

## Dicyanofuroxan and Its Charged Forms - A DFT Study

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### Abstract

Dicyanofuroxan is a new and interesting high explosive that can be used instead of some classical explosives. The present density functional treatment considers dicyanofuroxan and its ring opened dinitroso isomer. The treatment has been based on density functional theory at the level of UB3LYP/6-311++G(d,p). Within the constraints of the theory and the basis set employed the results indicated that the ring form of dicyanofuroxan is electronically more stable and thermodynamically more favored compared to its ring-opened dinitroso isomer. Transition state geometry and energy have been obtained for the ring opening reaction of dicyanofuroxan. Furthermore its charged forms are the focus of interest. Its monoanionic and dicationic forms decompose but mono cation form undergoes some bond elongations tending to decompose. Additionally some quantum chemical properties are presented and discussed.

### 1. Introduction

Among a variety of energetic structural patterns considered in order to design high density energetic materials with thermal stability and moderate sensitivity to external stimuli in the same molecular moiety is a tricky issue. The 1,2,5-oxadiazole-2-oxide (often referred to as furoxan or furoxane) ring is indeed prominent due to its desirable oxygen balance, high density of energetic derivatives, and high positive enthalpy of formation [1-9].

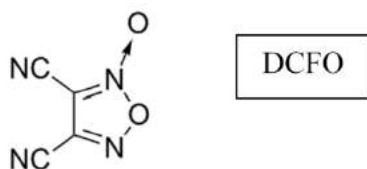
Simple nitro derivatives of furoxan have not attracted much interest for use as practical energetic materials due to their poor thermal stability and the reactivity of the nitro groups to nucleophilic displacement reactions [10].

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Dicyanofuroxan (3,4-dicyano-1,2,5-oxadiazole-2-oxide, DCFO) is a new and interesting high explosive that can be used instead of TNT, NG or PETN. It possesses remarkable stability and thermally stable up to 200°C. It forms white to flocculated slightly yellow crystals with a mean mp. of 40°C. The crystals are readily insoluble in water but soluble in CH<sub>2</sub>Cl<sub>2</sub>. It has remarkable resistance to shock, friction, percussion and impact [11]. It is readily detonated by any standard blasting caps and can be used for making booster charges in place of tetryl. DCFO can be readily melted and casted into any desired shape [11]. Homewood et al., have patented a safe explosive containing dicyanofuroxan [12]. Johnson et al., described another method for its synthesis [13]. They claimed that when detonated in a liquid and/or solid form by the addition of energy, such as heat, through an electrical resistance means, or preferably, by means of conventional blasting caps, DCFO exhibits considerable explosive force [12]. It can be alloyed with TNT, RDX, HMX or any other explosive having mp., in the range of 40-180°C to form melt cast explosive charges and for military applications such as artillery shells and missile warheads [11].



Gumanov and Korsunskii studied the thermal decomposition mechanism of dicyanofuroxan [14]. Homewood et al., has patented a safe explosive containing dicyanofuroxan [12]. Larin et al., reported various nitro-, cyano-, and methylfuroxans [15].

## 2. Method of Calculation

Initially all the structures were subjected to MM2 geometry optimizations leading to energy minima followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [16,17] at the restricted level [18]. Then, the structure optimizations have been achieved within the framework of Hartree-Fock (HF) and finally by using density functional theory (DFT) at the level of UB3LYP/6-311++G(d,p) [19,20]. 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 [21]. It is worth mentioning that the correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [22] and Lee, Yang, Parr (LYP) correlation

correction functional [23]. The normal mode analysis for each structure presently considered yielded no imaginary frequencies for the  $3N-6$  vibrational degrees of freedom. Note that  $N$  is the number of atoms in the system and the present normal mode analysis indicates that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. Furthermore, all the bond lengths were thoroughly searched in order to find out whether any bond cleavage occurred or not during the geometry optimization process. A rather high-level basis set has been employed in order to minimize the effect of basis set superposition error (BSSE) which accompanies in the case of open-shell systems. All these computations were performed by using SPARTAN 06 [24].

### 3. Results and Discussion

It is known that replacement of nitro groups by furaxano groups on aromatic ring can increase density, detonation velocity and energy of explosives. However, nitro derivatives of furoxan have not been favored for use as practical energetic materials due to their some unlikable properties as mentioned above [10]. Cyano groups act similar to nitro groups in many respects. Furoxan ring system in dicyanofuroxan (DCFO) is under the influence of electron withdrawing cyano groups which make the ring more electron deficient as compared to furoxan itself. It is to be mentioned that furoxans until 1960s were assumed to be o-dinitroso compounds [25].

