Tautomerism in a DADNE embedded pull-push type structures-A DFT treatise

Lemi Türker

Middle East Technical University, Department of Chemistry, Üniversiteler, Eskişehir Yolu No:1, 06800, Çankaya/Ankara, TURKEY

Abstract:

1,5-Type proton tautomerism of 2-(dinitromethylene)-4,5-dinitro-2,3-dihydro-1H-imidazole structure is considered within the constraints of density functional theory at the level of B3LYP/6-311++G(d,p). One of the pentad tautomers has been found to be almost as stable as the parent structure. The local aromaticity search (NICS(0)) indicated that both of the structures have an embedded aromatic imidazole ring system, which is not expected at first sight for the parent structure and possible causes of it are sought. Also, various quantum chemical results, calculated IR, and UV spectra are obtained and discussed.

Key words: DADNE, explosives, tautomerism, pull-push, aromaticity, NICS.

1. Introduction

Three structural isomers of diaminodinitroethylene are *geminal, cis-* and *trans* ones, of which the *geminal* one is known as FOX-7 [Agrawal ,2010]. FOX-7 is a novel high-energy insensitive material having good

geminal-DADNE   *cis-DADNE*   *trans-DADNE*
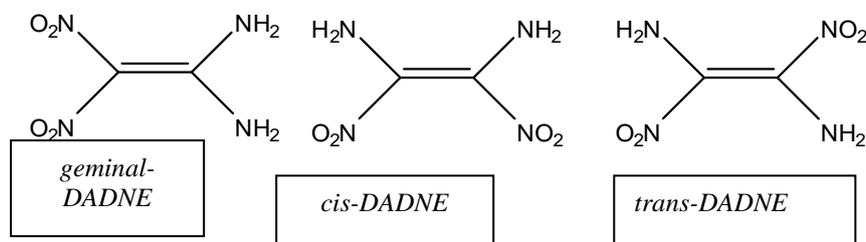
thermal stability and low sensitivity. The presence of amino and nitro groups in DADNE isomers makes them, in different extents, some push-pull type structures. The push-pull behavior dictates various properties of them of which tautomerism if possible in those structures is to be mentioned particularly.

Tautomers having different structures possess dual reactivity, depending on its tautomer content (allelotropic mixture [Reutov, 1970]). Note that substances which are isomeric under certain conditions are tautomeric under more drastic conditions [Reutov, 1970; Anslyn and Dougherty,2006]. The proton tautomerism is a special kind of cationotropic tautomeric transformations. 1,3-Type tautomerism is more often encountered one however, less likely 1,5- type proton tautomerism occurs in some structures. Some nitro compounds may exhibit 1,3- or 1,5-type proton tautomerism which is known as nitro-*aci* tautomerism. 1,5-Type tautomerism is also known as pentad tautomerism [Nemeyanov and Nemeyanov,1977]. A large number of allelotropic mixtures have been successfully separated by isolating individual tautomers (desmotropic forms) each of which yields its own series of derivatives [Reutov, 1970].

Because of the strong electron attracting properties of the nitro group, in many nitro compounds nitro-*aci* tautomerism arises [Nemeyanov and Nemeyanov, 1976; Bharatam and Lammertsma, 2003; Lammertsma and Bharatam, 2000; Dhaked and Bharatam, 2013]. In contrast to very weakly electrolytically dissociating nitro compounds their isomers, *aci*-nitro, compounds are rather strong acids. The equilibrium is therefore shifted to the side of slightly dissociated true nitro compound. However, *aci*-nitro forms act as *pseudo*-acids which react with alkali to form salts [Nemeyanov and Nemeyanov, 1976].

In the present study, a novel push-pull system originating from structural combination of *geminal* and *cis*-DADNE that is 2-(dinitromethylene)-4,5-dinitro-2,3-dihydro-1H-imidazole has been treated computationally. Up to the best knowledge of the author the compound has not been synthesized yet, although somewhat a similar compound, 2-(dinitromethylene)-4,5-imidazolidinedione, has been reported [Cai, Shu, Huang, Cheng, and Li, 2004].

