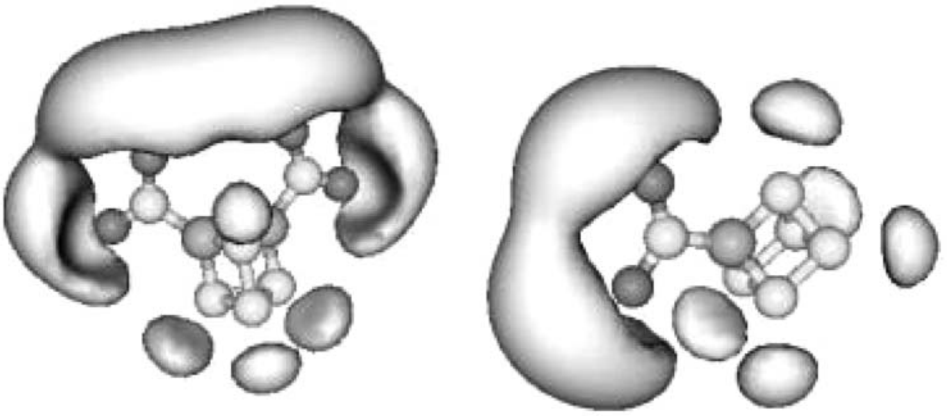


1,3,4,5-tetranitroazatriprismanes

1,2,5,6-tetranitroazatriprismanes

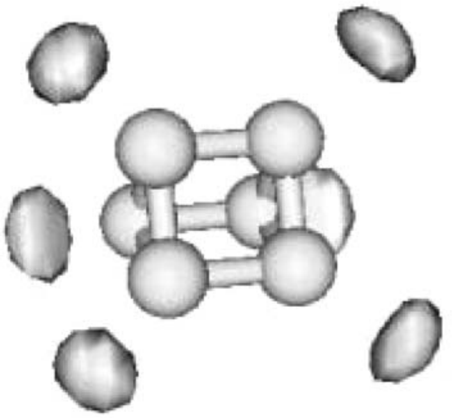
Fig. 3 (Contd.)

the ballistic parameters of high-energy molecules. As may readily be noticed, the ΔH_f increases with increasing number of nitrogens in a triprismane framework. In the case of di-, tri- and tetranitroazatriprismanes, it is dependent on the interactions of nitro groups and nitrogen sites in the triprismane skeleton. In different isomers, the ΔH_f turns out to be the largest when both the nitro group and nitrogen atoms in triprismane occupy vicinal positions, i.e., for the isomer,



1,2,3,4-tetranitroazatriprismanes

1,2,3,4,5-pentanitroazatriprismanes



Hexaazatriprisamanes

Fig. 3 (Contd.)

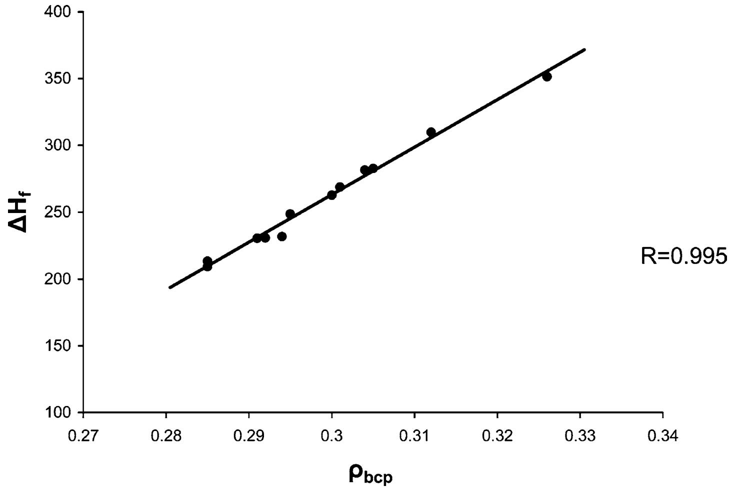


Fig. 4 The heat of formation (in kJ mol^{-1}) versus the ρ_{bcp} of X—N bonds in nitroazatriprismanes

which have the largest dipole moment and are largely destabilized. A plot of ΔH_{f} as a function of average ρ_{bcp} (of the X—N bonds) turns out to be linear (cf. Fig. 3) with a correlation coefficient of 0.995.