An analogous furoxan compound, 4,6-dinitrobenzofuroxan were studied extensively for its ring opening reaction to its dinitroso isomer [26-28]. Note that one of the striking features of benzofuroxan (BFO) is its intramolecular isomerization to 1,2-dinitroso benzene intermediate to yield the starting compound eventually [29].

Optimized structures of the presently considered DCFO isomers and direction of dipole moment vectors of them are shown in Figure 1.



**Figure 1.** Optimized structures of DCFO isomers considered.

Table 1 shows some properties of the DCFO isomers considered. As seen in the table, isomer-I has a greater dipole moment value but owes slightly less polarizability compared to isomer-II, most probably due to its highly symmetrical structure.

**Table 1.** Some properties of the DCFO isomers considered.

Structure	Dipole moment	Polarizability	Log P
I	1.82	49.23	3.38
II	1.57	50.10	-0.54

Dipole moment in debye units.

Table 2 includes some thermo chemical properties of DCFO isomers considered. According to the data presented, structure-I possesses more favorable  $H^\circ$  and  $G^\circ$  compared to isomer-II but due to its cyclic structure it has less favorable entropy value.

**Table 2.** Some thermo chemical properties of DCFO isomers.

Structure	$H^\circ$	$S^\circ$ (J/mol $^\circ$ )	$G^\circ$
I	-1369876.949	358.22	-1369983.753
II	-1369767.822	382.03	-1369881.725

Energies in kJ/mol.

Table 3 lists some energies of the DCFO isomers and the transition state considered. where  $E$ , ZPE and  $E_c$  stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively.

**Table 3.** Some energies of the DCFO isomers and the transition state considered.

Structure	$E$	ZPE	$E_c$
I	-1370006.48	120.62	-1369885.86
II	-1369888.46	108.64	-1369779.82
TR	-1369824.80	110.21	-1369714.59

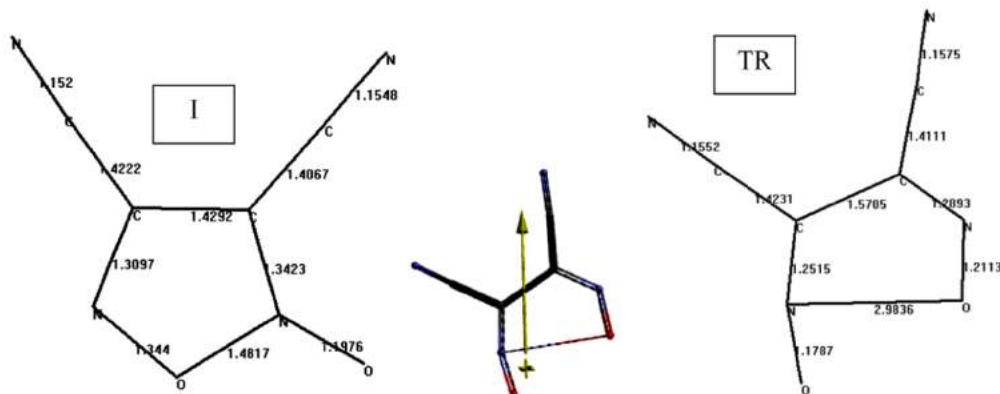
Energies in kJ/mol.

The electronic stability order follows the sequence of TR<II<I. Based on the corrected total electronic energies considered, the activation energy for the ring opening

reaction of DCFO is 171.27 kJ/mol., whereas the dinitroso isomer requires only -65.23 kJ/mol., of energy to pass through the same activation state for the ring closure process.

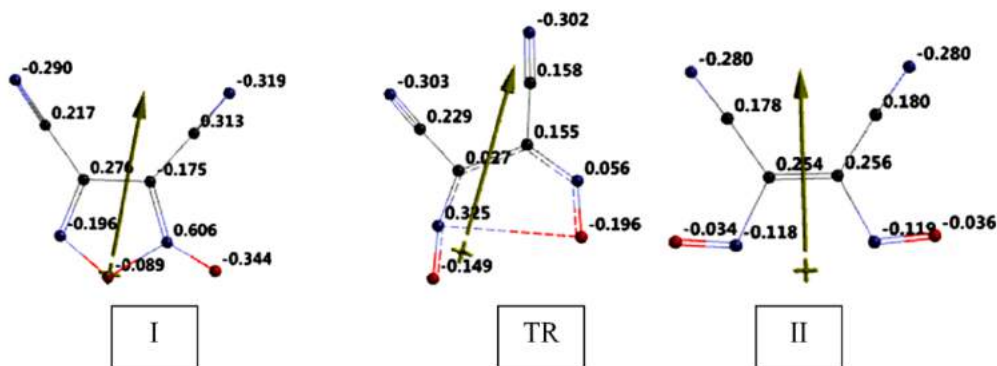
As seen in Table 3, the cyclic isomer is more stable than the nitroso form albeit the fact that former one is entropically less favored.

