



## ***cis*- and *trans*-2,5,7,9-Tetranitro-2,5,7,9-tetraazabicyclo[4,3,0]nonan-8-one and Some of its Isomers-A DFT Treatise**

**Lemi Türker**

Department of Chemistry, Middle East Technical University, Üniversiteler, Eskişehir Yolu No: 1, 06800 Çankaya/Ankara, Turkey; e-mail: lturker@gmail.com; lturker@metu.edu.tr

### **Abstract**

Some geometrical isomers of tetranitro-tetraazabicyclononones (the titled compounds) and some of their constitutional isomers are investigated quantum chemically at the level of B3LYP/6-311++G(d,p). The constitutional isomers differ from the title compounds by the position of the carbonyl group. All the structures are nitramines (actually nitramides of organic sense). The constitutional isomers considered are capable of exhibiting proton tautomerism (keto-enol type). The tautomers have also been subjected to density functional treatment at the same level of calculation. For all the structures various electronic, energetic and spectral data have been collected and discussed.

### **1. Introduction**

A typical submunition fill employing RDX as the main explosive charge could exhibit significant deleterious environmental effects on water supplies. RDX also has high to moderate mobility in soil, and its natural (aerobic) biodegradation is very slow. As a potential solution to persistent environmental problems posed by such ingredients, a class of explosive energetic ingredient has received some development over the last couple of decades such as cyclic *N,N'*-dinitrourea derivatives. Specific examples investigated included tetranitroglycoluril (TNGU or Sorguyl) and hexanitrohexaazatricyclododecanedione (HHTDD). They are significantly more hydrolytically reactive than simple alicyclic nitramines such as RDX. With processing

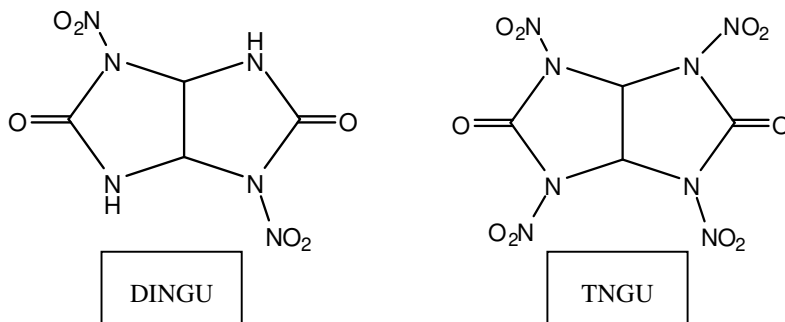
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problems technologically solved, these ingredients would offer attractive performance advantages, particularly in the case of HHTDD, which is recognized to be the most powerful easily accessible explosive compound, surpassing even CL-20 in explosive performance (TNGU is comparable in performance to HMX.) [1, 2]. Because of this hydrolytic reactivity, ordnance fills that employ any of these ingredients must account for it in their formulation and processing, RDX has been classified as a possible human carcinogen, based on the presence of liver tumors found in mice that ingested food contaminated with RDX over a one to two year period [3]. On environmental grounds, replacements for RDX are being sought.

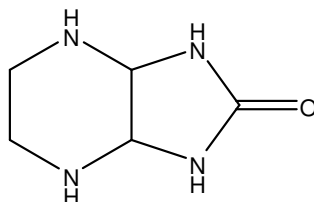
The date of synthesis of nitrourea explosives goes back to 1974. N-nitroureas are very attractive because mono-nitroureas and di-nitroureas proved to have a good explosive performance. Some N-nitroureas such as TNGU and 1,4-Dinitroglycouril (DINGU) are to be mentioned [4, 5].



