

Short communication

Quantum chemical, ballistic and explosivity calculations on 2,4,6,8-tetranitro-1,3,5,7-tetraaza cyclooctatetraene: A new high energy molecule

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Abstract

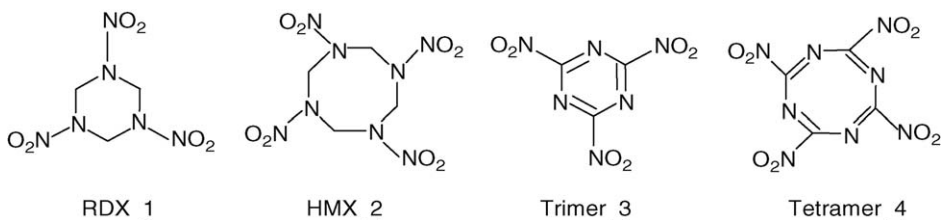
Ab initio molecular orbital calculations have been carried out on 2,4,6,8-tetranitro-1,3,5,7-tetraazacyclooctatetraene, the tetramer of the series $(\text{NO}_2\text{CN})_n$ where $n = 1-4$, using the Hartree–Fock theory with the 6-31 G(d) basis set. These calculations yield three conformers for the tetramer with D_{4h} , C_{4h} and C_2 symmetries. The nonplanar conformer with the C_2 symmetry turns out to be 99.0 and 164.4 kJ mol^{-1} , respectively, lower in energy than the C_{4h} and D_{4h} conformers. The electron density topography – the density at the bond critical point – has been used as a measure of the C–NO₂ strengths. Based on these bond strengths, heats of formation [obtained from the parametric model 3 (PM3) method] and specific decomposition energies, it may be concluded that $(\text{NO}_2\text{CN})_4$ is a promising candidate in the class of high energy molecules. Theoretically computed explosive (velocity of detonation, detonation pressure, etc.) and ballistic (characteristic velocity, specific impulse, etc.) parameters support these conclusions.

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1. Introduction

A conjugated C–NO₂ analog of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), viz. 2,4,6,8-tetranitro-1,3,5,7-tetraazacycloocta tetraene possesses several features that make it interesting. The molecular set (1–4) of interest in the present study is:



The title compound, **4** the tetramer in the series $(\text{NO}_2\text{CN})_n$, $n = 1-4$, is analogous to HMX. Members of the $(\text{NO}_2\text{CN})_n$ series are potential high energy molecules and being C–NO₂ compounds may have an edge over the corresponding nitramines in insensitivity towards external stimuli. The trimer **3** and tetramer **4**, C–NO₂ analogs of cyclotrimethylene trinitramine (RDX) and HMX have in them an aromatic ring and conjugated double

bonds, respectively. This is expected to enhance the density and thermal stability of these systems as compared to the corresponding nitramines, RDX and HMX.

In the present study quantum chemical ab initio molecular orbital calculations have been carried out on the series

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(NO₂CN)_n, n = 1–4. Based on the heat of formation and mass density, the trimer (NO₂CN)₃, analogue of RDX has been predicted [1,2] to be a high energy molecule. It should be noted that the tetramer of (NO₂CN)_n, the HMX analogue, however, has not been studied in this respect. With this view we have carried out systematic ab initio molecular orbital calculations on the series (NO₂CN)_n, n = 1–4.

Velocity of detonation (VOD), Chapman–Jouget (CJ) pressure and the specific impulse are some of the parameters governing the explosive nature of a compound. These data predicted for the trimer and tetramer are compared with RDX and HMX data in the present work.

2. Computational methods

Ab initio Hartree–Fock (HF) self consistent field molecular orbital calculations have been performed by using the GAUSSIAN 94 [3] program with the internally stored 6-31 G(d) basis set. The equilibrium geometries in the HF calculations were obtained by the analytical gradient relaxation method.

For the tetramer, different conformers, viz. (A) planar (B) the nitro groups perpendicular to the planar ring and (C) a nonplanar cyclic structure, have been considered. Detailed topographical analysis of the electron density (ED) distribution has been performed for the series. This includes location of the critical points (CP), the sites where the gradient of the ED vanishes. The critical points of molecular electron density distribution can be characterized from its rank and signature (excess of positive eigen values over negative ones). Thus, maxima are denoted as (3, –3), minima are denoted as (3, +3) and two types of saddles are denoted as (3, –1) and (3, +1). The ED is maximum at the nuclear sites and a (3, –1) saddle is found between every bonded pair of atoms. The presence of a ring or cage in the system can be identified from occurrence of (3, +1) saddle and minimum, respectively, in the ED distribution. These CPs further may be characterized as minima, saddles and the maxima [4]. Each bond in a bound molecular system thus exhibits a CP between the nuclei, referred to as the bond CP. It follows that the ED at the bond CP and its Laplacian may be taken as the measure of the bond strength, one of the crucial parameters responsible for the explosive behaviour [5]. The other important parameters determine the energetic behaviour of an explosive molecule is oxygen balance and the heats of formation. The heats of formation for the conformers of (NO₂CN)₄ have been obtained from the semi-empirical PM3 method [6]. The ΔH_f values from the PM3 method typically show a deviation of 5–8 kcal mol^{–1} from the experimental ones and is found to be most suitable amongst the semi-empirical methods.