2. Method

Structure optimizations leading to energy minima were initially achieved by using MM2 method which is followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [J.J.P. Stewart, 1989] at the restricted level [Leach, 1997; Fletcher, 1990]. Subsequent optimizations were achieved at Hartree-Fock level by using various basis sets. Then, the optimizations were managed within the framework of density functional theory (DFT) using B3LYP functional [Kohn and Sham, 1965; Parr and Yang, 1989] at the level of 6-311++G(d,p). The exchange term of B3LYP consists of hybrid Hartree–Fock and local spin density (LSD) exchange functions with Becke's gradient correlation to LSD exchange [Parr and Yang, 1989; Becke, 1988]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [Vosko, Vilk and Nusair, 1980] and Lee, Yang, Parr (LYP) correlation correction functional [Lee, Yang and Parr, 1988]. The present vibrational analyses have been also done at the same level of calculations which had been performed for the optimizations. The total electronic energies (E) are corrected for the zero point vibrational energy (ZPE) to yield E_c values. The normal mode analysis for each structure yielded no imaginary frequencies for the $3N-6$ vibrational degrees of freedom, where N is the number of atoms in the system. This indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. All these calculations were done by using the Spartan 06 package program [Spartan, 2006]. The NICS(0) values were calculated (B3LYP/6-311++G(d,p)) by the use of Gaussian 03 package program [Frisch et al.,2004].

3. Results and discussion

Structurally, presently considered push-pull system, structure-A, (2-(dinitromethylene)-4,5-dinitro-2,3-dihydro-1H-imidazole) can be designed, from the *geminal* and *cis* DADNE by their intermolecular union [Dewar,1969; Dewar and Dougherty, 1975]. It has a hydrogen on each nitrogen atom, thus may form
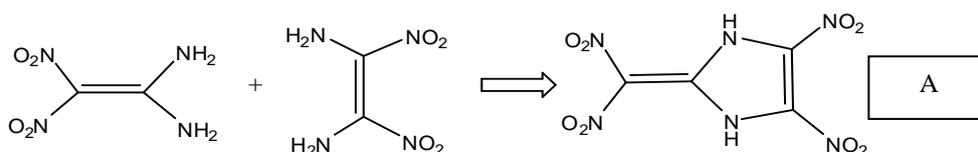
hydrogen bonds with oxygen atoms of the nearby nitro groups. Although, 1,3-type proton tautomerism seems to be possible, via migration of proton to the carbon atom of each double bond, the presence of nitro groups on those carbon atoms makes that proton shift less likely
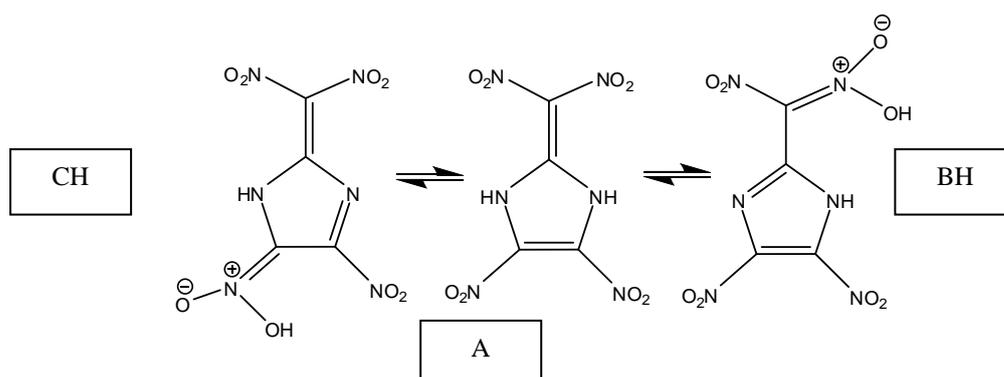
than the 1,5-proton (pentad) tautomerism to the oxygen atom of a nitro group which is a kind of nitro-*aci* tautomerism (structures BH and CH).

