The Structure and Chemical Bond of FOX-7: The AIM Analysis and Vibrational Normal Modes

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ABSTRACT: *FOX-7 (1,1-diamino-2,2-dinitroethylene) recently is expected as a relatively new energetic material with high-performance and low sensitivity. The RHF and MP2 levels and DFT method with B3LYP functional with aug-cc-pVDZ basis set have been used for obtaining equilibrium geometry and Rho function (electron density distribution). By the aid of fundamental physical theorems implemented in the Quantum Theory of Atoms In Molecules (QTAIM), the structure, the physical nature of chemical bonds and all Bond Critical Points (BCPs) properties have been determined for FOX-7 at the mentioned theoretical levels. Existence of resonance due to "electron-withdrawing" nitro groups and "electron-donating" amine groups in ethene backbone and intra-molecular hydrogen bonding are shown with AIM analysis and then the resonance structures of FOX-7 are found. Also the calculated IR spectrum of FOX-7 is compared with the experimental IR spectrum. It is demonstrated that the mathematical properties of molecular graph derived from charge density analysis are in good correlation with that of the vibrational normal modes derived from ab initio computations.*

KEY WORDS: *FOX-7, QTAIM, Molecular graph, Chemical bond, Vibrational normal mode.*

INTRODUCTION

In 1998, the FOA Defence Research Establishment (Sweden) reported the successful synthesis of FOX-7 (1,1-diamino-2,2-dinitroethylene), an explosive which they claim exhibits both high performance and low sensitivity [1-3]. FOX-7 can be described as a push-pull ethene compound, consisting of two electron donating amino groups (“head”) and two electron withdrawing nitro groups (“tail”) [2,3]. The length of the ethylene bond (1.45 Å) is in between the length of a single (1.54 Å) and a double bond (1.34 Å) suggesting that the order of the ethylene bond is about 1.5 [4].

Compared with typical C-H-N-O explosives, FOX-7 is a small and relatively symmetric species. The structure of solid FOX-7 is also simple, consisting of a small crystal unit cell containing four molecules. These characteristics make FOX-7 an attractive system for theoretical studies,

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particularly as a prototype for modeling the complex physics and chemistry associated with initiation and growth of reaction to detonation in solid energetic materials. For this purpose, *ab initio* quantum chemical calculations provide the most accurate and detailed description of the reaction chemistry in the absence of empirical data. B3LYP/aug-cc-pVDZ predictions of the structures and energies of FOX-7 and its isomers is obtained by *Dorsett* [1], are nearly identical to those obtained by *Politzer et al*. using B3P86/6-31+G** [5].

Heats of formation in gas phase, Relative specific Impulses (RIs) vs. octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), heats of detonation, detonation velocities and pressures of FOX-7, were calculated by quantum chemistry, molecular mechanics and Monte Carlo methods by *Chaoyang et al*. [6] In this study heat of formation was calculated by G2 method [6].

Experimental electron densities was determined for the FOX-7 from single-crystal diffraction data and was compared with theoretical bond-topological properties [DFT, projected onto the multi pole model, basis B3LYP/6-31++G(d,p)] [7].

The close proximity of aminohydrogens to nitro oxygens has prompted speculation that the stability of FOX-7 is due to hydrogen bonding within the molecule. However, part of the increased stability can be attributed to other electronic effects. It is well known that the presence of amino groups tends to desensitize nitroaromatic molecules to shock or impact initiation. For example, TATB is much more stable than trinitrobenzene, which contains no amine groups [1].

A theoretical study by *Politzer et al*., [5] confirmed the presence of push-pull electron delocalisation in FOX-7. By comparing various amino/nitro derivatives of ethylene, *Politzer et al*. conclude that the stability FOX-7 is due more to resonance effects than to hydrogen bonding.

In the present study, by the aid of fundamental physical theorems implemented in the Quantum Theory of Atoms in Molecules (QTAIM), the structures and the physical nature of chemical bonds of FOX-7 have been determined.