Figure 2 shows bond lengths/distances in structure-I and the transition state for the ring-opening of DCFO during the isomerization of structure-I to II.



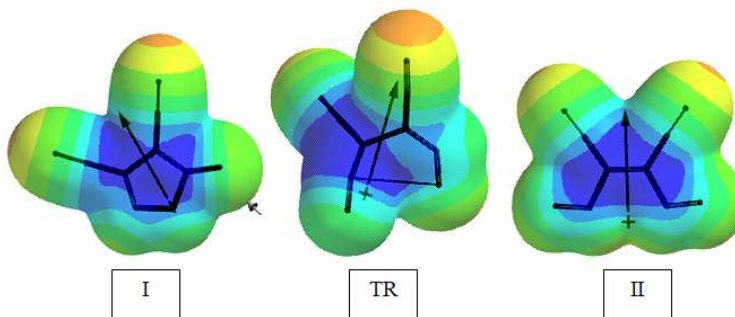
**Figure 2.** Bond lengths/distances in structure-I and the transition state for the ring-opening of DCFO (Bond lengths/distances in Å).

Figure 3 shows the electrostatic potential (ESP) charges on the atoms of the systems presently considered. 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 [24].



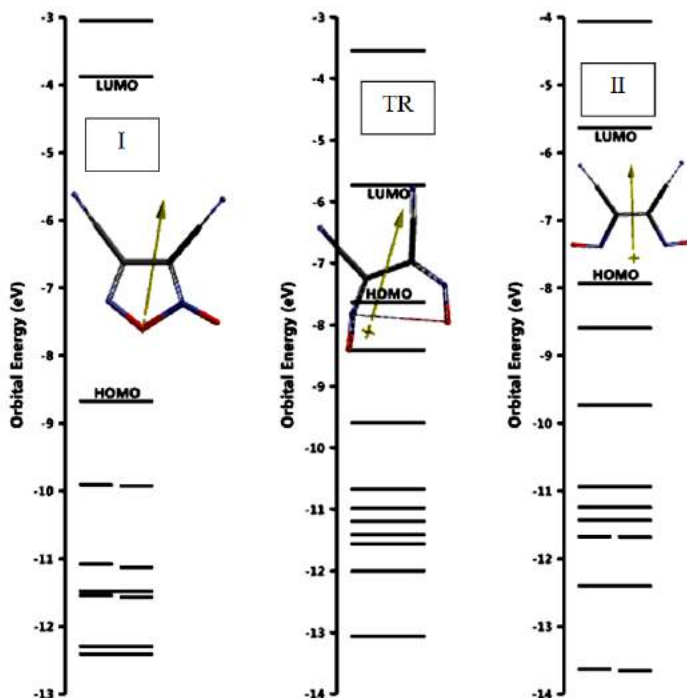
**Figure 3.** The ESP charges on the atoms of structures-I and II and the transition state considered.

Figure 4 shows the electrostatic potential maps of the systems considered. Note that blue and orange to green regions stand for electro positive and negative potential fields, respectively. In structures-I and II positive potential field spreads over the furoxan ring while in the transition state structure it is somewhat shifted one side. The direction of the dipole moment vectors changes accordingly.



**Figure 4.** Electrostatic potential maps of the systems considered.

Figure 5 displays some molecular orbital energy levels of the systems considered.



**Figure 5.** Some molecular orbital energy levels of the systems considered.

As seen in the figure, in the transition state the HOMO energy level raises up but the LUMO level decreases with respect to the corresponding orbital energies of structure-I (see also Table 4).

