ORIGINAL PAPER

A B3LYP and MP2(full) theoretical investigation into the strength of the C-NO$_2$ bond upon the formation of the molecule-cation interaction between Na$^+$ and the nitro group of nitrotriazole or its methyl derivatives

Qing-guo Wei · Wen-jing Shi · Fu-de Ren · Yong Wang · Jun Ren

Abstract The changes of bond dissociation energy (*BDE*) in the C–NO$_2$ bond and nitro group charge upon the formation of the molecule-cation interaction between Na$^+$ and the nitro group of 14 kinds of nitrotriazoles or methyl derivatives were investigated using the B3LYP and MP2(full) methods with the 6-311++G**, 6-311++G(2df,2p) and aug-cc-pVTZ basis sets. The strength of the C–NO$_2$ bond was enhanced in comparison with that in the isolated nitrotriazole molecule upon the formation of molecule-cation interaction. The increment of the C–NO$_2$ bond dissociation energy (ΔBDE) correlated well with the molecule-cation interaction energy. Electron density shifts analysis showed that the electron density shifted toward the C-NO$_2$ bond upon complex formation, leading to the strengthened C-NO$_2$ bond and the possibly reduced explosive sensitivity.

Keywords Bond dissociation energy in C-NO$_2$ bond · Molecule-cation interaction · MP2(full)

Q.-g. Wei
College of Mechatronic Engineering, North University of China, Taiyuan 030051, China

W.-j. Shi (✉)
The Third Hospital of Shanxi Medical University, Taiyuan 030053, China
e-mail: wenjingfd@126.com

F.-d. Ren (✉) · Y. Wang · J. Ren
College of Chemical Engineering and Environment, North University of China, Taiyuan 030051, China
e-mail: fdren888@126.com

Introduction

The search for new and thermally stable insensitive explosives has been a primary goal in the field of energetic material chemistry in order to avoid the catastrophic explosion in use and meet the requirement of military application [1, 2]. It has been extensively shown from many experimental and theoretical results that introducing cation into the structure of explosive can lead to a dramatic change of explosive sensitivity [3]. In 2005, the experimental sensitivity data indicated that the Co (III) / Ni (III) / Cu (II) complexes with mono-(5-nitro-*H*-tetrazolato-*N*) triammine were more friction sensitive than mono-(5-nitro-*H*-tetrazolato-*N*) triammine zinc (II) perchlorate [4]. In 2006, Talawar et al. found that the electrostatic spark sensitivity of explosives decreased in the order of AgN$_3$=nickel hydrazinium nitrate>PbN$_6$>mercury salt of 5-nitro tetrazole>cobalt hydrazinium nitrate>bis-5-nitrotetrazolato tetra amino cobalt (III) perchlorate [5]. Anniyappan et al. observed that the impact and friction sensitivities of potassium salt of FOX-7 were far higher than those of guanidinium salt [6]. In 2007, the investigation into the explosive properties of potassium salts of trinitrophloroglucinol indicated that, the more metal atoms that entered the molecular structure, the lower the sensitivity [7]. In 2009, Klapötke et al. observed that 5-nitriminotetrazole was sensitive toward outer stimuli but its copper complex was insensitive [8]. In 2010, copper (II) chlorate (VII) coordination polymer with 4-amino-1,2,4-triazole was characterized to be low-sensitive to friction (10 N) [9]. In 2011, Fischer et al. stated that the NH$_4^+$ cation strongly influenced the friction sensitivity of 1-nitratoethyl-5-nitriminotetrazole

[10]. In theoretical investigations, the electronic structure and relationship between structure and sensitivity of α-Pb(N$_3$)$_2$ were studied by *ab initio* method [11]. A report dealing with thermolysis of 5-nitro-2,4-dihydro-3*H*-1,2,4-triazole-3-one (NTO) and its salts was thoroughly reviewed. The metal complexes were found to be more insensitive than NTO [12]. All these results indicate indirectly that the molecule-cation interaction between the explosive molecule and cation strongly influences the sensitivity of explosive.

In nitro explosives, the X-NO$_2$ (X = C, N or O) bond is usually relatively weak, and the homolysis of the X-NO$_2$ bond might occur easily in the case of shock or impact. This phenomenon is known as "trigger linkage" and, in most cases, the X-NO$_2$ bond could be termed as "trigger bond" [2, 13–15]. Recently many researchers have found that, in some cases, the explosive sensitivity of nitro explosive exhibits a good linear relationship with the bond dissociation energy (*BDE*) of trigger bond or the charge of nitro group [16–22]. Song, Owens and Xiao et al. found that, the stronger the C-NO$_2$ trigger bond, the lower the explosive sensitivity turned [19, 23, 24]. Cao, Zhang and Rice et al. confirmed that the more positive the nitro group charge, the higher the shock sensitivity of a nitro compound was [17, 20, 21]. Tan et al. stated that, despite it needing a different shock initiation mechanism to interpret with different kinds of explosives, evaluating the shock sensitivity applying *BDE*s of the weakest X-NO$_2$ (X = C, N, O) bond and the Mulliken charges of nitro group could be used in wide ranges, including aliphatic nitro compounds, aromatic nitro compounds, nitramines and nitric acid esters [22]. These investigations show that the explosive sensitivities of nitro compound could be evaluated by the *BDE* of the X-NO$_2$ trigger bond and the charge of nitro group.

Since molecule-cation interaction strongly influences the explosive sensitivity and the explosive sensitivity shows a good linear relationship with the *BDE* of trigger bond or the charge of nitro group, the molecule-cation interaction might also influence the strength of the X-NO$_2$ trigger bond and the charge of nitro group. However, in the previous investigations, the influence of the molecule-cation interaction on the strength of the X-NO$_2$ bond was not considered. Thus, researchers believed that the cation only played a structure-creating role (i.e., coordinates other molecules) providing the stability. Furthermore, they declared that the complex needed only more energy to destroy the molecule-cation interaction in the process of the detonation [3]. Very recently we have investigated theoretically, for the first time, the influence of the molecule-cation interaction on the strength of trigger bond and the charge of nitro group for the 3,4-dinitropyrazole (DNP) complex with Na$^+$ using the B3LYP and MP2(full) methods. The result showed that the C-NO$_2$ trigger bond was strengthened and the explosive sensitivity might be reduced upon the formation of molecule-cation interaction [25].

As a follow-up to our investigation into the influence of molecule-cation interaction on the strength of the C-NO$_2$ bond, in this paper, we investigated systematically changes of the *BDE* in the C-NO$_2$ bond upon the formation of the molecule-cation interaction between Na$^+$ and the nitro group of 14 kinds of nitrotriazoles or methyl derivatives.