In summary, the molecular attributes such as large bond strengths in triprismanes (which leads to high-content) and the less electron-rich centers either in triprismane framework (as in azatriprismanes) or near the NO_2 groups (in nitroazatriprismanes) facilitate their use as potential energy-rich explosives. This is demonstrated by the use of molecular electrostatic potential and the molecular electron density topography.

4 Conclusions

The conclusions of this work are summarized in the following (i) For azatriprismanes and nitroazatriprismanes as well the lowest energy isomers have more number of nitrogen atoms spatially arranged in opposite corners of rectangular faces of triprismanes skeleton. (iii) B3LYP frequencies of the lowest vibration predict a relatively rigid structure for aza derivatives in contrast to nitroazatriprismanes. (iv) A linear correlation (correlation coefficient > 0.992) of ΔH_f as a function of ρ_bcp of the X—N (X = C or N) has been obtained for both the nitroazatriprismanes and the azatriprismane series.

References

1. Katz TJ, Acton N (1973) J Am Chem Soc 95:2738
2. Schultz HP (1965) J Org Chem 30:1361
3. Dai YA, Dunn K, Boggs JE (1984) J Mol Struct 109:127
4. Politzer P, Jayasuriya K, Zilles BA (1985) J Am Chem Soc 107:121
5. Politzer P, Seminario JM, Concha MC, Murray JS (1993) Theor Chim Acta 85:128
6. Engelke R (1989) J Phys Chem 93:5722
7. Engelke R (1992) J Phys Chem 96:10789
8. Murray JS, Seminario JM, Lan P, Politzer P (1990) J Mol Struct 207:193
9. Murray JS, Redfern PC (1993) Struct Chem 4:73
10. Murray JS, concha M, Seminario JM, Politzer P (1991) Phys Chem 95:1601
11. Gimarc BM, Zhao M (1996) Inorg Chem 35:3289
12. Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Robb MA, Cheeseman JR, Keith T, Peterson GA, Montgomery JA, Raghavachari K, Al–laham MA, Zakrzewski VG, Oritz JV, Forseman JB, Cioslowski J, Stefanov BB, Nanayakkara A, Challacombe M, Peng CY, Ayala PY, Chen W, Wong MW, Andres JL, Replolge ES, Gomperts R, Martin RL, Fox DJ, Binkley JS, Defrees DJ, Baker J, Stewart JJP, Head–Gordon M, Gonzalez C, Pople JA (1995) Gaussian 94. Gaussian Inc., Pittsburgh, PA
13. Pulay P (1969) Mol Phys 17:197
14. Becke D (1993) J Chem Phys 98:5684
15. Lee C, Yang W, Parr RG (1988) Phys Rev B37:785
16. Scrocco E, Tomasi J (1978) Adv Quantum Chem
17. Tomasi J, Bonaccorsi R, Cammi R (1991) In: Maksic ZB (ed) Theoretical models of chemical bonding, vol 4. Springer, Berlin Heidelberg New York, p 228
18. Naray-Szabo G, Ferenczy GC (1995) Chem Rev 4:829
19. Limaye AC, Gadre Sr (2001) Curr Sci (India) 80:1298
20. Gadre SR, Shirsat RN (2000) Electrostatics of atoms and molecules. Universities Press, Hyderabad
21. Gadre Sr, Shrivastava IH (1991) J Chem Phys 94:4384
22. Gadre SR, Kulkarni SA, Shrivastava IH J Chem Phys (1992) 96:5253
23. Cremer D, Kraka E (1985) J Am Chem Soc 107:3800
24. Grimme S (1996) J Am Chem Soc 118:1529