

A comparative theoretical investigation into the strength of the trigger-bond in the Na^+ , Mg^{2+} and HF complexes involving the nitro group of $\text{R}-\text{NO}_2$ ($\text{R}=-\text{CH}_3$, $-\text{NH}_2$ and $-\text{OCH}_3$) or the $\text{C}=\text{C}$ bond of $(\text{E})-\text{O}_2\text{N}-\text{CH}=\text{CH}-\text{NO}_2$

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Abstract A comparative theoretical investigation into the change in strength of the trigger-bond upon formation of the Na^+ , Mg^{2+} and HF complexes involving the nitro group of RNO_2 ($\text{R}=-\text{CH}_3$, $-\text{NH}_2$, $-\text{OCH}_3$) or the $\text{C}=\text{C}$ bond of $(\text{E})-\text{O}_2\text{N}-\text{CH}=\text{CH}-\text{NO}_2$ was carried out using the B3LYP and MP2(full) methods with the 6-311++G**, 6-311++G(2df,2p) and aug-cc-pVTZ basis sets. Except for the $\text{Mg}^{2+}\cdots\pi$ system with $(\text{E})-\text{O}_2\text{N}-\text{CH}=\text{CH}-\text{NO}_2$ (i.e., $\text{C}_2\text{H}_2\text{N}_2\text{O}_4\cdots\text{Mg}^{2+}$), the strength of the trigger-bond $\text{X}-\text{NO}_2$ ($\text{X}=\text{C}$, N or O) was enhanced upon complex formation. Furthermore, the increment of bond dissociation energy of the $\text{X}-\text{NO}_2$ bond in the Na^+ complex was far greater than that in the corresponding HF system. Thus, the explosive sensitivity in the former might be lower than that in the latter. For $\text{C}_2\text{H}_2\text{N}_2\text{O}_4\cdots\text{Mg}^{2+}$, the explosive sensitivity might also be reduced. Therefore, it is possible that introducing cations into the structure of explosives might be more efficacious at reducing explosive sensitivity than the formation of an intermolecular hydrogen-bonded complex. AIM, NBO and electron density shifts analyses showed that the electron density shifted toward the $\text{X}-\text{NO}_2$ bond upon complex formation, leading to a strengthened $\text{X}-\text{NO}_2$ bond and possibly reduced explosive sensitivity.

Keywords Intermolecular hydrogen bond · Molecule-cation interaction · Bond dissociation energy in trigger-bond · MP2(full)

Introduction

The search for new and thermally stable insensitive explosive has been a primary goal in the field of energetic material chemistry in order to avoid catastrophic explosion in use and to meet the requirements of military application [1–4]. Therefore, much attention has been paid recently to investigation of the relationship between the sensitivity and structure of energetic compounds [5–17].

For nitro explosives, the $\text{X}-\text{NO}_2$ ($\text{X}=\text{C}$, N or O) bond is usually relatively weak, and, in most cases, homolysis of the $\text{X}-\text{NO}_2$ bond occurs easily in the case of shock or impact. Therefore, the $\text{X}-\text{NO}_2$ bond in nitro explosives is often termed the “trigger bond” [3, 5, 7, 18]. The results of many experimental and theoretical studies have shown that, sometimes, the stronger the $\text{X}-\text{NO}_2$ trigger-bond, the lower the explosive sensitivity becomes [13, 15]. Furthermore, explosive sensitivity often exhibits a good linear relationship with bond dissociation energy (BDE) in the $\text{X}-\text{NO}_2$ trigger bond [9, 10, 12–18]. Interestingly, for explosive complexes, we have shown recently for the first time that the BDE of the $\text{C}-\text{NO}_2$ trigger bond was increased in comparison with that in the monomer. Furthermore, the intermolecular hydrogen-bonding or molecule-cation interaction energy correlated well with the increment of the BDE in the $\text{C}-\text{NO}_2$ trigger bond. Therefore, it was proposed that both the intermolecular hydrogen-bonding and molecule-cation interactions might reduce explosive sensitivity owing to the increased BDE of the trigger-bond in the complex [19, 20]. This begs the question:

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which kind of interaction is more efficacious to reduce sensitivity, hydrogen bonds or molecule-cation interactions?

The strength of covalent bonds might change upon complex formation because shifts in electron density (electron rearrangements) could occur among chemical bonds. The bond will be strengthened by the accumulation of electron density and weakened when electron density is lost. For nitro explosives, explosive sensitivity might be reduced upon accumulation of electron density in the X–NO₂ trigger-bond, and increased if electron density is lost because, as mentioned above, sensitivity sometimes exhibits a linear relationship with trigger-bond strength.

In our recent investigations into the intermolecular hydrogen-bonded and molecule-cation systems of nitrotriazole, atoms-in-molecules (AIM) [21], natural bond orbital (NBO) [22] and electron density shifts [23] analyses have shown that the electron density shifts toward the C–NO₂ trigger-bond upon complex formation, leading to a strengthened C–NO₂ bond. Furthermore, the increase in BDE and shifts in the electron density of the C–NO₂ bond in the Na⁺ complex are far more notable than those in the corresponding HF complex, perhaps leading to lower explosive sensitivity in the former compared to that in the latter. From these results, it was concluded that molecular cation interactions between Na⁺ and the nitro group of nitrotriazoles are more efficacious at reducing sensitivity of nitrotriazoles than the corresponding hydrogen-bonding interactions involving HF [19, 20].

In this paper, our interest was to clarify whether introducing cations into the structure of nitro explosive is more efficacious to reduce explosive sensitivity than the formation of the intermolecular hydrogen-bonded complex. For this purpose, both hydrogen-bonded and molecule-cation interaction complexes are considered.