Most of the compounds containing triazole ring can be used as outstanding explosives because the heterocyclic ring system confers a high density, thermal stability, high nitrogen content, high volume of detonation products and insensitivity to impact [26, 27]. Recently various nitrotriazole explosives with the structural unit 1,2,3-triazole or 1,2,4-triazole have been synthesized and tested as insensitive high energy explosives [28–32]. Furthermore, lots of experimental and theoretical investigations have indicated that, for the nitrotriazole compounds, a key initiating step appears to be the rupture of the C-NO$_2$ bond, which might be as a "trigger linkage" [33–41]. The thermal decomposition mechanisms of hydrazine 3-nitro-1,2,4-triazol-5-one (HNTO) and dimethylamine salt of 3-nitro-1,2,4-triazol-5-one ((CH$_3$)$_2$NH$_2$C$_2$N$_4$O$_3$H) were studied by means of differential scanning calorimetry, thermogravimetry and derivative thermogravimetry. The results showed that the nitryl group broke away first from HNTO and (CH$_3$)$_2$NH$_2$C$_2$N$_4$O$_3$H [33, 34]. The thermal decomposition experiment for Co(H$_2$O)$_6$](NTO)$_2$·2H$_2$O indicated that ligand water was dissociated first and the NO$_2$ group had priority of leaving [35]. Wang et al. found that the direct scission of C-NO$_2$ was the initial step of the unimolecular decomposition of NTO at MP2/6-31G** level [36]. In 2010, a good linear correlation was found between the drop energy and the *BDE* of the C-NO$_2$ bond for 26 energetic compounds including 3-nitro-1,2,4-triazole-5-one and 4-methyl-3,5-dinitro-1,2,4-triazole, implying that these compounds ignited through the C-NO$_2$ dissociation mechanism [37]. Another linear correlation between the impact sensitivity $h_{50\%}$ and the ratio (*BDE*/*E*) of the *BDE* in the C-NO$_2$ bond to the total energy *E* was also confirmed using density functional theory for nine triazole energetic explosives [38]. Moreover, some results of population analysis also showed that the C-NO$_2$ bond was the weakest bond in some nitrotriazole compounds [33, 34]. Very recently, the C-NO$_2$ bond has been regarded as the trigger linkage in some nitrotriazoles [39]. These results suggest that the C-NO$_2$ bond might be broken preferentially and the nitro group might be easier to be dissociated when nitrotriazole are decomposed. The C-NO$_2$ bond dissociation energy in nitrotriazoles is possibly one of the important factors affecting the sensitivity.

The theoretical investigation on the changes of the *BDE* in the C-NO$_2$ bond upon the formation of the Na$^+$ complexes with nitrotriazole or its methyl derivatives might reveal, in a way, the nature of the change of sensitivity. It will be important for keeping, transporting, safe using, molecular design and synthesis of the important energetic nitrotriazole and its methyl derivatives.

Computational details

As a cost-effective approach, in most cases, geometry optimization by density functional theory (DFT) methodology is feasible for high energetic compounds. However, to investigate complexation energy, the MP2(full) method is more reliable [42–44]. In addition, a high quality basis set is crucial for calculating the properties of the complex [45, 46]. Taking all the above factors into account, we decided to use the DFT-B3LYP and MP2(full) methods with the 6-311++G**, 6-311++G (2df,2p) and aug-cc-pVTZ basis sets in this work.

All calculations were performed with Gaussian 03 programs [47]. All the nitrotriazole complexes with Na$^+$ were fully optimized using the DFT-B3LYP and MP2(full) methods with the 6-311++G** and 6-311++G(2df,2p) basis sets. The structures corresponding to the minimum energy points at the molecular energy hypersurface (NImag=0) were obtained. Single point energy calculations were carried out at the B3LYP/6-311++G**, B3LYP/6-311++G(2df,2p), MP2(full)/6-311++G**, MP2(full)/6-311++G(2df,2p) and MP2(full)/aug-cc-pVTZ levels. The shifts of the electron densities [48] that accompanied the formation of complex were displayed at MP2(full)/6-311++G** level.

The *BDE*s in the C-NO$_2$ bond were calculated at the B3LYP/6-311++G**, B3LYP/6-311++G(2df,2p), MP2 (full)/6-311++G**, MP2(full)/6-311++G(2df,2p) and MP2 (full)/aug-cc-pVTZ levels.

$$BDE = E_{(R\cdot)} + E_{(\cdot NO_2)}$$
$$- E_{(RNO_2)} for\ nitrotriazole\ molecule \qquad (1)$$

$$BDE = E_{(R\cdot)} + E_{(\cdot NO_2\cdots Na+)} - E_{(RNO_2\cdots Na+)} for\ complex \quad (2)$$

R· means the radical of triazole or its methyl derivative. The *BDE* was corrected with the basis set superposition error (BSSE) [49, 50] correction.

Molecule-cation interaction between Na$^+$ and the nitro group ($E_{int.}$) was expressed as follows:

$$E_{int.} = E_{(RNO_2\cdots Na+)} - E_{(RNO_2)} - E_{(Na+)}. \qquad (3)$$

$E_{int.}$ was also corrected with the BSSE and zero-point energy (ZPE) corrections.

The nitro group charge (Q_{NO2}) was calculated as Eq. 4.

$$Q_{NO_2} = Q_N + Q_{O1} + Q_{O2} \qquad (4)$$

The Q_N, Q_{O1} and Q_{O2} are the charges on the N and the O atoms, respectively.

Results and discussion

In this work, the studied Na$^+$ complexes of nitrotriazole with the structural unit 1,2,3-triazole are 4-nitro-1*H*-1,2,3-triazole Na$^+$ (I–1), 4-nitro-3*H*-1,2,3-triazole Na$^+$ (I–2), 1-methyl-4-nitro-1,2,3-triazole Na$^+$ (I–3), 3-methyl-4-nitro-1,2,3-triazole Na$^+$ (I–4), 5-methyl-4-nitro-1*H*-1,2,3-triazole Na$^+$ (I–5), 5-methyl-4-nitro-3*H*-1,2,3-triazole Na$^+$ (I–6) and 2-methyl-4-nitro-1,2,3-triazole-3-oxide Na$^+$ (I–7). Those with the structural unit 1,2,4-triazole are 3-nitro-1*H*-1,2,4-triazole Na$^+$ (II–1), 3-nitro-2*H*-1,2,4-triazole Na$^+$ (II–2), 1-methyl-3-nitro-1,2,4-triazole Na$^+$ (II–3), 2-methyl-3-nitro-1,2,4-triazole Na$^+$ (II–4), 5-methyl-3-nitro-1*H*-1,2,4-triazole Na$^+$ (II–5), 5-methyl-3-nitro-2*H*-1,2,4-triazole Na$^+$ (II–6) and 3-nitro-1*H*-1,2,4-triazole-5-oxide Na$^+$ (II–7). All the structures of complexes are shown in Fig. 1. The selected geometric parameters are listed in Table 1. The molecule-cation interaction energies and the *BDE*s in the C–NO$_2$ bond are presented in Tables 2 and 3, respectively. The nitro group charges are collected in Table 4.