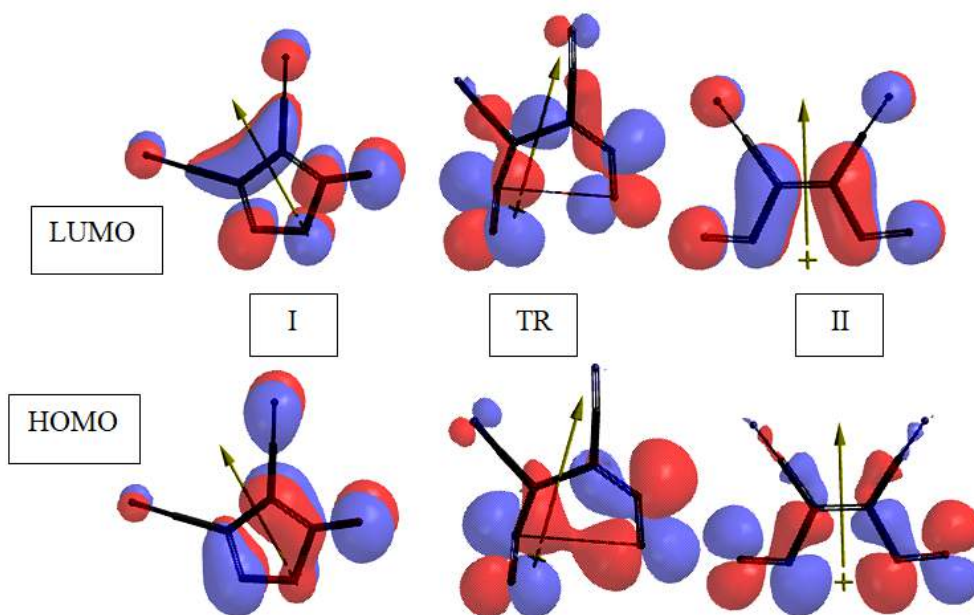
Table 4 lists some energies of structures-I and II and the transition state considered where  $\Delta\varepsilon = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$ .

**Table 4.** Some energies of structures I and II and the transition state considered.

Structure	HOMO	LUMO	$\Delta\varepsilon$
I	-836.72	-374.20	462.52
II	-765.00	-543.71	221.29
TR	-736.41	-552.63	183.78

Energies in kJ/mol.

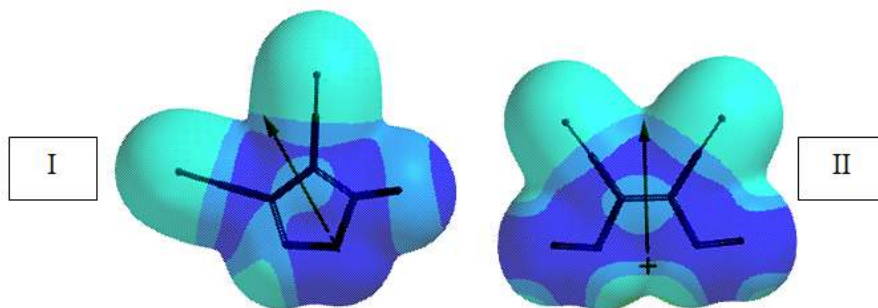
The HOMO order is I<TR<II while the LUMO energies follow the order of TR<II<I. Consequently, the interfrontier molecular orbital energy gap ( $\Delta\varepsilon$ ) values follow the order of TR<II<I. All these indicate that some extended conjugation occurs



**Figure 6.** The HOMO and LUMO patterns of the systems considered.

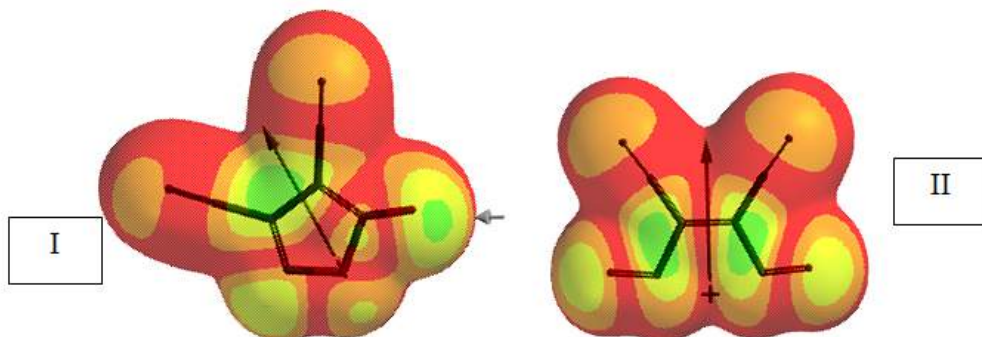
better in the transition state and structure-II compared to the cyclic structure. Because the extended conjugation raises up the HOMO but lowers the LUMO energy levels causing narrowing of interfrontier molecular orbital gap [30]. On the other hand, the impact sensitivity increases more and more as  $\Delta\epsilon$  value gets smaller and smaller [31,32]. Thus, structure-II is expected to be more sensitive to impact stimulus than isomer-I is.