COMPUTATIONAL METHODS

In the present study, we report new quantum chemical calculations for geometry optimization using RHF (Restricted Hartree Fock) and MP2 (Møller-Plesset second-order perturbation theory) levels and Density Functional Theory (DFT) method with the exchange-correlation potential that is constructed from *Becke*'s three parameter formula for exchange (B3) [8], along with the *Lee-Yang-Parr* parameterization for correlation (LYP) [9]. These calculations were performed within a valence double-zeta basis set augmented with both diffuse and polarization functions (aug-cc-pVDZ). This basis set was contracted as: (10s5p2d/4s3p2d) and used pure spherical harmonic (i.e. 5 d-type), one-particle Gaussian functions. Vibrational frequencies were calculated at the same level for characterization of stationary point (no imaginary frequencies was observed).

The coalescence of the ring and the bond critical point of the FOX-7 structures were obtained with 2.800, 2.810 and 2.820 Å O(t)-O(t) distances. So these structures are calculated with MP2/aug-cc-pVDZ level as a single point to obtain theoretical electron dencities.

All *ab initio* calculations have been performed using Spartan'06 [10], and PC GAMESS 7.1.5 [11], and QTAIM calculations and wave function analysis have been done using AIM2000 package [12].

RESULTS AND DISCUSSION

Since this paper is based on the QTAIM methodology, some relevant important points of this theory seems worth-mentioning although, a detailed discussion may be found elsewhere [13-18]. The molecular optimized geometry of FOX-7 is shown in Fig. 1a and their selected geometric parameters are given in Table 1. The Molecular Graph (MG) of studied molecule has been depicted in Fig. 1b.

The calculated inter-nuclear distances and angles of FOX-7 are listed in Table 1, along with corresponding experimental values for solid FOX-7. Aside from the N-H distances, the calculated gas-phase data are quite similar to the experimental structure. However, the isolated molecule has C_2 symmetry, whereas interaction between neighboring molecules in solid FOX-7 causes an accentuated twist of one nitro group [1,19].

Bonding Scheme and vibrational normal mode

The major classification of bonded interactions [17,20], in the framework of QTAIM has been proposed based on the sign of Laplacian of electron density ($\nabla^2\rho_b$) and total energy density (H_b) evaluated at the BCPs. H_b is sum of the kinetic energy density (G_b) and electronic potential energy density (V_b) at a BCP.

The AIM analysis for the optimized structures (Fig. 1a) has been performed to obtain the topological properties of

Table 1: Selected geometric parameters for FOX-7 (Å, degrees).

parameter	Expt. [18]	Calc.*	Parameter	Expt. [18]	Calc.*
C-C	1.456	1.409	N-H(t)	0.88, 0.87	1.013
C-NH_2	1.319, 1.325	1.358	N-H(s)	0.84	1.018
C-NO_2	1.399, 1.426	1.436	N-O(t)	1.252, 1.242	1.238
O(s)-H(s)	1.97, 2.03	1.849	N-O(s)	1.249, 1.242	1.255
∠H_2N-C-NH_2	118.4	116.2	∠O-N-O	120.9, 121.0	123.6
∠O_2N-C-NO_2	116.3	115.9	∠H(t)-N-C	121.0, 121.1	117.6
∠H_2N-C-C	120.7, 120.8	121.9	∠H(s)-N-C	119.8, 121.9	116.1
∠O_2N-C-C	120.7, 120.8	122.1	∠O(s)-N-C	118.6, 118.9	118.0
∠H-N-H	118.3, 118.1	119.8	∠O(t)-N-C	120.1, 120.4	118.3
∠H_2N-C-C-NO_2	172.9, 177.8	164.7			
∠H(t)-N-C-C	179.6, -178.3	-154.4	∠O(t)-N-C-C	171.0, 143.6	150.7
∠H(s)-N-C-C	0.5, 10.1	2.6	∠O(s)-N-C-C	-5.8, -34.3	-27.0

** The calculated parameters are in MP2/aug-cc-pVDZ level*
(t) terminal bond (bond nearly parallel to C=C axis), (s) side bond