Structure of the complex

From Fig. 1, the Na$^+$ complexes with nitrotriazole are C_s symmetry, and those with the methyl derivatives are C_1 symmetry. All the five membered triazole rings have planar geometry and the interatomic distances within the triazole ring are not equal. From Table 1, the O3 Na5 distance is in the range between 2.396 and 2.457 Å at MP2(full)/6-311++G** level, which is close to that in the molecule-cation interaction complex DNP Na$^+$ (2.438 Å) [25]. On the other hand, the N2-O3 bond length in complexes increases in comparison with that in the isolated nitrotriazole molecules. These results suggest that the molecule-cation interactions between Na$^+$ and the nitro group might be formed.

Interestingly, from Table 1, the bond length of the C-NO$_2$ bond in complexes decreases in comparison with that in the isolated nitrotriazole molecules at three levels of theory. In most cases, shortening of a bond length might lead to strengthening of the bond [51]. Thus, the C-NO$_2$ bond might turn stronger upon the formation of the molecule-cation interaction between Na$^+$ and the nitro group.
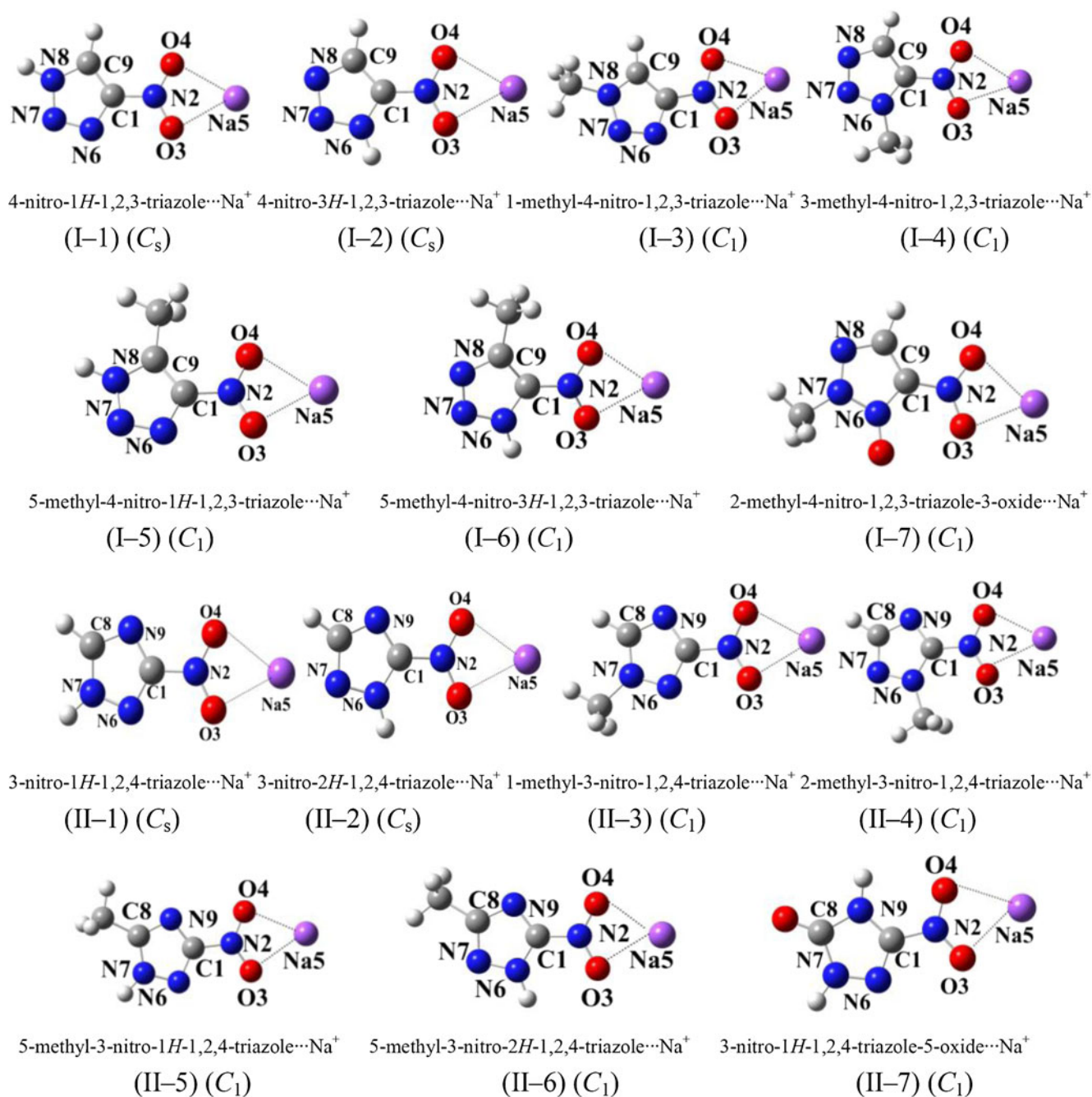
Fig. 1 Molecular structures of complexes at MP2(full)/6-311++G** level

Molecule-cation interaction and *BDE* in the C-NO₂ bond

From Table 2, the values of the molecule-cation inter-
action energies between Na⁺ and the nitro group calcu-
lated using the B3LYP method are larger than those
obtained from the MP2(full) method. As mentioned
above, the intermolecular interaction energy by the
MP2(full) method with the high quality basis set is
usually close to the experimental result. Therefore, the
results at the MP2(full)/aug-cc-pVTZ level were used to

elucidate the trends in the molecule-cation interaction
energies.

In the Na⁺ complexes with the 1,2,3-triazole unit, the
values of the molecule-cation interaction energies are
within the range of 90.4–135.8 kJ mol⁻¹ at MP2(full)/
aug-cc-pVTZ level (see Table 2). For the complexes
with the 1,2,4-triazole unit, they are stronger slightly
than those of the complexes with the 1,2,3-triazole unit,
up to the range of 100.7–141.5 kJ mol⁻¹. At five levels
of theory, the molecule-cation interaction decreases in

Table 1 Selected geometric parameters (in Å)[a]