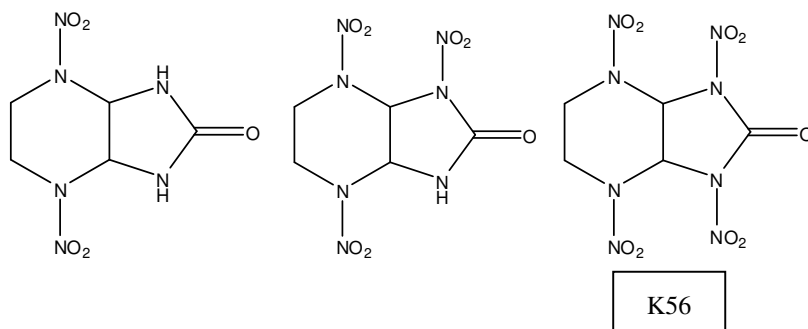
TNGU is a powerful explosive with high detonation velocity and crystal density [5]. However, it is readily hydrolyzed by cold water and of limited use as a practical explosive. DINGU is hydrolytically more stable [5]. Li and coworkers recognized the potentiality of cyclic N-nitroureas as energetic materials and synthesized various bicyclic nitroureas [6].

Pagoria et al., reported the synthesis and characterization of several bicyclic mono- and dinitrourea compounds as energetic materials and discuss their use as precursors to other energetic compounds [7]. Sikder et al., managed the synthesis and characterization of some other urea embedded heterocyclic energetic materials such as 2,4,6,8-Tetranitro-2,4,6,8-tetraazabicyclo[3.3.1]nonane-3,7-dione (TNPDU) and 2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo[4.3.0]nonane-8-one (TNABN) [8].

The nitration of 2,5,7,9-tetraazabicyclo[4,3,0]nonan-8-one ring system has been investigated [9]. Some trinitro-2,5,7,9-tetraazabicyclo[4.3.0]nonan-8-one derivatives were also investigated [10, 11].



Three products have been observed from the N-nitration of the dihydrochloride salt with various nitrating agents and conditions [12]. It is observed that the nitration of amino nitrogens of the salt is considerably more facile than its urea nitrogens producing,



the tetra nitro product is known as K56. A similar compound ( $C_5H_7N_7O_7$ ), contains fused five- and six-membered rings in a flattened envelope and a twist-boat conformation, respectively, with a *cis* junction between the two heterocyclic rings [10]. However, up to the best knowledge of the author, stereochemistry of the explosive compound labeled K56 is obscure in the literature.

Also, a series of high energy density compounds (HEDCs) based on N-nitrourea were designed and their theoretical performances were calculated using the Gaussian programs. The predicted values of the energy density of these compounds are in the range  $1.848\text{--}1.93\text{ g/cm}^3$ , and their calculated VODs are in the range  $6700\text{--}8305\text{ m/s}$  [13]. Generally, nitrourea energetic materials have better thermal stability, higher density and higher energy level, but bisnitrourea-compounds have the poor hydrolytic stability, which restricts their application. The synthesis and performance determination of nitrourea energetic materials are in progress.

In the present study, the *cis*- and *trans*-isomers of nitrourea explosive, K56, and some of its isomers are considered within the realm of density functional theory (DFT).