Fig. 1 shows the optimized structures of the 1,5-type tautomers (as well as the direction of the dipole moment vectors) presently considered. As seen in the figure, in structure-BH, hydrogen bonding is
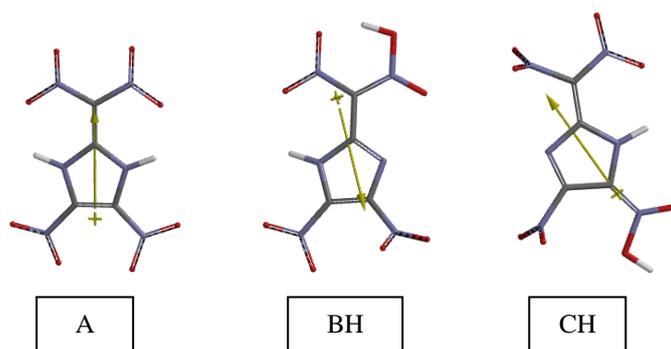
Fig. 1. Optimized structures of the tautomers considered.

possible between the migrated proton and the oxygen atom of the nitro group to form a six-membered ring system. Due to this fact the direction of the dipole moment vector in BH is almost opposite to the ones in A and CH.

Table 1 lists some properties of the tautomers. The order of calculated dipole moments is CH>BH>A, whereas the polarizability order is CH>A>BH.

Table 1. Some properties of the tautomers considered.

Tautomer	Dipole (Debye)	Ovality	Log P	Polarizability	Area (Å^2)	Volume (Å^3)
A	2.58	1.39	1.72	55.06	212.73	177.89
BH	5.62	1.40	3.07	54.99	214.41	177.56
CH	7.46	1.44	3.07	55.31	221.55	179.56

Fig. 2 shows the ESP charge distribution of the tautomers. Note that the ESP charges are obtained by the program based on a numerical method that generates charges that reproduce the electrostatic potential field from the entire wavefunction [Spartan, 2006]. The charge distribution is symmetrical in A (it has C2 symmetry).
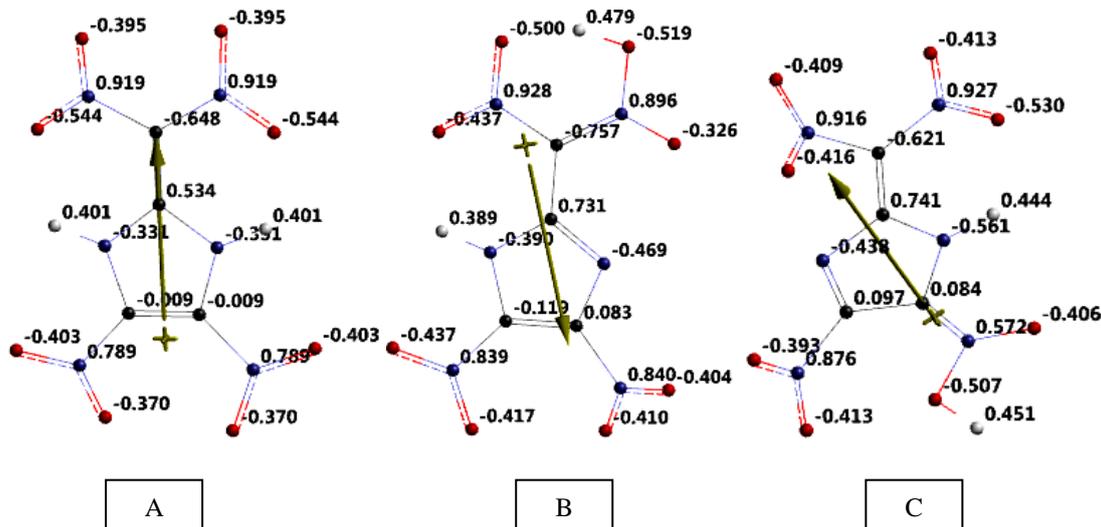
Fig. 2. The ESP charge distribution of the tautomers.