Figure 7 shows the local ionization maps of DCFO isomers. In a local ionization potential map, conventionally red regions on the density surface indicate areas from which electron removal is relatively easy, meaning that they are subject to electrophilic attack. On the other hand, regions having blue color represent areas where ionization is relatively difficult.



**Figure 7.** The local ionization maps of DCFO isomers.

Figure 8 displays the LUMO maps of DCFO isomers. A LUMO map displays the absolute value of the LUMO on the electron density surface. In a LUMO map, the blue colored region stands for the maximum value of the LUMO and the color red, the minimum value.

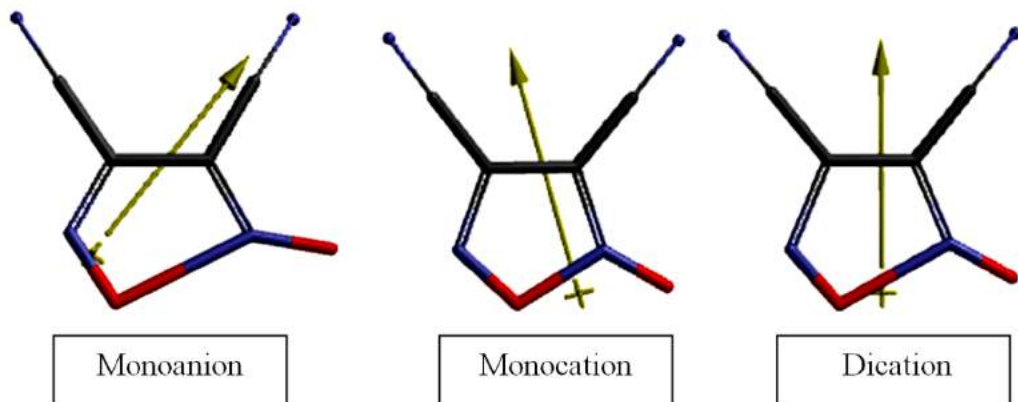


**Figure 8.** The LUMO maps of DCFO isomers.



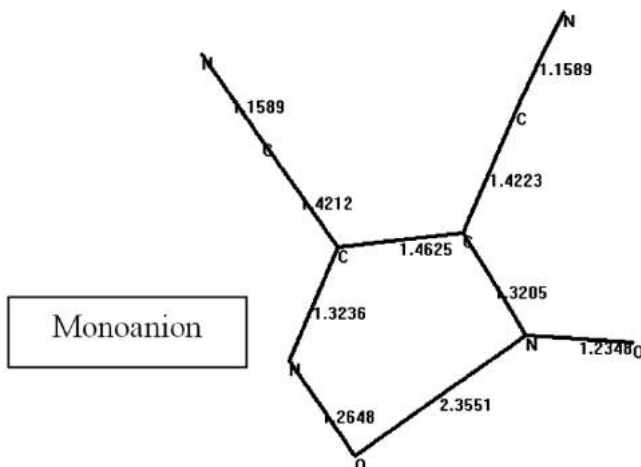
## The charged forms

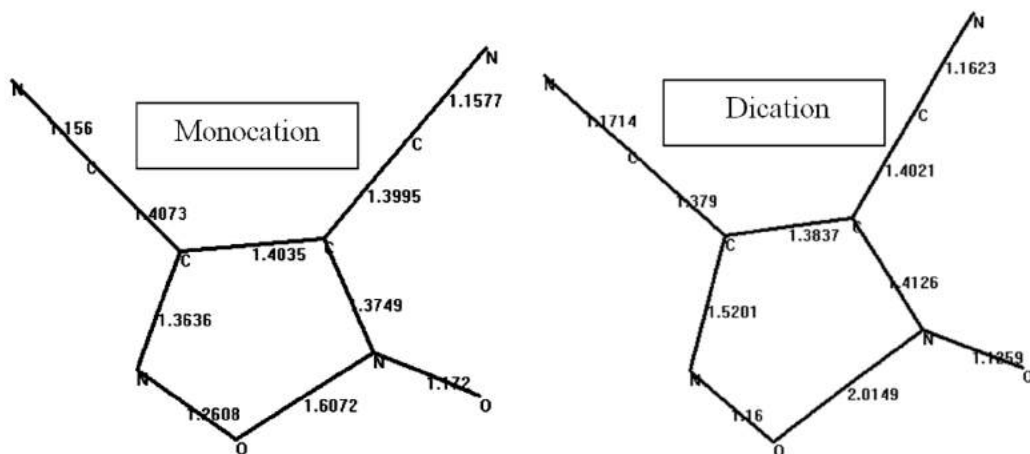
Electric spark sensitivity of an energetic material is very important for safety during the storage and/or handling purposes. Ionized forms of an energetic material put some light on the stability of it against the static electric charge accumulation. Figure 9 shows the optimized structures of some ions of DCFO.