Parameters	(I-1)	(I-2)	(I-3)	(I-4)	(I-5)	(I-6)	(I-7)
O3···Na5	2.379[b]	2.409	2.365	2.382	2.389	2.350	2.374
	2.367[c]	2.398	2.356	2.371	2.379	2.339	2.361
	2.418[d]	2.457	2.408	2.430	2.441	2.396	2.410
C1-N2	1.412[b]	1.396	1.408	1.393	1.386	1.402	1.385
	(1.450)[b]	(1.435)	(1.448)	(1.436)	(1.428)	(1.444)	(1.430)
	1.408[c]	1.393	1.404	1.390	1.383	1.398	1.381
	(1.445)[c]	(1.430)	(1.443)	(1.431)	(1.424)	(1.439)	(1.426)
	1.427[d]	1.412	1.425	1.410	1.407	1.420	1.393
	(1.452)[d]	(1.438)	(1.451)	(1.438)	(1.434)	(1.448)	(1.431)
N2-O3	1.233	1.240	1.235	1.244	1.251	1.237	1.242
	(1.217)	(1.221)	(1.217)	(1.223)	(1.224)	(1.217)	(1.221)
	1.232	1.237	1.234	1.242	1.249	1.235	1.240
	(1.215)	(1.219)	(1.215)	(1.221)	(1.222)	(1.215)	(1.219)
	1.235	1.239	1.236	1.241	1.246	1.236	1.245
	(1.225)	(1.228)	(1.226)	(1.229)	(1.230)	(1.225)	(1.230)
Parameters	(II-1)	(II-2)	(II-3)	(II-4)	(II-5)	(II-6)	(II-7)
O3···Na5	2.407	2.400	2.391	2.370	2.400	2.396	2.387
	2.396	2.388	2.380	2.358	2.381	2.384	2.374
	2.441	2.436	2.428	2.407	2.427	2.430	2.429
C1-N2	1.437	1.418	1.432	1.414	1.414	1.434	1.405
	(1.470)	(1.456)	(1.469)	(1.457)	(1.456)	(1.469)	(1.451)
	1.434	1.415	1.429	1.411	1.411	1.430	1.401
	(1.466)	(1.451)	(1.464)	(1.452)	(1.451)	(1.464)	(1.446)
	1.439	1.421	1.435	1.417	1.415	1.436	1.413
	(1.460)	(1.448)	(1.459)	(1.448)	(1.446)	(1.459)	(1.446)
N2-O3	1.232	1.230	1.235	1.234	1.231	1.234	1.238
	(1.219)	(1.212)	(1.219)	(1.214)	(1.213)	(1.220)	(1.215)
	1.230	1.228	1.232	1.232	1.230	1.232	1.235
	(1.217)	(1.211)	(1.217)	(1.212)	(1.211)	(1.217)	(1.213)
	1.237	1.236	1.238	1.238	1.238	1.238	1.239
	(1.228)	(1.225)	(1.229)	(1.226)	(1.226)	(1.229)	(1.225)

[a] The values in parenthesis are the geometric parameters for isolated nitrotriazole molecules

[b] At B3LYP/6-311++G** level

[c] At B3LYP/6-311++G(2df,2p) level

[d] At MP2(full)/6-311++G** level

the same order of (I-7)>(I-3)>(I-6)>(I-1)>(I-4)>(I-5)>(I-2) and (II-3)>(II-6)>(II-1)>(II-4)>(II-5)>(II-7)>(II-2).

Table 3 gives both uncorrected and corrected BDEs of the C-NO₂ bond after correction of the BSSE by means of the counterpoise method. The proportion of corrected BDEs for the complexes to their total BDEs, defined as [BDE-BDE$_{(BSSE)}$]/BDE, is only 2.59%, 1.73%, 7.49%, 6.84% and 6.88% at B3LYP/6-311++G**, B3LYP/6-311++G(2df,2p), MP2(full)/6-311++G**, MP2(full)/6-311++G(2d,p) and MP2(full)/aug-cc-pVTZ levels, respectively. These results indicate that the BSSE corrections for BDEs are not notable. In general, the BSSE corrections are not negligible. There is a standard computational protocol: only in the case of complete basis set, is the correction for BSSE not needed.

From Table 3, the BDEs in the C-NO₂ bond calculated using the B3LYP method are all lower than those obtained by the MP2(full) method. This result is expected: dispersion interaction is not accounted using B3LYP method but given by MP2 method. Thus, the MP2(full) method is more feasible to elucidate the trends in the calculated BDEs than the B3LYP method. However, recently many theoretical investigations have shown that the B3LYP method correctly describes the BDE value while the MP2 method cannot be used to adequately describe it [52–54]. In 1996, Jursic et al. found that, for the O-O and O-C bond dissociation energies, the MP2 model gave unsatisfactory results, and calculation with the DFT-B3LYP method was required [55]. In 2002, Budyka et al. found that electron correlation correction at the MP2/6-31G*//HF/6-31G* level overestimated the C-N BDE value by about 67 kJ mol^{-1} compared to experiment for PhNHCH₃, and B3LYP-calculated BDE value was in good agreement with experimental one [52]. For the C-H and N–H bonds in monocyclic aromatic molecules, the B3LYP method yields BDEs that were on average lower than experiment by ~5–10 kJ mol^{-1} while the MP2 BDEs calculated were about 72.0 kJ mol^{-1} higher than those from

Table 2 Molecule-cation interaction energy ($-E_{int.}$(kJ mol^{-1}))[a]

Parameters	(I-1)	(I-2)	(I-3)	(I-4)	(I-5)	(I-6)	(I-7)
B3LYP/6-311++G**	139.4	110.1	150.9	121.5	123.1	150.9	153.1
	(137.2)	(108.2)	(148.6)	(119.2)	(120.8)	(148.6)	(150.8)
	134.5	*106.4*	*146.6*	*117.3*	*117.9*	*146.1*	*148.0*
B3LYP/6-311++G(2df,2p)	140.2	110.2	151.8	122.9	124.0	151.8	154.3
	(136.7)	(106.7)	(148.2)	(119.3)	(120.3)	(148.3)	(150.6)
	134.1	*104.8*	*146.1*	*117.4*	*118.6*	*145.8*	*147. 9*
MP2(full)/6-311++G**	117.7	85.1	127.3	95.2	93.8	125.7	130.7
	(108.9)	(76.6)	(118.4)	(86.4)	(85.2)	(116.7)	(121.5)
MP2(full)/6-311++G(2df,2p)	121.6	89.4	131.4	99.7	98.4	129.9	134.4
	(114.4)	(82.5)	(124.1)	(92.5)	(91.2)	(122.5)	(126.9)
MP2(full)/aug-cc-pVTZ	122.9	90.4	130.1	115.1	98.0	129.3	135.8
	(111.8)	(80.7)	(126.7)	(104.3)	(81.7)	(112.6)	(128.0)
Parameters	(II-1)	(II-2)	(II-3)	(II-4)	(II-5)	(II-6)	(II-7)
B3LYP/6-311++G**	144.8	114.2	155.6	128.0	124.7	155.5	122.6
	(142.8)	(112.1)	(153.4)	(125.7)	(122.9)	(153.5)	(121.3)
	139.5	*110.1*	*150.7*	*123.7*	*121.3*	*150.3*	*119.0*
B3LYP/6-311++G(2df,2p)	145.7	114.8	161.1	128.6	125.6	156.0	120.4
	(142.5)	(111.4)	(162.8)	(125.1)	(122.2)	(152.6)	(116.9)
	139.3	*109.4*	*160.2*	*123.0*	*120.4*	*149.4*	*114.5*
MP2(full)/6-311++G**	128.8	96.8	137.8	108.5	105.9	137.4	98.6
	(120.0)	(88.4)	(129.7)	(99.9)	(97.7)	(128.6)	(90.1)
MP2(full)/6-311++G(2df,2p)	132.5	101.6	141.8	113.0	110.6	141.6	102.5
	(125.3)	(94.1)	(134.6)	(105.8)	(103.6)	(134.3)	(95.5)
MP2(full)/aug-cc-pVTZ	131.9	100.7	141.5	115.3	110.4	141.1	101.9
	(116.4)	(85.5)	(125.8)	(104.8)	(101.0)	(94.9)	(86.4)

[a] The values in the parenthesis are BSSE-corrected ($-E_{int.(BSSE)}$), and those with BSSE and ZPE ($-E_{int.(BSSE-ZPE)}$) correction are in italic

experiment [56]. Furthermore, Barckholtz et al. found that the MP2 calculations of the radical species suffered from significant spin contamination, with $<S^2>$ as high as 1.4 for the radicals formed from benzene and the azabenzenes [56]. We also found that, for the MP2 method, the values of $<S^2>$ were up to 1.15 for the nitropyrazole radical, while for the B3LYP method, they were about 0.75 [25]. The data from the MP2 method could not be close to experimental values perhaps due to the serious spin contamination. In the title compounds, for the MP2 method, the values of $<S^2>$ are up to 1.14 for the 14 kinds of triazole radicals, while for the B3LYP method, they are about 0.75. Therefore, in this paper, the B3LYP/6-311++G(2df,2p) method is selected to elucidate the trends in the calculated *BDEs*.