Fig. 3 displays the electrostatic potential maps of the tautomers where the blue/bluish and red/reddish regions stand for electropositive and electronegative potential regions, respectively.
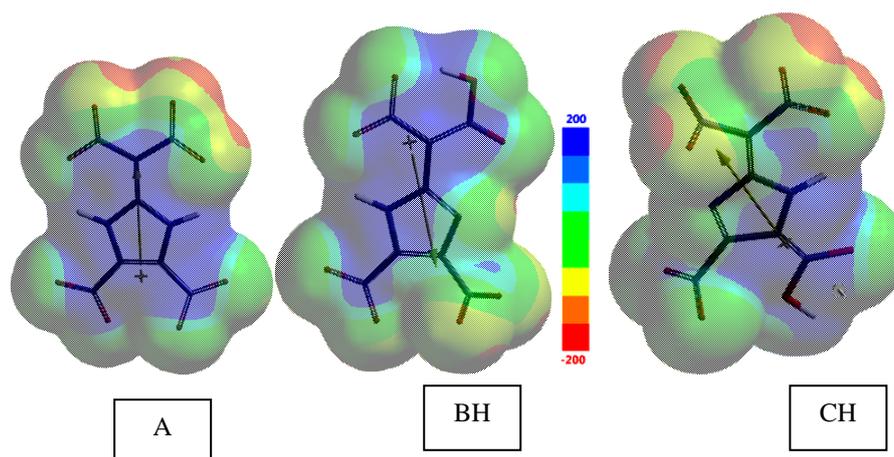
Fig. 3. Electrostatic potential maps of the tautomers considered.

Table 2 shows some energies of the tautomers, where E, ZPE and E_C are the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. The order of E_C values is A<BH<CH. Thus, electronically A is the most stable one which is followed by BH.

Table 2. Some energies of the tautomers considered.

Tautomer	E	ZPE	E_C
A	-2845529.36	282.39	-2845246.97
BH	-2845516.77	280.45	-2845236.32
CH	-2845463.66	278.77	-2845184.89

Energies in kJ/mol.

Fig. 4 shows some resonance structures of A. In the resonance structure B, planar imidazolium ring system contains 6π electrons having cyclic conjugation. Therefore, it meets the criteria of Hückel's aromaticity test and structure B is expected to be an aromatic structure. So tautomer BH which is a resonance assisted tautomer, has to be aromatic. That might be one of the reasons why BH is almost electronically as stable as A. The other reason is possibly the hydrogen bonding existing in BH (see Fig. 1).
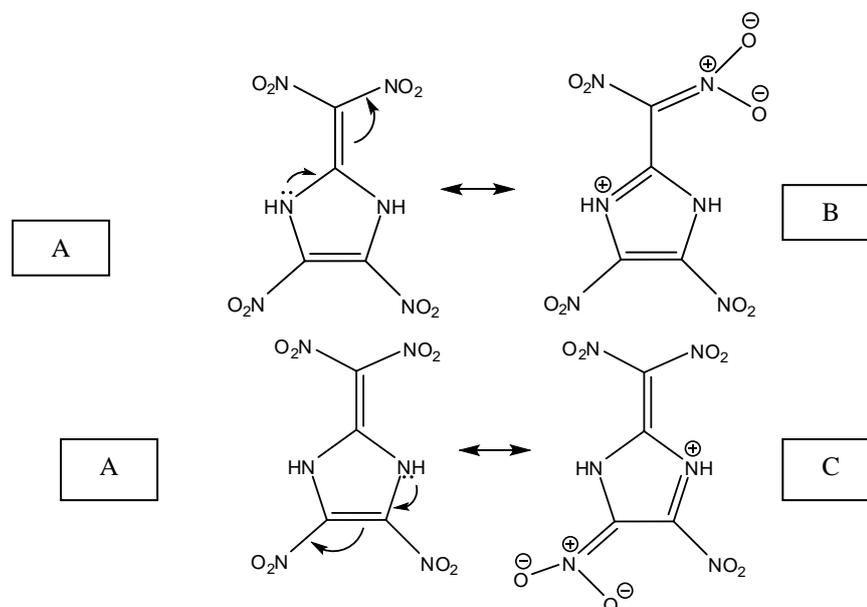
Fig. 4. Some resonance structures of tautomer-A.