Prediction of the explosive and ballistic parameters was carried out from the molecular formula, density and ΔH_f data. Crystal densities of the trimer and the tetramer of (NO₂CN)₄ were calculated using the group-additivity approach [7]. The explosive parameters such as VOD and CJ pressure were computed from the Becker–Kistiakowsky–Wilson (BKW) equation of state [8]. Ballistic parameters, e.g. specific impulse (I_{sp}), mean molecular weight of exhaust gases and characteristic

velocity (C^*) were computed using NASA-CEC-71 program [9].

3. Results and discussion

The HF calculations reveal that the dimer (NO₂CN)₂ is unstable. This, in fact, may be attributed to the enhanced nuclear repulsion in the four membered ring system. As depicted in Fig. 1, the conformer (A) belongs to D_{4h} point symmetry group whereas conformers (B) and (C) have C_{4h} and C_2 symmetries, respectively. Selected geometrical parameters of these conformers are given in Table 1. The C=N in conformer A has more double bond character than in (B) or (C) and the C–NO₂ bond is more stretched in conformer (A), due to the planarity of the system, than in the conformers (B) or (C). The C–N–C and N–C–N bond angles generally show a variation of 10° in different conformers of the tetramer.

At the HF/6-31 G(d) level of theory, the conformers (A), (B) and (C) are stabilized by –42.7, –58.3 and –82.1 kcal mol^{–1}, respectively, with reference to the monomer whereas the trimer is by 88.4 kcal mol^{–1}. The ΔE_{dec} of the tetramer is nearly 300 kcal mol^{–1} higher than that for the trimer and nearly 450 kcal mol^{–1} higher than that for the monomer (see Table 1). The specific decomposition energy (ΔE_{sd}) of the tetramer is typically 1.8 times higher than that for the trimer. Calculation of the heat of formation from the HF theory is rather difficult. As pointed out earlier, we have employed semi-empirical PM3 calculations for obtaining the ΔH_f for all the conformers of (NO₂CN)₄. The ΔH_f for the conformer A thus turns out to be 114.9 kcal mol^{–1}. The energy of isodesmic reaction (1) predicted from the present HF calculations as well as from the PM3 method turn out to be –50.9 kcal mol^{–1}. Interestingly, the ΔH_f value (46.0 kcal mol^{–1}), for the trimer obtained from the highly sophisticated theories compares well with 43.4 kcal mol^{–1}, the

Table 1
Energies^a and selected geometry parameters of the NO₂CN tetramer (the bond lengths and angles in angstroms and degrees, respectively)

	Conformer A	Conformer B	Conformer C
$r(\text{C–N})$	1.372	1.358	1.378
$r(\text{C=N})$	1.235	1.254	1.243
$r(\text{C–NO}_2)$	1.524	1.476	1.479
$a(\text{N–C–N})$	137.5	139.8	130.6
$a(\text{C–N–C})$	132.5	130.2	120.3
$a(\text{N–C–NO}_2)$	116.0	107.9	112.6
$d(\text{N–C–N–O})$	0.0	90.3	–123.6
$d(\text{N–C–N–C})$	0.0	0.0	59.9
ΔE_m^b	–42.70	–58.37	–82.07
ΔE_{dec}^c	–646.03	–661.64	–685.37
ΔE_{sd}^d	–2243	–2297	–2380
ΔH_f	114.96	93.12	109.46

^a All energies are in kcal mol^{–1} except for ΔE_{sd} which is in cal g^{–1}.

^b Stabilization energy of tetramer with reference to monomer, $\Delta E_m = [E_{\text{tetramer}} - 4(E_{\text{monomer}})]$.

^c The decomposition energy, ΔE_{dec} is calculated from the energy of a reaction (NO₂CN)₄ → 4N₂ + 4CO₂.

^d The specific decomposition energy, $\Delta E_{sd} = \Delta E_{dec}/\text{molecular mass}$.