As can be seen from Table 3, the order of the *BDEs* in the C-NO$_2$ bond for the Na$^+$ complexes with the 1,2,3-triazole unit is I-6>I-7>I-3>I-1>I-5>I-4>I-2 at B3LYP/6-311++G (2df,2p) level. For the complexes of 1,2,4-triazole, the *BDEs* are the same order of II-6≈II-3>II-1>II-4>II-5>II-7>II-2 at five levels. Except for the complexes I-3, I-6 and II-6, the order of the *BDEs* is in accordance with that of the molecule-cation interaction energy. Furthermore, the *BDEs* in the Na$^+$ complexes with nitrotriazole are weaker than those in the systems with the methyl derivative.

Interestingly, from Table 3, the *BDEs* of the C-NO$_2$ bond in complexes are about 1.5 times larger than those in the corresponding isolated nitrotriazole molecules. This result suggests that the strength of the C-NO$_2$ bond is enhanced upon the formation of molecule-cation interaction between Na$^+$ and the nitro group, which is in agreement with the analysis of structure and similar to the result of the investigation on the DNP complex with Na$^+$ [25]. The stronger the C-NO$_2$ trigger bond in nitro explosives, in most cases, the lower the explosive sensitivity turned [19, 23, 24]. Thus, it is possible that the explosive sensitivity is reduced upon the formation of molecule-cation interaction if the C-NO$_2$ bonds are proved to be the trigger linkages in all the title compounds and breaking of the C-NO$_2$ bond is the mechanism for initiating detonation. It should be noted that, for the C-nitro explosives, breaking of the C-NO$_2$ bond is not the only mechanism for initiating detonation. There are many others, such as nitro-nitrite isomerization, formation of nitrosoaromatic intermediates, reactions of the −NO$_2$ group with an *ortho* substituent, etc. [57–59]. For example, Yim et al. found that the departing NO$_2$ could capture a H atom from the NTO ring to form HONO, by either a concerted bond breaking mechanism or by a bimolecular reaction between the NO$_2$ group and the triazol ring [60]. In fact, many factors

Table 3 Bond dissociation energy (BDE (kJ mol^{-1})) in the C-NO$_2$ bond[a]

Parameters	(I-1)	(I-2)	(I-3)	(I-4)	(I-5)	(I-6)	(I-7)
B3LYP/6-311++G**	441.6	412.7	457.9	426.89	437.9	465.5	458.4
	(431.2)	(402.8)	(447.5)	(416.4)	(427.3)	(454.4)	(447.5)
	306.7	*308.6*	*309.8*	*307.6*	*317.6*	*316.3*	*306.5*
	(298.9)	*(301.5)*	*(302.1)*	*(299.9)*	*(309.9)*	*(308.2)*	*(298.8)*
B3LYP/6-311++G(2df,2p)	448.9	421.3	465.3	432.4	443.3	470.4	467.3
	(444.5)	(417.8)	(460.8)	(426.0)	(435.7)	(462.7)	(463.2)
	313.6	*316.3*	*316.3*	*315.7*	*324.3*	*322.4*	*314.0*
	(309.5)	*(312.5)*	*(312.2)*	*(312.5)*	*(319.2)*	*(317.2)*	*(310.9)*
MP2(full)/6-311++G**	504.9	479.8	510.8	523.3	497.4	555.9	559.8
		(476.5)	(487.2)			(519.4)	(519.3)
	385.0	*392.6*	*385.3*	*423.7*	*416.8*	*395.6*	*426.9*
	(376.4)	*(380.1)*	*(379.0)*	*(391.6)*	*(387.4)*	*(388.7)*	*(389.3)*
MP2(full)/6-311++G(2df,2p)	519.4	496.8	525.2	505.2	519.5	573.4	580.2
	(488.7)	(466.5)	(494.0)	(472.6)	(492.1)	(542.2)	(544.4)
	434.9	*399.6*	*401.1*	*408.7*	*455.8*	*418.4*	*449.2*
	(407.2)	*(379.4)*	*(375.5)*	*(378.3)*	*(431.9)*	*(393.4)*	*(416.5)*
MP2(full)/aug-cc-pVTZ	541.1	519.4	547.3	529.2	548.2	600.6	603.2
	(509.4)		(514.7	(494.1		593.2	590.2
	428.9	*465.2*	*423.9*	*433.3*	*479.0*	*436.2*	*465.4*
	(411.5)	*(439.8)*	*(405.7)*	*(417.0)*	*(453.7)*	*(406.5)*	*(431.3)*
Parameters	(II-1)	(II-2)	(II-3)	(II-4)	(II-5)	(II-6)	(II-7)
B3LYP/6-311++G**	427.7	398.2	443.6	414.6	412.5	443.7	411.5
	(417.7)	(388.5)	(433.6)	(403.9)	(402.8)	(433.7)	(401.6)
	289.8	*290.0*	*294.0*	*289.5*	*291.8*	*293.6*	*287.0*
	(282.4)	*(282.9)*	*(286.6)*	*(281.6)*	*(284.7)*	*(286.3)*	*(279.7)*
B3LYP/6-311++G(2df,2p)	429.8	407.6	447.7	424.8	417.6	446.6	416.4
	(424.7)	(406.3)	(442.9)	(422.6)	(411.6)	(440.7)	(411.8)
	293.5	*298.7*	*294.4*	*299.0*	*299.2*	*298.6*	*294.7*
	(289.2)	*(296.3)*	*(290.3)*	*(297.5)*	*(295.5)*	*(294.1)*	*(290.9)*
MP2(full)/6-311++G**	506.3	481.1	515.7	497.5	493.2	518.2	449.4
	(473.1)	(447.6)	(481.9)	(461.3)	(459.2)	(484.7)	(415.7)
	343.3	*344.8*	*347.5*	*342.6*	*346.8*	*345.7*	*345.5*
	(313.7)	*(316.1)*	*(311.0)*	*(312.9)*	*(313.8)*	*(314.0)*	*(311.9)*
MP2(full)/6-311++G(2df,2p)	484.6	462.1	493.7	477.5	473.9	497.1	465.5
	(454.7)	(432.0)	(462.9)	(444.8)	(443.1)	(466.6)	(434.9)
	358.5	*363.0*	*374.2*	*363.6*	*360.9*	*377.5*	*360.3*
	(330.5)	*(334.8)*	*(351.4)*	*(333.3)*	*(332.4)*	*(358.1)*	*(332.0)*
MP2(full)/aug-cc-pVTZ	537.4	515.2	514.4	500.3	495.3	517.4	487.6
	(496.4)	(485.1)	(483.0)	(465.8)	(462.6)	(485.0)	(454.8)
	377.6	*384.7*	*390.2*	*386.8*	*382.5*	*380.6*	*378.2*
	(352.3)	*(357.1)*	*(369.3)*	*(357.0)*	*(354.1)*	*(352.6)*	*(349.1)*