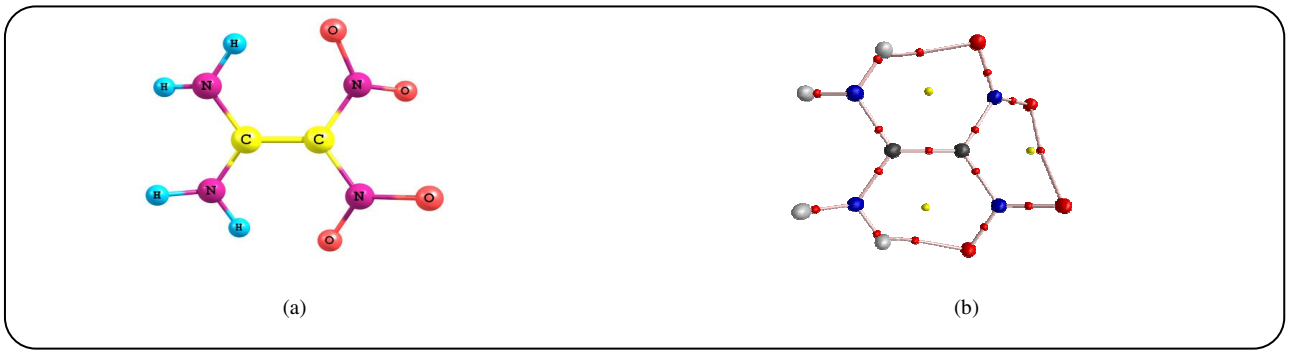


Fig. 1; (a) The optimized geometry of FOX-7 at level of MP2/aug-cc-pVDZ.
(b) The 3D molecular graph (MGs) of the equilibrium geometry of FOX-7. (Bold points are Bond Critical Points: BCPs; Pale points are Ring Critical Points: RCPs. The lines are Bond Paths: BPs.)

the bonds, such as the Laplacian of ρ_b ($\nabla^2\rho_b$), total energy density (H_b) at BCPs, Bond Critical Points (BCPs),ring critical points (RCPs) and also the bond paths (BPs). As is known, $\nabla^2\rho_b$ and/or H_b identifies whether the charge of the region is shared interactions ($\nabla^2\rho_b > 0$ and/or $H_b > 0$) or closed shell interactions ($\nabla^2\rho_b < 0$ and/or $H_b < 0$). The former characterizes shared interactions (covalent bonds), where the electron density concentrates in the inter nuclear region, whereas the latter is typically associated with interactions between closed-shell systems (ionic bonds, hydrogen bonds, and vander waals molecules).

The complete list of bond critical points of electron density (where $\nabla\rho = 0$) and their mathematical characters have been gathered in Table 2 for FOX-7 with RHF, B3LYP and MP2 levels and aug-cc-pVDZ basis set. The completeness of CP analysis has been checked by the satisfaction of Poincare-Hopf rule [17,20].

$$n - b + r - c = 1 \quad (1)$$

Table 2: Bond properties and mathematical characters of CPs of the Rho(r) function.

Connected atoms	RHF, B3LYP						
	BL	ρ_b	$\frac{1}{4}\nabla^2\rho_b$	ε	G_b	V_b	H_b
C-C	1.413	0.287	-0.165	0.353	0.088	-0.340	-0.252
C-NH_2	1.334	0.339	-0.294	0.151	0.199	-0.693	-0.494
C-NO_2	1.427	0.279	-0.181	0.444	0.165	-0.511	-0.347
O(s)-H(s)	1.881	0.040	0.036	0.008	0.035	-0.033	0.001
N-H(t)	0.993	0.338	-0.388	0.004	0.483	-0.485	-0.436
N-H(s)	0.996	0.326	-0.389	0.037	0.045	-0.479	-0.434
N-O(t)	1.183	0.504	-0.366	0.106	0.385	-1.035	-0.650
N-O(s)	1.212	0.465	-0.228	0.109	0.336	-0.900	-0.564
O(t)-O(t)	2.597	0.019	0.018	0.113	0.017	-0.017	0.0007
Connected atoms	MP2						
	BL	ρ_b	$\frac{1}{4}\nabla^2\rho_b$	ε	G_b	V_b	H_b
C-C	1.409	0.295	-0.171	0.396	0.104	-0.380	-0.275
C-NH_2	1.358	0.325	-0.278	0.143	0.202	-0.683	-0.481
C-NO_2	1.436	0.276	-0.182	0.387	0.169	-0.520	-0.351
O(s)-H(s)	1.849	0.036	0.031	0.014	0.031	-0.031	-0.0001
N-H(t)	1.013	0.329	-0.378	0.042	0.055	-0.488	-0.433
N-H(s)	1.018	0.323	-0.386	0.037	0.052	-0.489	-0.437
N-O(t)	1.238	0.477	-0.227	0.115	0.387	-1.001	-0.614
N-O(s)	1.255	0.457	-0.214	0.125	0.359	-0.932	-0.573
O(t)-O(t)	2.645	0.019	0.018	0.446	0.018	-0.018	-0.00007