**Figure 9.** Optimized structures of some ions of DCFO.

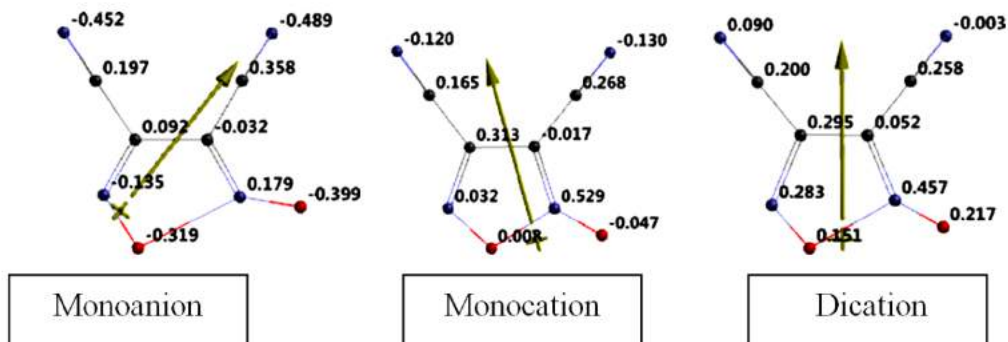
Figure 10 displays the bond lengths/distances (in Å) of some ions of DCFO. Since the monoanion is the decomposed form of structure-I, its dianion form is not considered. As evident from the figure, the positive or negative ionization causes the cleavage of ring N-O bond by the exocyclic N-O moiety. Note that the length of the respective N-O bond in structure-I is just 1.48 Å (see Figure 2).





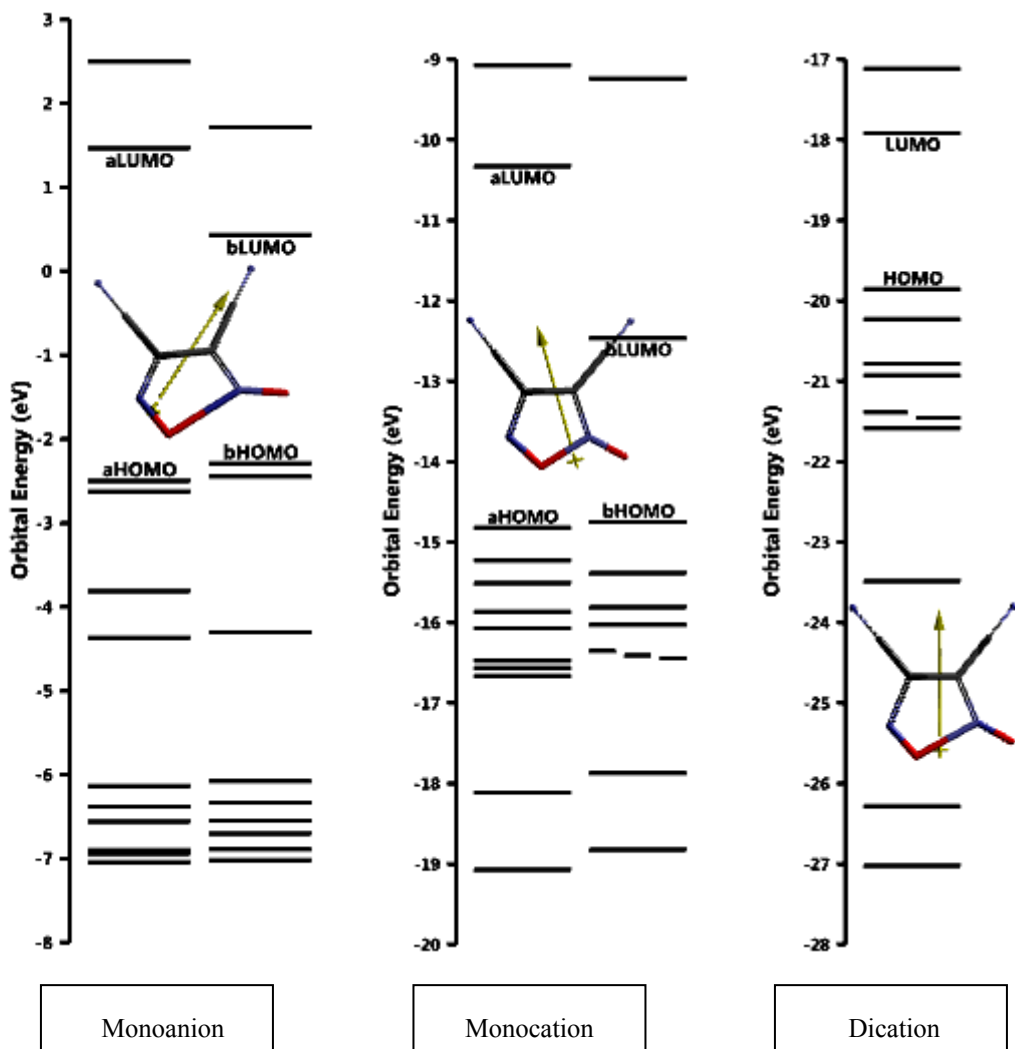
**Figure 10.** Bond lengths/distances (in Å) of some ions of DCFO.