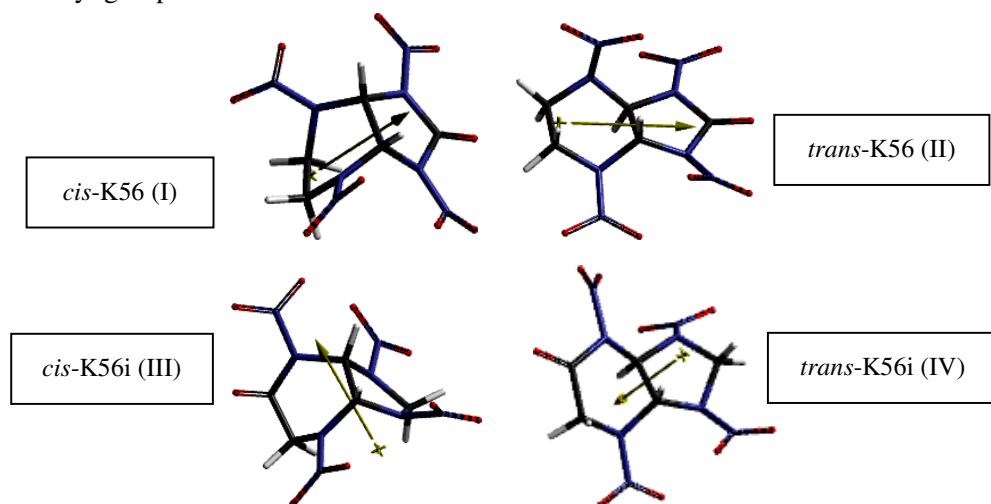
## 2. Method of Calculation

In the present study, the initial geometry optimizations of all the structures leading to energy minima have been achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [14, 15] at the restricted level [16, 17]. Subsequent optimizations were achieved at Hartree-Fock level using various basis sets. Then, geometry optimizations were managed within the framework of density functional theory (DFT) [18, 19] at the level of B3LYP/6-311++G(D,P) [17, 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 [19, 21]. 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]. Also, the vibrational analyses were done. The total electronic energies are corrected for the zero point vibrational energy (ZPE). 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 [24].

## 3. Results and Discussion

Figure 1 shows the optimized structures of the K56 and its geometrical and constitutional isomers presently considered. They are all nitramides. As seen in the figure *cis* and *transness* of the systems of present concern are determined by the relative positions of the hydrogens at the fusion points of the two rings. The presently defined configurational isomers of K56 structure (*cis*-K56i and *trans*-K56i) differ from the parent structures only by the location of the carbonyl group (nitramide moiety), namely in the isomeric structures the six-membered ring possesses the carbonyl moiety. Note that in *cis* and *trans* K56 structures the carbonyl moiety is in conjugation with two of the nitramide groups whereas in the isomers, *cis*-K56i and *trans*-K56i, only one of the nitramine groups can be conjugatively interacts with the carbonyl group of the nitramide moiety. Those isomers presently are also called carbonyl containing isomers.

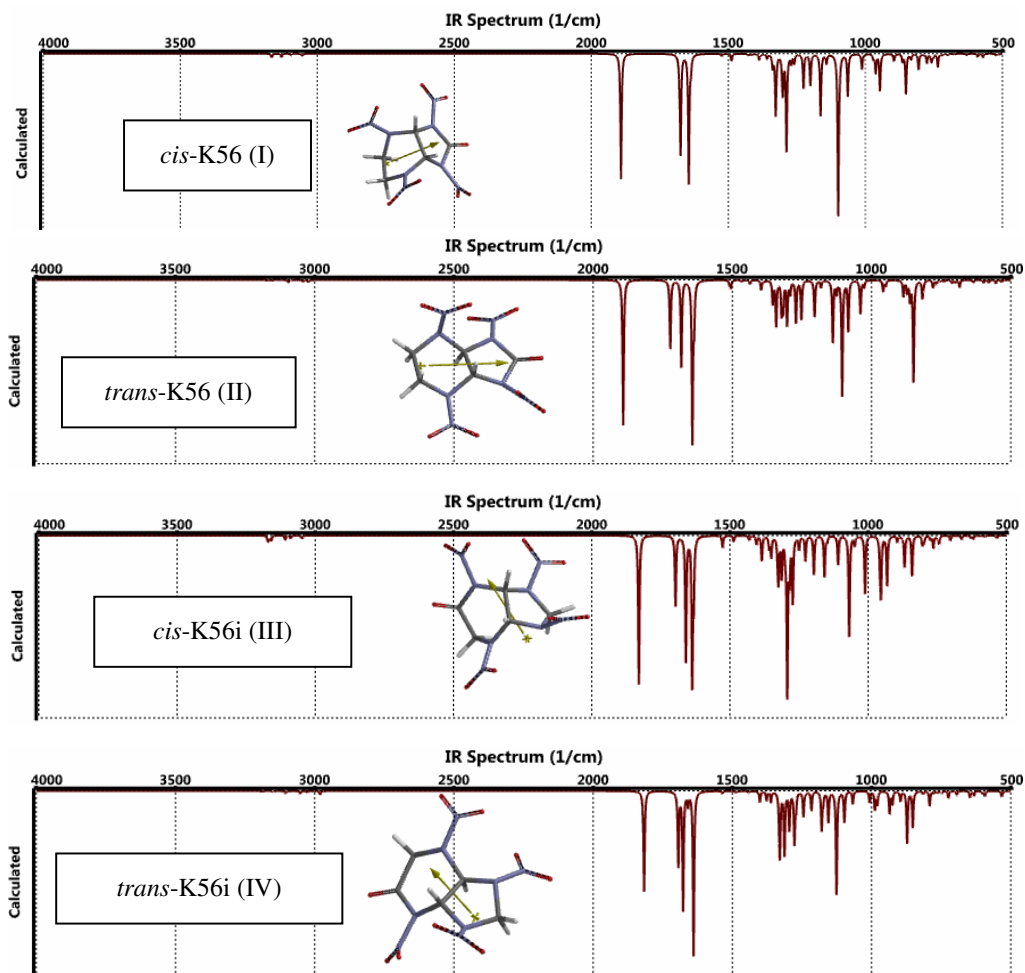
Figure 1 also shows the labels of these four structures as I-IV. Note that the dipole moment vectors (Figure 1) in I and II originate from some point of six-membered ring to five-membered ring. In III it originates from somewhere in the bay region formed by the five and six-membered rings and points to the other bay region. In structure IV the vector is from somewhere around the five-membered ring to the six-membered ring nearby the carbonyl group.