All enteries in a.u. exept Bond Lengths (BL) listed in Å.

Where n is the number of nuclei and b, r and c are the number of bond, ring and cage critical points, respectively.

The calculated IR spectrum of FOX-7 in the gas phase are obtained (Fig. 2) with MP2 level. There is currently experimental IR spectrum for FOX-7 (Fig. 3)* , however it is shown that measured vibrational frequencies had red-shifted with respect to the calculations in gas phase due to significant intermolecular bonding; the same as hydrogen bonding within the solid.

The relative changes in vibrational frequencies on going from the gas phase to the liquid or solid phases are usually small. Usually there is a small decrease in vibrational frequencies in the liquid and solid states as compared to the gas state [21].

In the basis of the calculated and experimental IR spectrum, the vibrational normal modes of the molecule have been analyzed carefully to characterize chemical bonds in FOX-7. The assigned values of frequencies for each pair of nuclei are gathered in Table 3. The analysis of normal modes in this paper is in discrepant with that obtained by *Dorsett* [1]. It seems the previous analysis by *Dorsett* is mistake.

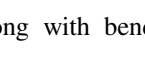
In attention to *Gillespie-Popelier* discussion [20], and Table 2, represent the following bonding natures: the most of bonded interactions are shared covalent ($\nabla^2\rho_b < 0$, $H_b<0$ and ρ_b order of 10^{-1} a.u.) and O(s)-H(s) and O(t)-O(t) interactions with $\nabla^2\rho_b > 0$ and $H_b>0$ are closed shell. O(s)-H(s) is hydrogen bond and O(t)-O(t) is not meaning classically. The vibrational mode of O(t)-O(t) interaction along with bending of  in RHF, B3LYP and MP2 levels are 313.6, 293.2 and 268.4 cm^{-1} respectively. So the normal mode is populated in room

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Table 3: Vibrational normal modes of FOX-7. Frequencies are in wavenumbers (cm^{-1}).

Connected atoms	Normal mode (cm^{-1})			
	RHF	B3LYP	MP2	Exp.
C-C	1315	1215	1233	1164
$C-NH_2$	1752, 1765	1624, 1633	1623, 1660	1500, 1517
$C-NO_2$	1480, 1529	1266, 1335	1334, 1388	1207, 1345
N-H(t), N-H(s)	3793, 3805, 3950, 3954	3430, 3445, 3657, 3659	3485,3494, 3669, 3670,	3302,3328, 3414, 3448
N-O(t), N-O(s)	1774, 1834	1563, 1595	1690, 1711	1603, 1629

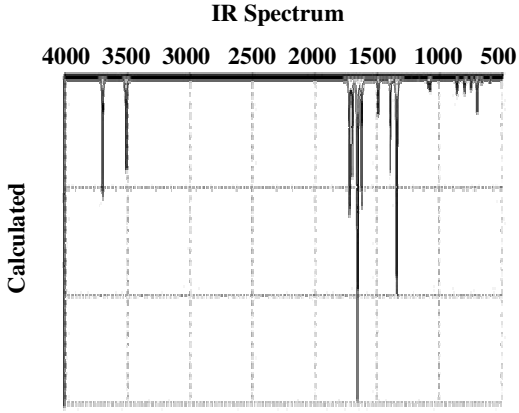


Fig. 2: Calculated IR spectrum of FOX-7 in the gas phase.