[a] The values in the parenthesis are BSSE-corrected ($-E_{int.(BSSE)}$), and those of the BDEs for isolated nitrotriazole molecules are in italic

are related to sensitivity. Therefore, the strengthened C-NO$_2$ bond does not in all cases lead to the reduced sensitivity.

As can be seen from Tables 2 and 3, the value of the increment of the BDE in the C-NO$_2$ bond in complex in comparison with that of the corresponding isolated nitrotriazole molecule (ΔBDE) is very close to the molecule-cation interaction between Na$^+$ and the nitro group. For instance, for the Na$^+$ complexes with the 1,2,3-triazole unit, the difference between the interaction energy and the value of ΔBDE is no more than 6.0 kJ mol^{-1} at B3LYP/6-311++G (2df,2p) level. This is pleasing information! It tells us that the explosive complex needs more energy to destroy the molecule-cation interaction and to counteract the increment of the BDE in the C-NO$_2$ bond in the process of detonation.

Table 4 Charges (in e) of nitro group[a]

Parameters	(I-1)	(I-2)	(I-3)	(I-4)	(I-5)	(I-6)	(I-7)
Mulliken charge[b]	−0.207	−0.306	−0.240	−0.382	−0.359	−0.259	−0.313
	(−0.218)	(−0.261)	(−0.230)	(−0.299)	(−0.292)	(−0.258)	(−0.273)
Mulliken charge[c]	−0.249	−0.303	−0.270	−0.363	−0.364	−0.321	−0.310
	(−0.263)	(−0.288)	(−0.264)	(−0.319)	(−0.318)	(−0.308)	(−0.288)
Mulliken charge[d]	−0.292	−0.374	−0.218	−0.357	−0.328	−0.237	−0.368
	(−0.194)	(−0.237)	(−0.205)	(−0.278)	(−0.255)	(−0.228)	(−0.246)
Natural charge[d]	−0.357	−0.383	−0.366	−0.400	−0.418	−0.386	−0.398
	(−0.267)	(−0.268)	(−0.273)	(−0.276)	(−0.286)	(−0.280)	(−0.260)
APT charge[c]	−0.037	−0.017	−0.038	−0.033	−0.036	−0.054	−0.032
	(−0.035)	(−0.015)	(−0.034)	(−0.003)	(0.015)	(−0.035)	(0.044)
Parameters	(II-1)	(II-2)	(II-3)	(II-4)	(II-5)	(II-6)	(II-7)
Mulliken charge[b]	−0.191	−0.263	−0.214	−0.320	−0.346	−0.273	−0.304
	(−0.224)	(−0.250)	(−0.247)	(−0.279)	(−0.288)	(−0.262)	(−0.241)
Mulliken charge[c]	−0.239	−0.280	−0.262	−0.333	−0.375	−0.339	−0.300
	(−0.268)	(−0.271)	(−0.277)	(−0.304)	(−0.306)	(−0.297)	(−0.253)
Mulliken charge[d]	−0.303	−0.345	−0.235	−0.323	−0.358	−0.292	−0.361
	(−0.227)	(−0.241)	(−0.251)	(−0.272)	(−0.286)	(−0.269)	(−0.230)
Natural charge[d]	−0.328	−0.348	−0.341	−0.368	−0.360	−0.337	−0.373
	(0.253)	(0.242)	(−0.259)	(−0.259)	(−0.256)	(−0.258)	(−0.251)
APT charge[c]	−0.059	−0.013	−0.005	−0.027	−0.017	−0.061	−0.041
	(0.060)	(0.013)	(0.060)	(−0.016)	(−0.013)	(0.064)	(0.010)

[a] The values in parenthesis are the charges for isolated nitrotriazole molecules
[b] At B3LYP/6-311++G** level
[c] At B3LYP/6-311++G(2df,2p) level
[d] At MP2(full)/6-311++G** level

That is to say, if the C-NO$_2$ bonds are the trigger linkages, the origin of the change of explosive sensitivity is not only due to the formation of the molecule-cation interaction but also due to the increment of the C-NO$_2$ bond dissociation energy. In the previous investigations, the influence of the molecule-cation interaction on the strength of the C-NO$_2$ bond was not considered, and only the formation of molecule-cation interaction was regarded as the origin of the change of explosive sensitivity [3].

Two good linear relationships between $E_{int.}$ and ΔBDE for the Na$^+$ complexes with the 1,2,3-triazole and 1,2,4-triazole units were shown in Fig. 2 at B3LYP/6-311++G(2df,2p) level. They fitted Eqs. 5 and 6, respectively:

$$\Delta BDE = 0.924(-E_{int.}) + 14.151 \quad (5)$$

$$\Delta BDE = 1.102(-E_{int.}) + 7.637 \quad (6)$$

ΔBDE and $(-E_{int.})$ are in kJ·mol^{-1}. This result shows again that the molecule-cation interaction between Na$^+$ and the nitro group has an important effect on the strength of the C-NO$_2$ bond.

Charge analysis

Lots of recent investigations have indicated that, the more negative charges the nitro groups carry, the less sensitive the explosives are [20–22]. From Table 4, except for the complexes I-1, II-1 and II-3, the Mulliken charges of nitro group in complexes are more negative than those in the corresponding isolated nitrotriazole molecules. For the natural charge and APT charge, the values in all the complexes are also more negative than those of the corresponding nitrotriazoles. In particular,
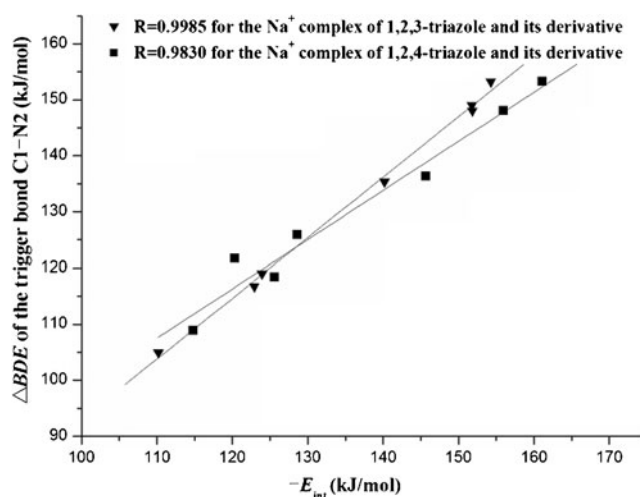