**Figure 1.** *cis*- and *trans*-K56 and their carbonyl containing isomers.

Figure 2 shows the calculated IR spectra of the structures considered. The peak at  $1892\text{ cm}^{-1}$  stands for carbonyl stretching in *cis*- and *trans*-K56 structures (I and II). The corresponding peak in isomers III and IV occurs somewhat at lower values. The cause of it might be due to inductively electron supply to the carbonyl group by the  $\text{CH}_2$  group. Note that in I-IV, adjacent nitrogen(s) should not supply electron population to the carbonyl group due to the nitro group they possess. The carbonyl peak in the *trans* isomer is somewhat at lower value than the *cis*-isomer in all the cases.

Table 1 tabulates some energies of the structures of the present concern, where  $E$ , ZPE and  $E_c$  stand for the total electronic energy, zero point vibrational energy and the corrected total electronic energy, respectively. The  $E_c$  values indicate that the *cis* isomer of each set of structures is more stable than the *trans* ones.



**Figure 2.** IR spectra of the carbonyl containing structures considered.

**Table 1.** Some energies of the carbonyl containing structures considered.

Structures	E	ZPE	E <sub>c</sub>
<i>cis</i> -K56 (I)	-3436941.88	464.12	-3436477.76
<i>trans</i> -K56 (II)	-3436876.62	464.40	-3436412.22
<i>cis</i> -K56i (III)	-3436910.37	462.75	-3436447.62
<i>trans</i> -K56i (IV)	-3436823.99	462.38	-3436361.61

Energies in kJ/mol

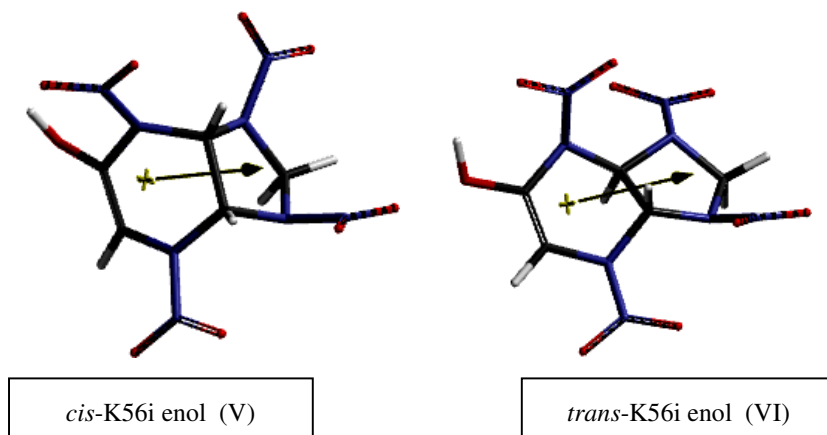
The stability order of structures I-IV is I > III > II > IV. This order is probably dictated by the over all effects of charge-charge, charge-dipole and dipole-dipole interactions.

The calculated UV-VIS spectra (time-dependent DFT) of these structures are very similar to each other and absorbs below 400 nm, having only a single  $\lambda_{\max}$  value at ca. 275 nm.