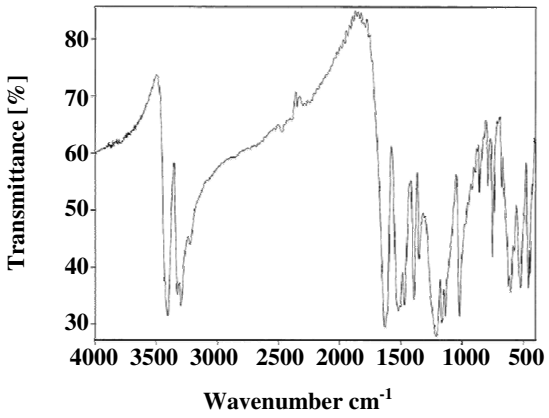


Fig. 3: Experimental IR spectrum of FOX-7.

temperature and the BCP between O(t)-O(t) can be disappeared. Of course the vibrational normal modes in Table 3 are found to be in very good correlation with other bond indices of shared covalent bond in Table 2.

It was shown by *Bader* [13], that the opening of a ring structure resulted from the coalescence of the ring and a bond critical point. Thus we have increased the distance of O(t)-O(t) from equilibrium (2.645 Å) to 2.800, 2.810 and 2.820 Å with MP2 method, it results the coalescence of the ring and the bond critical point at 2.810 Å and opening and disappearing of the bond critical point at 2.820 Å (Fig. 4).

Bond Ellipticity

The electron density of a bond that in an orbital model possesses "π" character is elliptically disposed about the BP. The electron density is preferentially accumulated in a plane that in ethene is perpendicular to the plane of the nuclei, the plane determined by the major axis of the ellipse. The extent of this accumulation is determined by the ellipticity (ε) defined as $(\frac{\lambda_1}{\lambda_2})$-1 and ranges from zero to infinity, where λ_1 and λ_2 are the negative eigenvalues of the Hessian of the electron density with respect to position [13,17]. That is, the curvatures of the density at the BCP perpendicular to the bond path, with $|\lambda_1| > |\lambda_2|$, λ_2 being the curvature along the major axis of the ellipse, that is, the direction of the "soft" curvature. The ellipticities of the C-C bonds in cylindrical bonds including single bond (ethane) and triple bond (acetylene) is equal to zero at BCP, and in benzene and ethylene are 0.18, and 0.30, respectively. The ellipticity has the property of determining the presence of a π-like component to the density, even in situations where the bond order is less than unity. Obviously, this parameter is available only in cases where a bond path connects two atoms.

Comparing the ε values in Table 2, denotes that the C-C, $C-NH_2$, $C-NO_2$, N-O(t) and N-O(s) bonds are not completely cylindrical. So they have some double bond

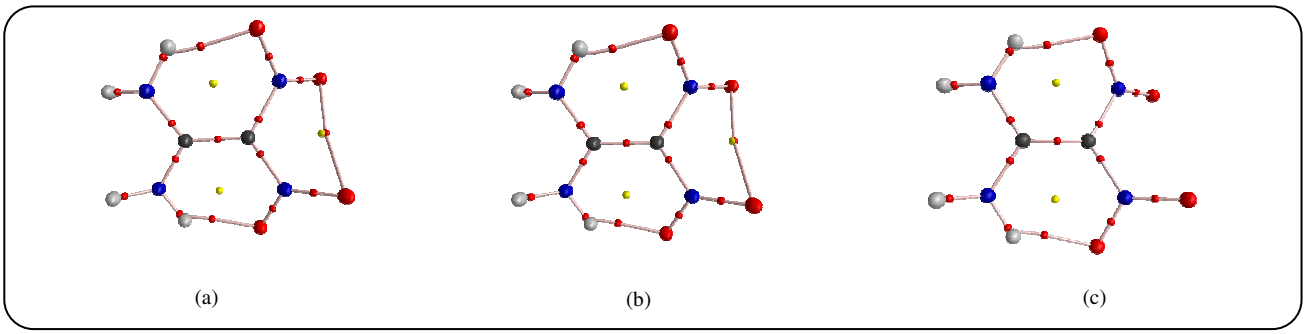
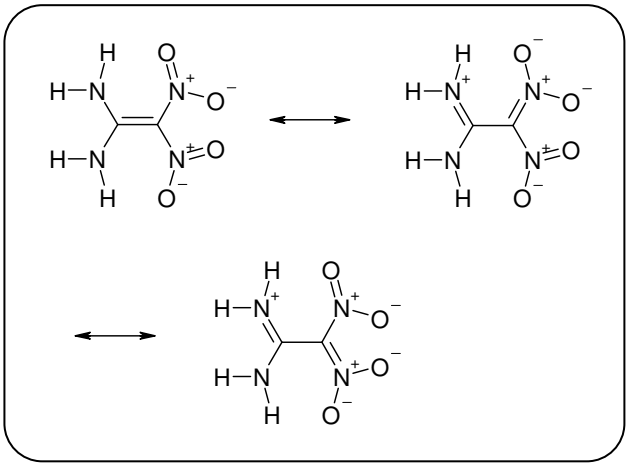