A combination of various properties in cyclic delocalized systems dictates aromaticity. In general, aromaticity is discussed in terms of energetic, structural and magnetic criteria [Minkin, Glukhovtsev and Simkin, 1994; Schleyer and Jiao, 1996; Glukhovtsev, 1997; Krygowski, Cyranski, Czarnocki, Hafelinger and Katritzky; 2000; Schleyer, 2001; Cyranski, Krygowski, Katritzky and Schleyer]. Schleyer introduced a simple and efficient probe for aromaticity that is "nucleus-independent chemical shift" (NICS) [Schleyer, Maerker, Dransfeld, Jiao and Hommes, 1996]. It is the computed value of the negative magnetic shielding at some selected point in space such as at a ring or cage center. The data calculated and piled in the literature indicate that negative NICS values denote aromaticity (e.g., -11.5 for benzene, -11.4 for naphthalene) whereas positive NICS values denote antiaromaticity (28.8 for cyclobutadiene) while small NICS values are indicative of non-aromaticity (-2.1 for cyclohexane, -1.1 for adamantane). NICS may be a useful indicator of aromaticity that most often correlates successfully with the other energetic, structural and magnetic criteria for aromaticity [Jiao and Schleyer, 1998; Schleyer, Kiran, Simion and Sorensen, 2000; Quinonero, Garau, Frontera, Ballaster, Costa and Deya, 2002; Patchkovskii and Thiel, 2002]. NICS has been proved to be an effective probe for local aromaticity of individual rings of polycyclic systems. In contrast, resonance energies and magnetic susceptibilities are measures of the overall aromaticity of a polycycle, but do not provide any information about the individual rings.

The NICS(0) value of the 5-membered ring in structure A is -13.3659 which indicates that the ring is highly aromatic. Similarly, the respective value of BH is -14.3949. All indicate that resonance structure B is an important contributor into the valence bond hybrid of the system. On the other hand, NICS(0) value of tautomer CH is just -8.0628. Its comparatively less aromatic nature could be rationalize by some resonance structures having charge separation on sites far away from each other compared to the cases in other tautomers.