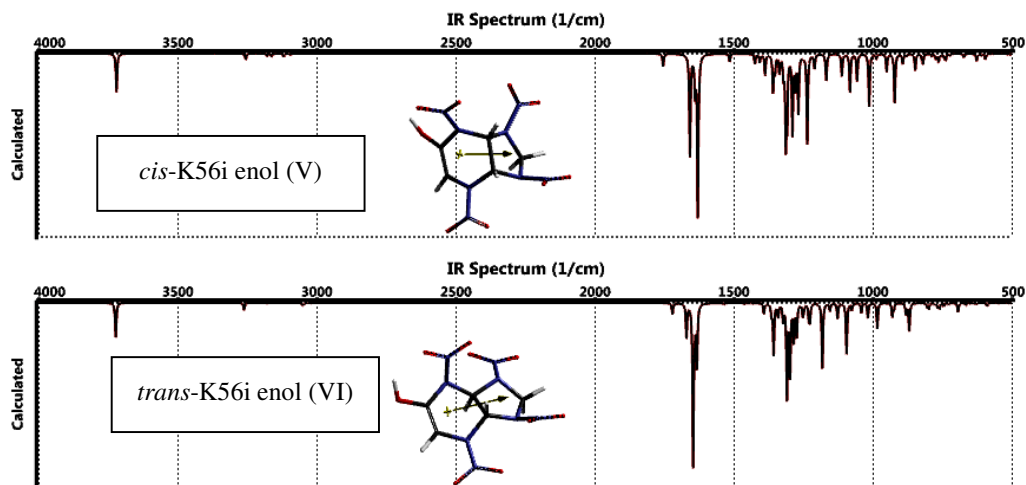
### Tautomerism

Tautomerism plays an important role on some properties of molecules. Tautomers having different structures possess dual reactivity, depending on its tautomer content (allelotropic mixture [25]). Note that substances which are isomeric under certain conditions are tautomeric under more drastic conditions [25, 26]. The proton tautomerism is a special kind of cationotropic tautomeric transformations.

Structures III and IV are capable of exhibiting keto-enol type proton tautomerism. Figure 1 shows the optimized structures of *cis*- and *trans*-K56 and their also carbonyl containing (nitramide) isomers. Whereas Figure 3 displays the optimized structures of the enol tautomers of the keto isomers considered. The respective structures are V and VI, respectively. Note that the keto isomers, *cis* and *trans* K56i, have two nitramine groups on the five-membered ring and one nitramine and one nitramide group on the six-membered ring. Whereas, the enolic structures V and VI possess four nitramine groups over all. Figure 4 shows the IR spectra of these enol structures.



**Figure 3.** Optimized structures of the enol tautomers considered.



**Figure 4.** IR spectra of the enol tautomers considered.

Table 2 tabulates  $E$ , ZPE and  $E_c$  values of the enol forms. The data indicate that enol form V of III is more stable than the respective enol form VI of IV. Combining the data presented in Table 1, the stability order of tautomers is obtained as III > V > IV > VI. Consequently, keto structures (actually nitramide) III and IV are more stable than their enol forms V and VI, respectively.

**Table 2.** Some energies of the enol tautomers considered.

	$E$	ZPE	$E_c$
<i>cis</i> -K56i enol (V)	-3436875.28	462.65	-3436412.63
<i>trans</i> -K56i enol (VI)	-3436801.67	462.60	-3436339.07