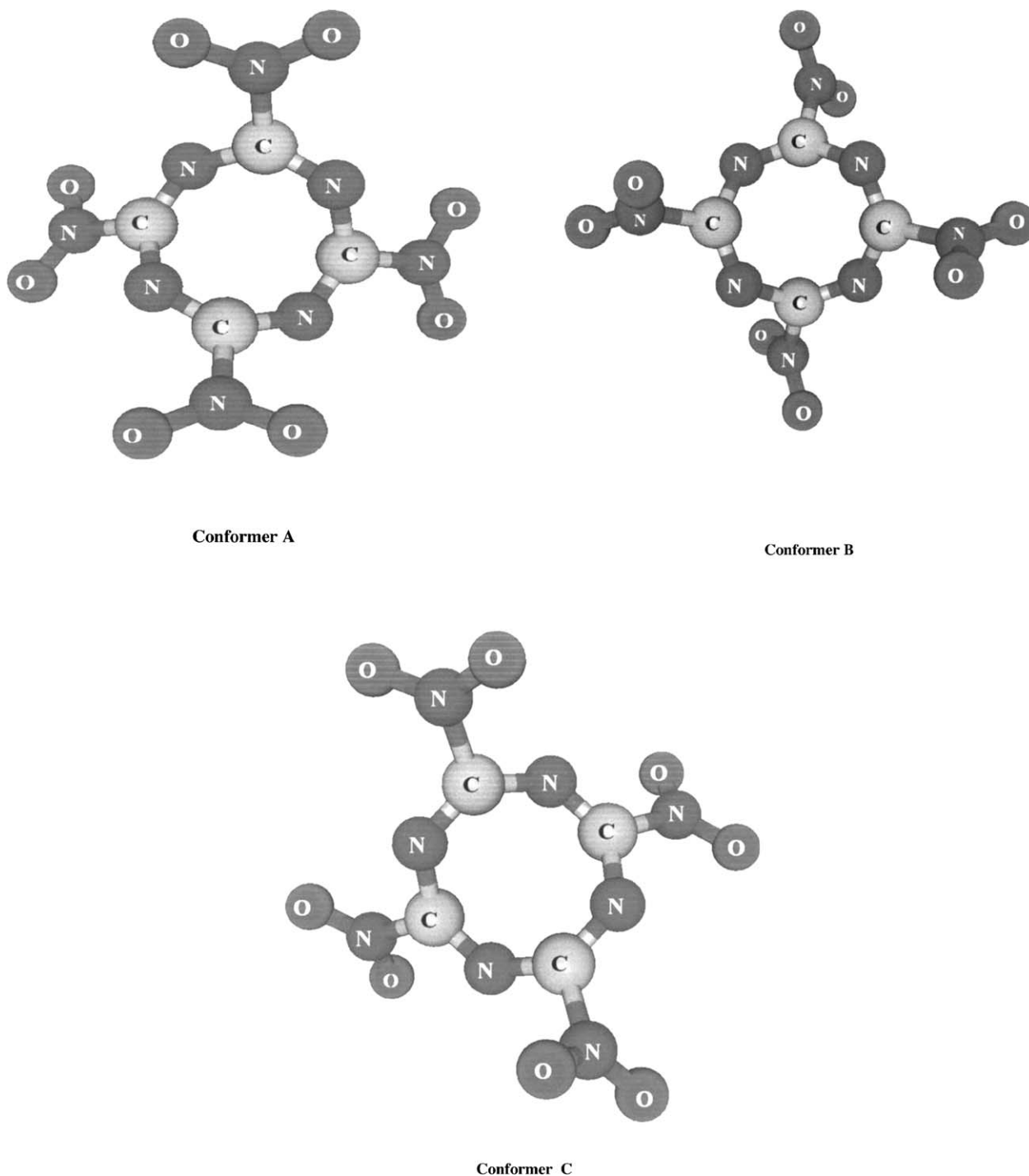


Fig. 1. Conformers (A, B and C) of tetramer.

one derived from the PM3 method [10] for the trimer $(\text{NO}_2\text{CN})_3$. Heat of formation values from the present calculations turn out to be $93.1 \text{ kcal mol}^{-1}$ for conformer B and $109.5 \text{ kcal mol}^{-1}$ for conformer (C).