Fig. 5 shows the calculated IR spectra of the tautomers. In structure-A, the N-H stretchings occur at 3464 cm^{-1} whereas in BH and CH spectrums N-H stretching happens at 3578 cm^{-1} and 3554 cm^{-1}, respectively. The O-H stretching in BH and CH occurs at 2803 cm^{-1} (hydrogen bonded) and 3707 cm^{-1}, respectively. The bending of O-H in BH is at 1710 cm^{-1} whereas in CH at 1729 cm^{-1}. In between 1500-1600 cm^{-1} various stretching and bending vibrations occur.
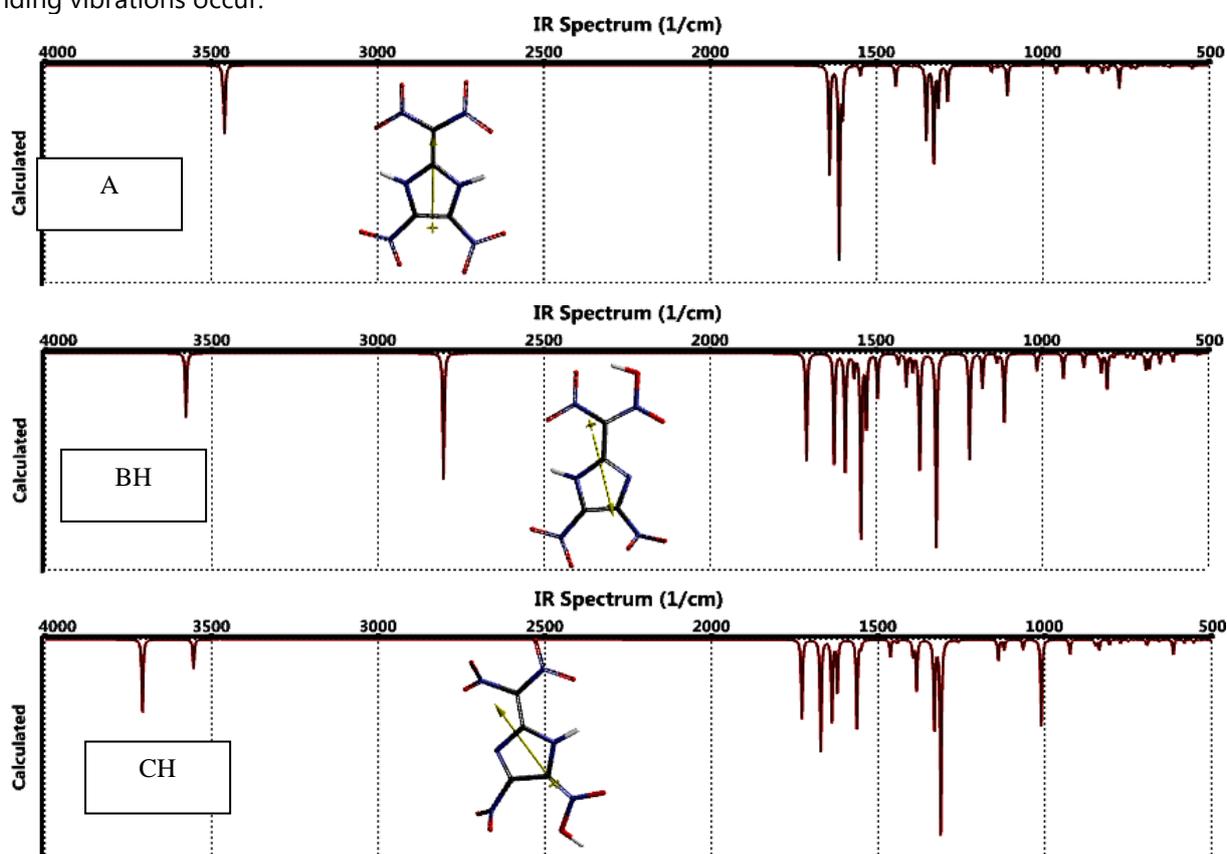
Fig. 5. IR spectra of the tautomers considered.

Table 3 displays the HOMO, LUMO energies and the interfrontier molecular orbital energy gaps (**Δε**) of the tautomers. The HOMO energy order is BH<A<CH whereas the LUMO energy order is A<CH<BH. Consequently, the order of Δε values become CH<A<BH. So the pentad proton tautomerism leading to BH lowers the HOMO but raises the LUMO energy levels with respect to A. Whereas, the same type tautomerism leading to CH raises up both the HOMO and LUMO energies compared to the respective values of A. It should be due to the conjugative differences between the endocyclic and exocyclic dinitroethylenic moieties present. In other words, the *geminal* and *cis* substituted nitro groups influence outcome of the effect highly different manner.

Table 3. The HOMO, LUMO energies and Δε values of the tautomers considered.

Tautomer	HOMO	LUMO	Δε
A	-784.70	-479.22	305.48
BH	-790.43	-469.12	321.31
CH	-735.68	-476.78	258.90

Energies in kJ/mol.

It is known that the impact sensitivity is correlated with the HOMO-LUMO energy difference adversely [Anbu, Vijayalakshmi, Karunathan, Stephen and Nidhin, 2019; Badders, Wei, Aldeeb, Rogers and Mannan, 2006]. Thus, tautomer CH having the smallest **Δε** value is expected to be more sensitive to an impulse stimulus.