Figure 11 shows the ESP charges on atoms of DCFO ions. As seen in the figure, in the case of monoanion opposite charges accumulate on the atoms of the broken N-O bond whereas similar charges appear in the case of cations considered. Thus, the anion formation possibly occurs via heterolytic whereas cation formation via homolytic cleavage of the N-O bond.



**Figure 11.** The ESP charges on DCFO ions.

Figure 12 shows some molecular orbital energy levels of the ions considered. Note that the mono anion and cation forms are open-shell systems, thus unrestricted calculations yield  $\alpha$ - and  $\beta$ -type orbitals which are represented in the figure by a- and b-types. Also note that inner lying orbitals of structure-I are more dense compared to the others which reflect thermal stability of structure-I.



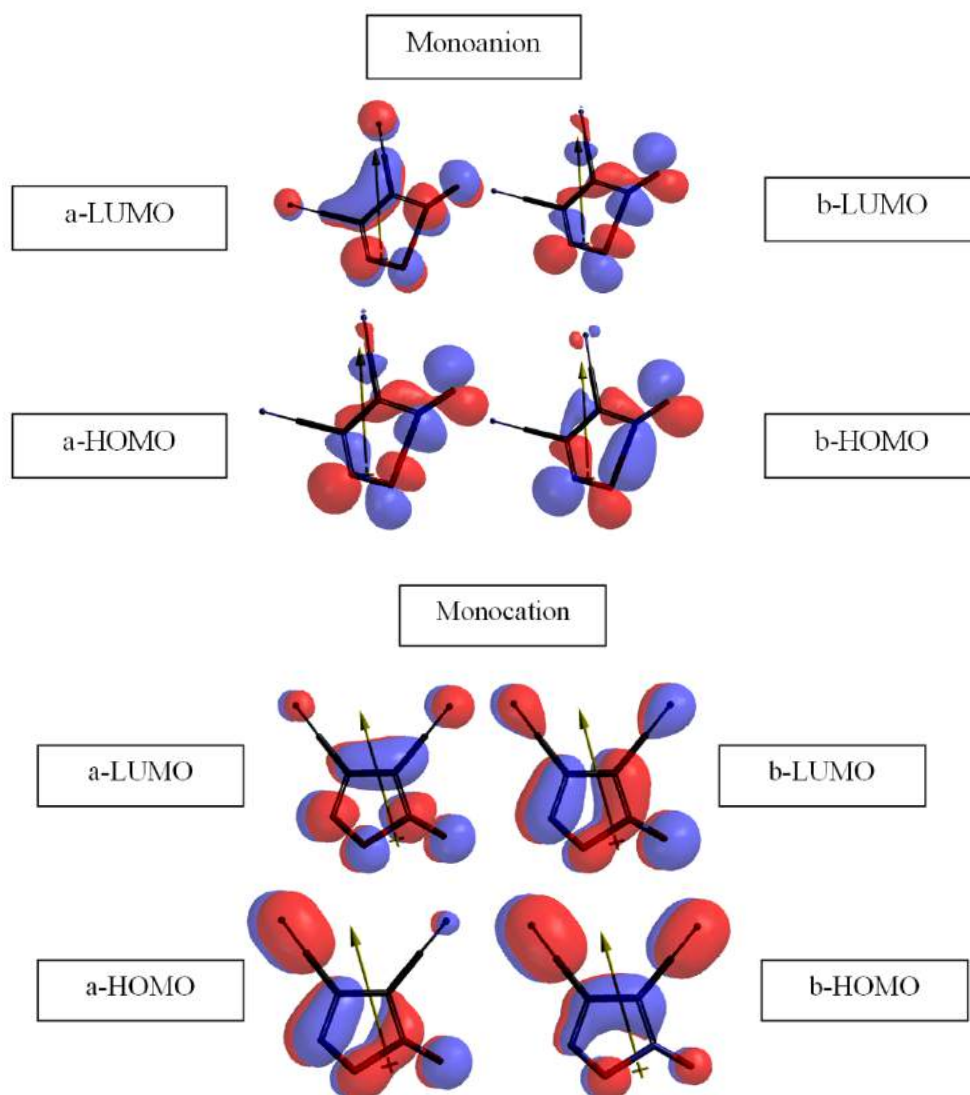
**Figure 12.** Some molecular orbital energy levels of the ions considered.