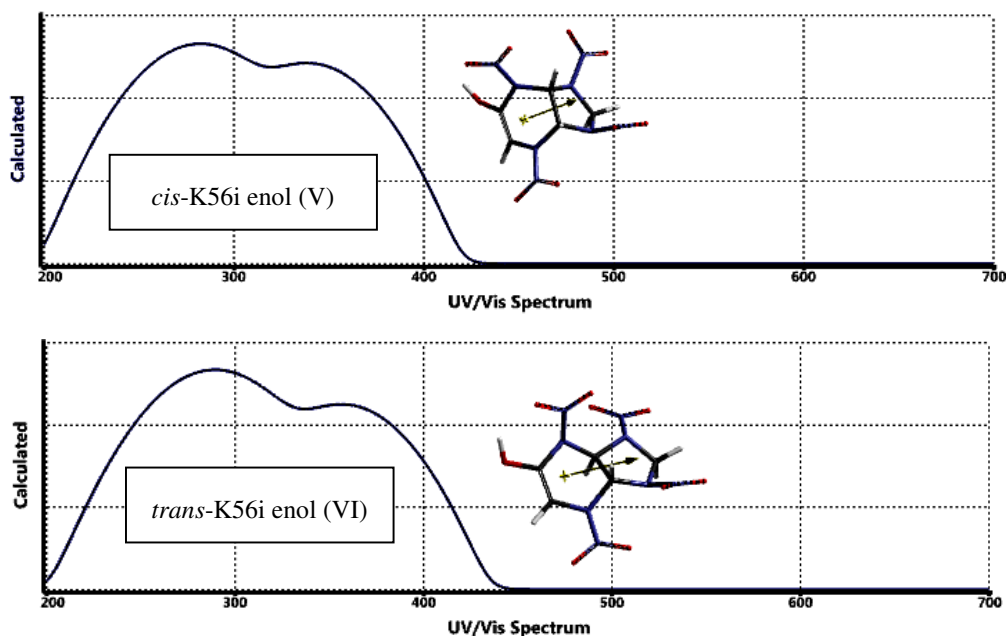
Energies in kJ/mol.

Figure 5 depicts the UV-VIS spectra of the enol forms V and VI. The enol forms have two  $\lambda_{\max}$  values and their spectra extend above 400 nm.

### Interfrontier molecular orbital energies

Table 3 shows the HOMO ( $\epsilon_{\text{HOMO}}$ ) and LUMO ( $\epsilon_{\text{LUMO}}$ ) energies and the interfrontier molecular orbital energy gaps ( $\Delta\epsilon = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$ ) of the structures considered. The order of HOMO energies is II < I < IV < III < V < VI. Whereas the order of LUMO energies is I < IV < III < VI < II < V. Consequently,  $\Delta\epsilon$  values follow the order of II > IV > I > III > V > VI.





**Figure 5.** UV-VIS spectra of the enol tautomers considered.

**Table 3.** The HOMO, LUMO energies and the interfrontier molecular orbital energy gaps of the structures considered.

Structure	$\epsilon_{\text{HOMO}}$	$\epsilon_{\text{LUMO}}$	$\Delta\epsilon$
<i>cis</i> -K56 (I)	-859.52	-342.46	517.06
<i>trans</i> -K56 (II)	-866.16	-317.07	549.09
<i>cis</i> -K56i (III)	-830.40	-323.80	506.6
<i>trans</i> -K56i (IV)	-851.73	-325.60	526.13
Enol <i>cis</i> (V)	-729.18	-315.54	413.64
Enol <i>trans</i> (VI)	-725.93	-318.49	407.44

Energies in kJ/mol.

It has been claimed that a reverse correlation exists between the impact sensitivity of an explosive and its HOMO-LUMO energy gap [27]. The present order of  $\Delta\epsilon$  values suggests that the impact sensitivities of them should follow the reverse order, namely VI > V > III > I > IV > II. Accordingly, the enolic structures (V and VI) should be more

sensitive than their corresponding keto (nitramide) tautomers (III and IV) (although the enols are less stable, see Tables 1 and 2). The structure I (five-membered ring nitramide) is more stable than II (six-membered ring nitramide). On the other hand, I is more sensitive to impact stimulus than its *trans* isomer II.

#### 4. Conclusion

The present DFT treatise has indicated that all the *cis* structures (including the enolic ones) are more stable than their *trans* counterparts. The interfrontier molecular orbital energy gaps ( $\Delta\epsilon$ ) (which have four nitramine groups) of all the *cis* forms of carbonyl containing species (I and II) are narrower than their *trans* forms (II and IV). Whereas, in the case of enolic structures the *trans* form has smaller  $\Delta\epsilon$  value. The enolic ones are less stable than their carbonyl containing ones (having one nitramide and three nitramine groups). As for the impact sensitivity and  $\Delta\epsilon$  relation, the *cis* isomers are more sensitive as compared to their *trans* forms, except the enolic ones.

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