Fig. 6 shows the HOMO and LUMO patters of the tautomers. They all show some sort of π-symmetry. As seen in the figure, in the case of A , dinitromethylene moiety does not contribute in to the LUMO at all. Whereas in BH case dinitroimidazoyl moiety does not have any contribution into the LUMO.
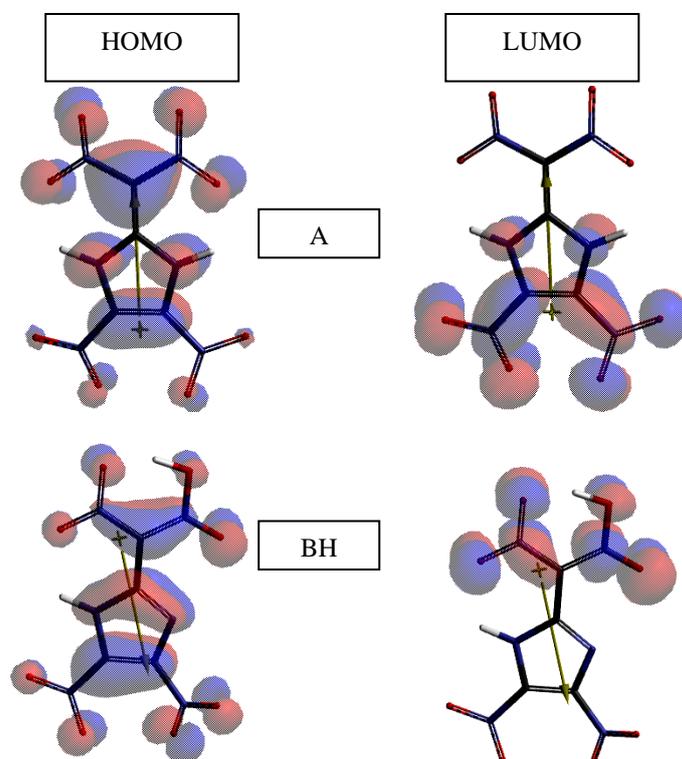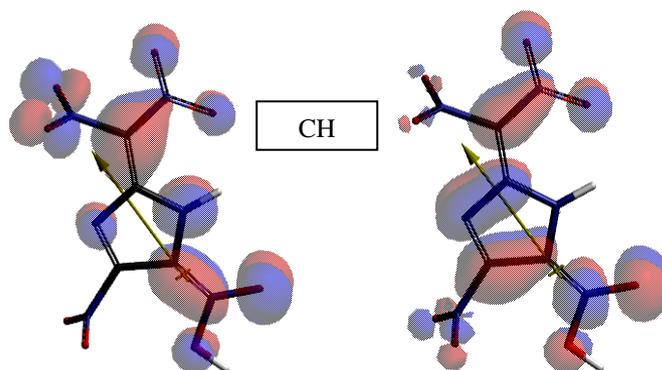
Fig. 6. The HOMO and LUMO patterns of the tautomers considered.

Table 4 shows the Gibbs free energies of formation values of the tautomers of the present concern. The data indicate that **Δ** G° values for conversion of A to BH and A to CH are 10.87 and 60.23 kJ/mol, respectively.

Table 4. G° (kJ/mol.) values of the tautomers considered.