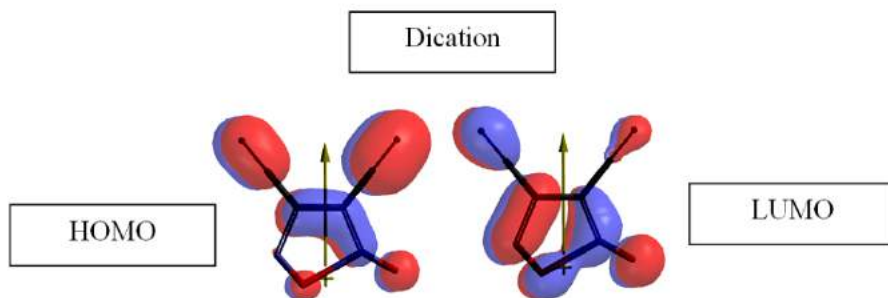
Table 5 lists some energies of the ions considered. The data in the table indicates that the monoanion formation raises up both the HOMO and LUMO energy levels of the parent structure while decreasing the  $\Delta\epsilon$  value. On the other hand, cation formation progressively lowers both the HOMO and LUMO levels compared to the levels of structure-I, meanwhile  $\Delta\epsilon$  value decreases.

**Table 5.** Some energies (in kJ/mol) of the ions considered.

Ion	HOMO	LUMO	$\Delta\epsilon$
Structure-I	-836.72	-374.20	462.52
Monoanion	-240.99	141.05	382.04
Monocation	-1429.65	-996.45	433.2
Dication	-1915.54	-1728.65	186.89

The effects of charging on the HOMO and LUMO patterns are shown in Figure 13.

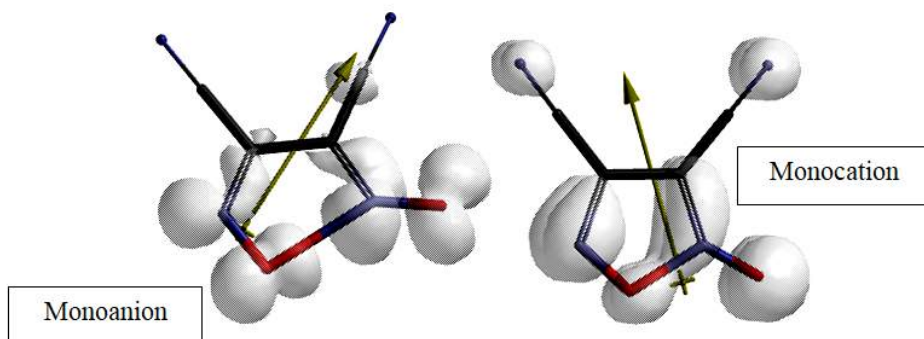




**Figure 13.** The HOMO and LUMO patterns of the charged DCFO species.

As seen in the figure the cation forms possess  $\pi$ -type symmetry in both the HOMO and LUMO.

Figure 14 displays the spin density maps of the open-shell ions considered. Note that in the monoanion case only one of the cyano groups has some spin density on the carbon atom while in the monocation both of them possess almost equivalent spin density on the nitrogen atoms.



**Figure 14.** Spin density maps of the open-shell ions considered.

#### 4. Conclusion

The present treatment, within the restrictions of the theory and the level of calculations, reveals that isomer-I is preferred over isomer-II and the isomerization process if occurs at all requires rather high activation energy compared to the ring closure. On the other hand, dicyanofuroxan is more insensitive to impact stimulus than its dinitroso isomer. However, dicyanofuroxan is sensitive to electrical charging and even more sensitive to negative charging.

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