Scalar fields such as electron density or its Laplacian offer a reliable tool to obtain the strength of different bonds in high energy molecules. We present the ED and its Laplacian at the bond critical points (BCP) in Table 2. The cleavage of C–NO₂ bonds in such systems is crucial in the manifestation of explosive

properties. The ED values at the BCP from Table 2 indicate that the C–NO₂ bonds in conformer A are weaker than those in (B) or (C) or even the trimer. Further, these ED values for the C–NO₂ bond in the minimum energy conformer (C) are lower by 0.03 a.u. than those in the monomer and 0.01 a.u. than in the trimer.

The explosive properties, VOD and CJ pressure and the ballistic parameters, I_{sp} , the density specific impulse, I_{spd} , C^* and the mean molecular weight of exhaust gases, derived for the NO₂CN

Table 2
Topographical parameters at BCP of electron density distribution of tetramer conformers (all values in a.u.)

System	CP Location of the bond	$\rho(r)$	$V^2 \rho(r)$
NO ₂ CN	C–NO ₂	0.317	–1.260
	C–N	0.485	–1.093
(NO ₂ CN) ₃	C–NO ₂	0.300	–1.204
	C=N	0.381	–1.061
(NO ₂ CN) ₄ [A]	C–NO ₂	0.266	–0.838
	C=N	0.413	–0.470
	C–N	0.329	–1.205
(NO ₂ CN) ₄ [B]	C–NO ₂	0.298	–1.155
	C=N	0.406	–0.804
	C–N	0.343	–1.357
(NO ₂ CN) ₄ [C]	C–NO ₂	0.290	–1.084
	C=N	0.412	–0.578
	C–N	0.388	–1.351

trimer and tetramer, are compared with those of RDX and HMX in Table 3. It may be noted that the trimer exhibits higher VOD and CJ pressure than the tetramer. This is a direct consequence of higher mass density, which may, in turn, be attributed to the planarity of the molecule. In order to test the sensitivity of the explosive parameters to the mass density the VOD values of the trimer were calculated in the density range of 1.9–2.1 kg m^{–3}. These calculations reveal that an increase of 0.1 units in the mass density enhances the VOD by ~450 m s^{–1}. Contrary to the expectation, the VOD of the trimer compares well with HMX and that of the tetramer with RDX. It is pertinent to state that the thermodynamic calculations for explosion processes including detonation have yielded significantly lower VOD values as

Table 3
Comparison of explosive and ballistic parameters of tetramer with the trimer, RDX and HMX

	Tetramer (C) (C ₄ N ₈ O ₈)	Trimer (C ₃ N ₆ O ₆)	RDX (C ₃ H ₆ N ₆ O ₆)	HMX (C ₄ H ₈ N ₈ O ₈)
Density (kg m ^{–3})	1.96	2.27	1.82	1.91
ΔH_f (kJ kg ^{–1})	1668	886	318	251
VOD (m s ^{–1})	8725	9993	8755	9158
CJ pressure (kbar)	375	518	347	395
I_{sp} at 6.86 MPa (s)	264	255	265	265
I_{spd} (s)	517	579	482	506
Characteristic velocity (C*) (m)	1524	1582	1651	1678
Mean molecular weight of exhaust gases	35	35	25	25
Oxygen balance (%)	0	0	–21.6	–21.6
Flame temperature (K)	3605	3790	3298	3376

compared to experimentally determined values in zero hydrogen organic explosives [11]. The actual explosive properties of the trimer and tetramer – zero-hydrogen high energy molecules – may be significantly higher than the theoretically computed values for these molecules (vide Table 3) due to the fact that the products of detonation of hydrogen free explosives are different from those of C, H, N and O explosives. The I_{sp} at 6.86 MPa of the tetramer is less than that of the trimer, both of which are less than those of RDX or HMX. However, the I_{spd} of the tetramer is close to RDX and that of the trimer is significantly higher than that of HMX, despite higher mean molecular of weight exhaust gases for both trimer and tetramer (35), compared to RDX or HMX (25). The trimer and tetramer in combination with hydrogen rich binders can give rise to lower mean molecular weight exhaust gases than in pure form and thus it is possible to achieve higher I_{spd} for such formulations. Both trimer and tetramer also posse's better oxygen balance than RDX or HMX and hence could be considered potential oxidizers.

4. Conclusion

HF/6-31 G(d) calculations yield three conformers for the (NO₂CN)₄. The C–NO₂ bond strengths in these conformers have been compared in terms of electron density topographical parameters. The explosive parameters are strongly dependent on the mass density and relatively not so sensitive to the heat of formation. Different conformers of the NO₂CN tetramer yield nearly identical velocity of detonation and specific impulse. The trimer and tetramer possess higher density specific impulse and flame temperature. They also have better oxygen balance. Therefore, these oxidizers in combination with hydrogen rich fuels can realize better performance.

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