Fig. 4: The 3D molecular graph (MGs) of the geometries of FOX-7 with O(t)-O(t) distances of (a) 2.800 Å, (b) 2.810 Å and (c) 2.820 Å. (Bold points are Bond Critical Points: BCPs; Pale points are Ring Critical Points: RCPs. The lines are Bond Paths: BPs.).

character. Therefore the following resonance structures are obtained.



These structures are nearly the same as structures that they are obtained by *Politzer et al.* [5]. The coalescence of the ring and a bond critical point makes decreasing in the magnitude of λ_2 and its eventual disappearance, it means that the ellipticity of the bond which is to be broken increases dramatically and becomes infinite at the geometry of the bifurcation point. In this work with increasing of O(t)-O(t) distance from equilibrium (2.645 Å) to 2.800 and 2.810 Å (Fig. 4), the ellipticities of O(t)-O(t) increase from 0.446 to 1.846 and 9.411 respectively. Thus, these structures possessing a bond with an unusually large ellipticity are potentially instable.

Bond Order

A bond order n within the context of QTAIM can be defined by successfully fitting the following expression, A and B being constants [13,17]:

$$n = \exp\left[A\left(\rho_b - B\right)\right] \qquad (2)$$

For defining the new bond orders, the accepted value of C-C bond orders in C_2H_6, C_2H_4 and C_2H_2 molecules at B3LYP/6-311+G(d,p) level have been used for obtaining the constants A, B in Eq. (2) by fitting procedures. In this case, A and B are obtained 6.2432 and 0.2346 respectively. So the bond order C-C in FOX-7 with B3LYP and MP2 levels are obtained 1.4 and 1.5 respectively. This result is in good correlation with classical vision [4].

The more interesting correlation can be found if normal mode frequencies are compared to that of experimental values of C-C, C=C and C≡C band stretching values. These values are (650-1550 cm^{-1}), (1550-1650 cm^{-1}) and (2000-2500 cm^{-1}) for C-C, C=C and C≡C respectively [22], and therefore Table 3 shows the C-C bond order is the upper limit of single bond.

CONCLUSIONS

For the first time the structures and the physical nature of chemical bonds of FOX-7 have been determined. We should attend that the geometry has a different meaning from structure.

Molecular graphs and mathematical characteristics of bond critical points of Rho(r) function confirm that the most of bonded interactions are covalent and there are two hydrogen bonds O(s)-H(s) in the molecule. The coalescence of the ring and the O(t)-O(t) interaction is obtained in O(t)-O(t) distance of 2.81 Å. This result with low vibrational mode of O(t)-O(t) interaction shows that this interaction is potentialy instable.

The comparison of the ε values denotes that the C-C, C-NH_2, C-NO_2, N-O(t) and N-O(s) bonds are not completely cylindrical. So, they possess some double

bond character. Therefore, we have represented the new resonance structures.

In this paper we are obtained the calculated IR spectrum and compared with the experimental spectrum. As a direct tool for deducing chemical bond between two nuclei (as is done in diatomic molecules), vibrational normal modes have been analyzed carefully. The normal modes with major contribution of each pair of nuclei were assigned. Again the value of C- C normal mode was found to be in good correlation with the QTAIM bond order and inter-nuclear distance of C-C bond. Therefore the bond order of C-C is obtained 1.5 at MP2 level.

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