Fig. 2 The increment of the C-NO$_2$ bond dissociation energy (ΔBDE) in complex in comparison with the isolated nitrotriazole molecules versus the molecule-cation interaction energy ($-E_{int.}$) at B3LYP/6-311++G(2df,2p) level

in 5-methyl-4-nitro-1H-1,2,3-triazole, 2-methyl-4-nitro-1,2,3-triazole-3-oxide, 3-nitro-1H-1,2,4-triazole, 3-nitro-2H-1,2,4-triazole, 1-methyl-3-nitro-1,2,4-triazole, 5-methyl-3-nitro-2H-1,2,4-triazole and 3-nitro-1H-1,2,4-triazole-5-oxide, the values of the APT charge are positive. However, in their corresponding complexes I-5, I-7, II-1, II-2, II-3, II-6 and II-7, they turn negative. These results show that much negative charge concentrates on the nitro group upon the formation of complexes. According to Rice et al. [21], it is possible that

the sensitivity is reduced with the formation of complexes, which is in accordance with the above analysis.

Analysis of the electron density shifts

In order to obtain deeper insight into the origin of the change of the $C-NO_2$ bond strength, the analysis of the electron density shifts which accompanied the formation of the molecule-cation interaction by the initial nitro-triazoles followed by addition of Na^+ was carried out.

Fig. 3 Shifts of electron density as a result of the formation of complexes
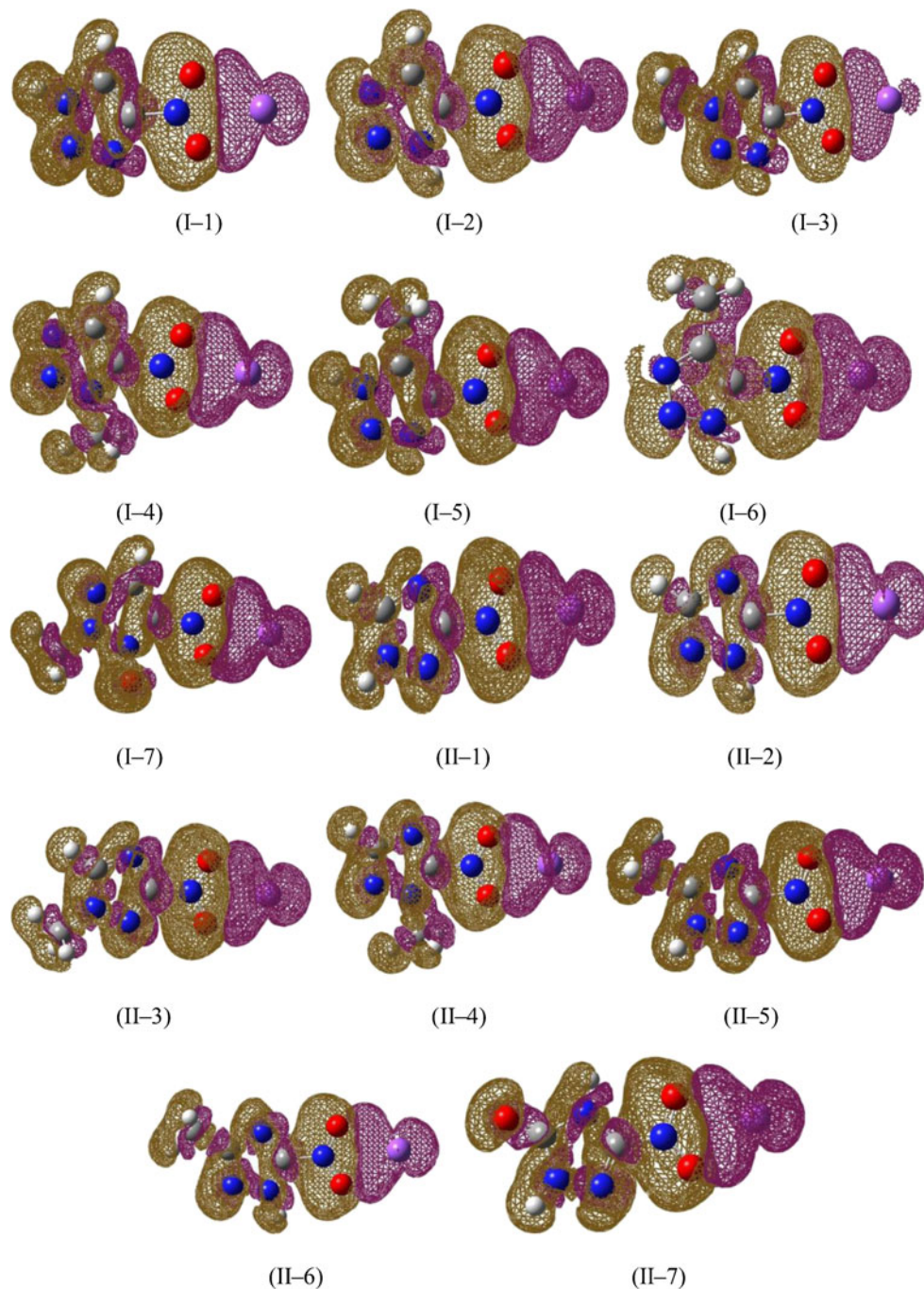
For this purpose, the electron density shift was calculated by evaluating the difference between the total electron densities of complexes and individual monomers. It was defined as:

$$\rho_{shift} = \rho_{(RNO_2\cdots Na+)} - \rho_{RNO_2} - \rho_{Na+}.$$

The shifts of electron density were illustrated in Fig. 3. Purple regions represented the accumulation of additional electron density; yellow regions indicated loss of density.

As can be seen from Fig. 3, for each complex, the Na^+ cation is filled with much purple area and the nitro group $-NO_2$ is around the yellow region, suggesting that the electron density of the nitro group is lost toward Na^+ and the molecule-cation interaction forms.

It is interesting that much purple area is around the C atom of the C-NO$_2$ bond and extends toward the C-NO$_2$ bond, showing that the electron density shifts toward the C atom and the C-NO$_2$ bond. It is well known that, the more intensive the electron between two atoms, the more chances of overlapping. As a result, the strength of the C-NO$_2$ bond is improved. Thus, we can draw a conclusion that the electron density shifts toward the C-NO$_2$ bond upon the formation of the molecule-cation interaction between Na^+ and the nitro group, leading to the enhanced C-NO$_2$ bond and the possibly reduced sensitivity of explosive.

Conclusions

We investigated the changes of the *BDE* in the C-NO$_2$ bond upon the formation of the molecule-cation interaction between Na^+ and the nitro group of 14 kinds of nitrotriazoles or methyl derivatives using the B3LYP and MP2(full) methods. The strength of the C-NO$_2$ bond was enhanced upon complexation. The value of ΔBDE correlated well with the molecule-cation interaction energy. The electron density shifted toward the C-NO$_2$ bond upon complex formation, leading to the strengthened C-NO$_2$ bond and the possibly reduced explosive sensitivity.