A	BH	CH
-2845376.392	-2845365.522	-2845316.189

Fig. 7 shows the calculated UV-VIS spectra (time-dependent DFT) of the tautomers. The spectrums of A and BH resemble each other in appearance but BH spectrum exhibits some hypsochromic effect (shift to lower wavelengths). as compared to the case of A.
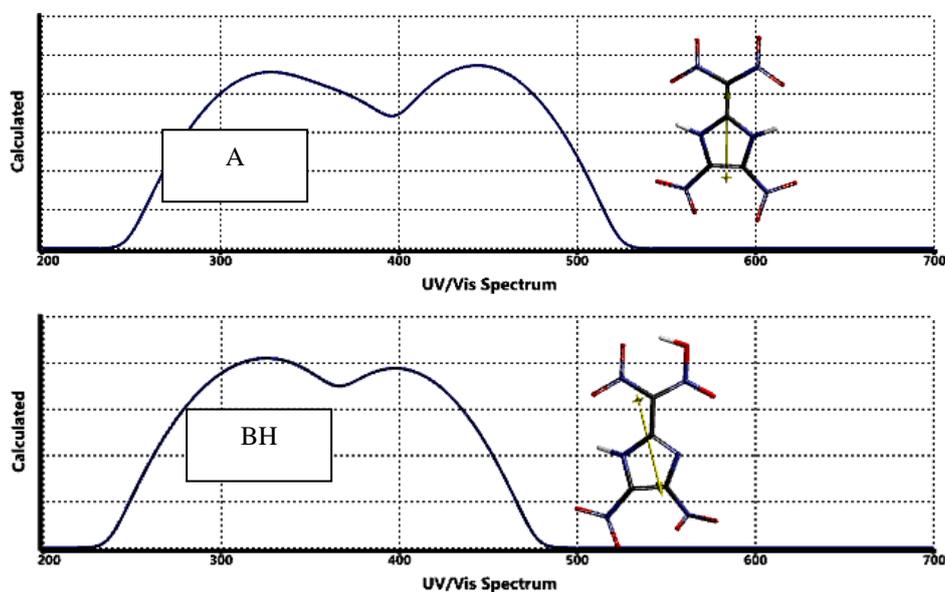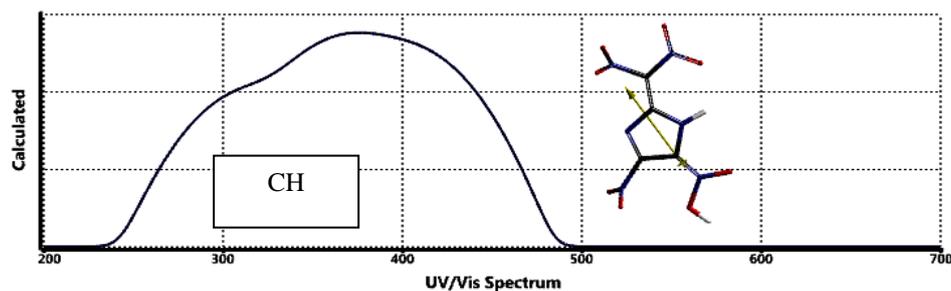
Fig. 7. UV-Vis spectra of the tautomers considered.

Some of the orbital energies of the tautomers considered are shown in Fig. 8. As seen in the figure NEXTHOMO and NEXTLUMO energy levels follow the order of A<BH<CH and BH<CH<A, respectively.
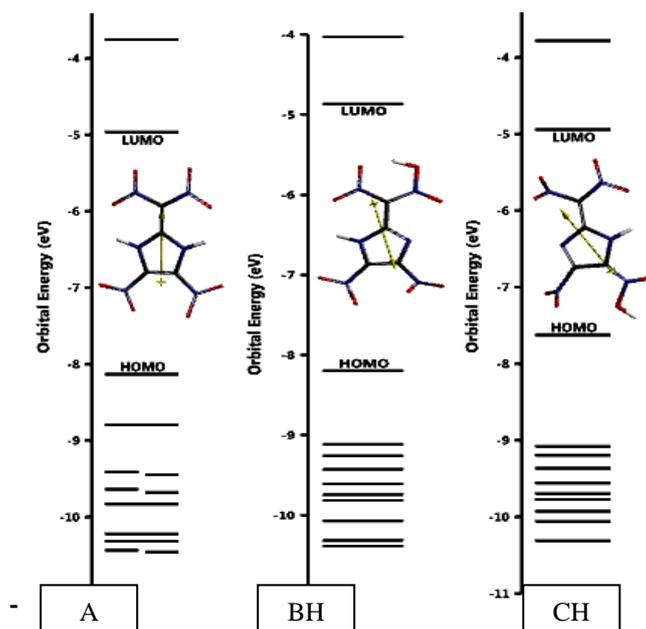
Fig. 8. Some of the orbital energies of the tautomers considered.

4. Conclusion

1,5 -type proton tautomerism of 2-(dinitromethylene)-4,5-dinitro-2,3-dihydro-1H-imidazole structure is considered within the constraints of density functional theory at the applied level of calculations, B3LYP/6-311++G(d,p). The results have indicated that the tautomer in which the proton has moved to one of the geminal nitro group (BH) is as stable as the parent structure. the NICS(0) values indicate that the 5-membered ring in all the cases are aromatic in the order of BH>A>CH. Thus, considerable degree of electron shuffling occurs in structures A and CH to generate an aromatic ring system.

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