References

1. Richard RM, Ball DW (2008) J Mol Struct (THEOCHEM) 851:284–293
2. Qiu L, Gong XD, Zheng J, Xiao HM (2009) J Hazard Mater 166:931–938
3. Ren WZ, Wang ZS (2004) Explosive Theory and Practice. China North Chemical Industries Corp Press, Nanjing
4. Talawar MB, Agrawal AP, Asthana SN (2005) J Hazard Mater A 120:25–35
5. Talawar MB, Agrawal AP, Anniyappan M, Wani DS, Bansode MK, Gore GM (2006) J Hazard Mater B 137:1074–1078
6. Anniyappan M, Talawar MB, Gore GM, Venugopalan S, Gandhe BR (2006) J Hazard Mater B 137:812–819
7. Wang L, Chen H, Zhang T, Zhang J, Yang L (2007) J Hazard Mater 147:576–580
8. Klapötke TM, Stierstorfer J, Weber B (2009) Inorg Chim Acta 362:2311–2320
9. Cudziło S, Nita M (2010) J Hazard Mater 177:146–149
10. Fischer N, Klapötke TM, Stierstorfer J, Wiedemann C (2011) Polyhedron 30:2374–2386
11. Ju XH, Xiao HM, Ji GF (2003) Acta Chim Sin 11:1720–1723
12. Singh G, Felix SP (2003) J Mol Struct 649:71–83
13. Liu Y, Gong XD, Wang LJ, Wang GX, Xiao HM (2011) J Phys Chem A 115:1754–1762
14. Pospíšil M, Vávra P, Concha MC, Murray JS, Politzer P (2010) J Mol Model 16:895–901
15. Delpuech A, Cherville J (1979) Propell Explos Pyrot 4:121–128
16. Li JS (2010) J Hazard Mater 180:768–772
17. Cao CZ, Gao S (2007) J Phys Chem B 111:12399–12402
18. Zhao J, Cheng XL, He B, Yang XD (2006) Struct Chem 17:501–507
19. Song XS, Cheng XL, Yang XD, He B (2006) Propell Explos Pyrot 31:306–310
20. Zhang CY, Shu YJ, Huang YG, Zhao XD, Dong HS (2005) J Phys Chem B 109:8978–8982
21. Rice BM, Hare JJ (2002) J Phys Chem A 106:1770–1783
22. Tan BS, Long XP, Peng RF, Li HB, Jin B, Chu SJ, Dong HS (2010) J Hazard Mater 183:908–912
23. Owens FJ, Jayasuriya K, Abrahmsen L, Politzer P (1985) Chem Phys Lett 116:434–438
24. Xiao HM (1994) Molecular orbital theory of nitro-compound. Publishing House of Defense Industry, Peking
25. Du S, Wang Y, Chen L, Shi W, Ren F, Li Y, Wang J, Cao D (2012) J Mol Model 18:2105–2115
26. Xue H, Gao Y, Wamley BT, Shreeve JM (2005) Chem Mater 17:191–198
27. Sikder AK, Geetha M, Sarwade DB, Agrrawal JP (2001) J Hazard Mater A 82:1–12
28. Vereshchyagin LI, Pokatilov FA, Kizhnyaev VN (2008) Chem Heterocycl Compd 44:3–25
29. Sukhanov GT, Sukhanova AG, Lukin AY (2007) Chem Heterocycl Compd 43:786–792
30. Sukhanova AG, Sakovich GV, Sukhanov GT (2008) Chem Heterocycl Compd 44:1368–1373
31. Duddu R, Dave PR, Damavarapu R, Surapaneni R, Parrish D (2009) Synth Commun 39:4282–4288
32. Darren LN, Michael AH, Herbert HH (2003) J Energ Mater 21:57–62
33. Yi JH, Zhao FQ, Ren YH, Xu SY, Ma HX, Hu RZ (2010) J Therm Anal Calorim 100:623–627
34. Ma HX, Song JR, Hu RZ, Zhai GH, Xu KZ, Wen ZY (2004) J Mol Struct (THEOCHEM) 678:217–222
35. Song JR, Ma HX, Huang J, Hu RZ (2004) Thermochim Acta 416:43–46
36. Wang YM, Chen C, Lin ST (1999) J Mol Struct (THEOCHEM) 460:79–102
37. Li JS (2010) J Phys Chem B 114:2198–2202
38. Zhao J, Xu D, Cheng X (2010) Struct Chem 21:1235–1240
39. Ravi P, Babu BK, Tewari SP (2012) J Mol Model. doi:10.1007/s00894-012-1515-z
40. Yi JH, Zhao FQ, Gao HX, Xu SY, Wang MC, Hu RZ (2008) J Hazard Mater 153:261–268
41. Pourmortazavi SM, Rahimi-Nasrabadi M, Kohsari I, Hajimirsadeghi SS (2011) J Therm Anal Calorim. doi:10.1007/s10973-011-1845-6

42. Richard RM, Ball DW (2007) J Mol Struct (THEOCHEM) 806:113–120
43. Suwattanamala A, Magalhaes AL, Gomes JANF (2005) Chem Phys 310:109–122
44. Ruan C, Yang Z, Hallowita N, Rodgers MT (2005) J Phys Chem A 109:11539–11550
45. Tanaka N, Tamezane T, Nishikiori H, Fujii T (2003) J Mol Struct (THEOCHEM) 631:21–28
46. Novoa JJ, Mota F (2000) Chem Phys Lett 318:345–354
47. Frisch MJ et al. (2003) Gaussian 03, Revision B.03. Gaussian, Inc., Pittsburgh, PA
48. Scheiner S, Kar T (2002) J Phys Chem A 106:1784–1789
49. Duijineveldt FB, Duijineveldt-van de Rijdt JCMV, Lenthe JHV (1994) Chem Rev 94:1873–1885
50. Boys SF, Bernardi F (1970) Mol Phys 19:553–566
51. Macaveiu L, Göbel M, Klapötke TM, Murray JS, Politzer P (2010) Struct Chem 21:139–146
52. Budyka MF, Zyubina TS, Zarkadis AK (2002) J Mol Struct (THEOCHEM) 594:113–125
53. Jursic BS (1996) J Mol Struct (THEOCHEM) 366:103–108
54. Brinck T, Haeberlin M, Jonsson M (1997) J Am Chem Soc 119:4239–4244
55. Jursic BS, Martin RM (1996) Int J Quantum Chem 59:495–501
56. Barckholtz C, Barckholtz TA, Hadad CM (1999) J Am Chem Soc 121:491–500
57. Brill TB, James KJ (1993) Chem Rev 93:2667–2692
58. Murray JS, Concha MC, Politzer P (2009) Mol Phys 107:89–97
59. Politzer P, Lane P, Murray JS (2011) Cent Eur J Energ Mater 8:39–52
60. Yim WL, Liu ZF (2001) J Am Chem Soc 10:2243–2250