For hydrogen-bonded and molecule-cation interaction systems with the nitro explosive, two kinds of interactions should be included: (1) the conventional interaction between the oxygen atom of the nitro group and H–X (X=F, Cl, O, etc.) or Mⁿ⁺ (M=Li, Na, Mg, etc.); (2) the interaction with π electrons, i.e., that between the multiple bond and H–X or Mⁿ⁺. Therefore, not only the simple model compounds R–NO₂ (R=–CH₃, –NH₂ and –OCH₃) but also six π -electron donors CH₂=CH–NO₂, CH₂=N–NO₂, HN=N–NO₂, (E)-O₂N–CH=CH–NO₂, O₂N–CH=N–NO₂ and O₂N–N=N–NO₂ were selected. For the Na⁺ or HF complexes with R–NO₂ (R=–CH₃, –NH₂ and –OCH₃), the structures corresponding to the minimum energy points at the molecular energy hypersurface (NImag=0) were obtained at HF/6-311++G** level. However, for each of the Na⁺··· π or F–H··· π complexes with the six π -electron donors, in which Na⁺ or the F–H bond was lying perpendicular to the double-bonds (C=C, C=N and N=N) and pointing toward to their midpoints, several imaginary frequencies were found. Then,

the Mg²⁺··· π , Al³⁺··· π , and X–H··· π (X=Cl, Br) complexes with the above six π -electron donors were chosen. Among these T-shaped structures, only the Mg²⁺··· π complex between Mg²⁺ and the C=C double bond of (E)-O₂N–CH=CH–NO₂ was found (NImag=0) at the HF/6-311++G** level. The other T-shaped complexes were either optimized as structures in which the cation and X–H bond were not lying perpendicular to the double bond but pointing toward to the oxygen atom of the nitro group, or it was difficult to find local minima perhaps due to the flat potential wells. Therefore, in this work, only the Na⁺ and HF complexes involving the nitro group of R–NO₂ (R=–CH₃, –NH₂ and –OCH₃) as well as the Mg²⁺··· π system with the C=C bond of (E)-O₂N–CH=CH–NO₂ were considered.

In this article, we present a comparative theoretical investigation into the strength of the trigger-bond in HF and Na⁺ complexes with the nitro group of RNO₂ (R=–CH₃, –NH₂, –OCH₃) or the Mg²⁺··· π system involving the C=C bond of (E)-O₂N–CH=CH–NO₂. An analysis of explosive sensitivity was also carried out. This theoretical study will be useful in the search for and synthesis of new and thermally stable insensitive mixed explosives that is critical to the storage, transport and safe use of energetic materials.

Computational details

According to our previous investigations, density functional theory (DFT) can be used to optimize the geometry of high energetic materials, while, for complexation energy, the MP2(full) method with high quality basis set is more reliable [1, 19, 20]. Therefore, we used the DFT-B3LYP and MP2(full) methods with the 6-311++G**, 6-311++G(2d,p) and aug-cc-pVTZ basis sets in this work.

All calculations were performed with Gaussian 03 programs [24]. The monomers CH₃–NO₂ (nitromethane, NM), NH₂–NO₂ (nitramide, NA), CH₃O–NO₂ (methyl nitrate, MN) and the corresponding Na⁺ and HF complexes as well as (E)-O₂N–CH=CH–NO₂ (C₂H₂N₂O₄) and its T-shaped system with Mg²⁺ were fully optimized using the DFT-B3LYP and MP2(full) methods with the 6-311++G** and aug-cc-pVTZ 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**, MP2(full)/6-311++G**, MP2(full)/6-311++G(2d,p) and MP2(full)/aug-cc-pVTZ levels, respectively. NBO [22] analysis and shifts in electron density [23] were investigated at the MP2(full)/6-311++G** level. The topological charge density was displayed by the AIM method [21] using the AIMPAC program [25] at the MP2(full)/aug-cc-pVTZ level.

The BDE in the C–NO₂, N–NO₂ or O–NO₂ bond was calculated at the B3LYP/6-311++G**, MP2(full)/6-311++

G**, MP2(full)/6-311++G(2d,p) and MP2(full)/aug-cc-pVTZ levels, respectively. BDE is defined as:

$$BDE = E_{(R\cdot)} + E_{(\cdot NO_2)} - E_{(RNO_2)} \text{ for monomer} \quad (1)$$

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

where $R\cdot$ means $\cdot CH_3$, $\cdot NH_2$, $\cdot OCH_3$ or $\cdot C_2H_2NO_2$ radical. BDE was corrected with the basis set superposition error (BSSE) [26, 27].

The interaction energy (E_{int}) was investigated by defining the energy difference between the complex and the isolated monomers.

$$E_{int} = E_{(RNO_2 \cdots Na^+ / Mg^{2+} / HF)} - E_{(RNO_2)} - E_{(Na^+ / Mg^{2+} / HF)} \quad (3)$$

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

The charge on the nitro group, Q_{NO_2} , was calculated as follows:

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

where Q_N , Q_{O1} or Q_{O2} is the charge on the N or O atom of the nitro group, respectively.

Results and discussion

The structures of seven complexes are shown in Fig. 1. Selected geometric parameters and charges on the nitro group are listed in Table 1. The interaction energies and the BDEs in trigger bonds are presented in Table 2. The

results of AIM are given in Table 3. The geometric parameters and BDEs in the trigger bond for monomers are given in the [Supplementary Material](#).

Structure of the complex

From Fig. 1, $NM \cdots Na^+$ and $MN \cdots Na^+$ are C_s symmetry, and $NA \cdots Na^+$ is C_{2v} symmetry. $C_2H_2N_2O_4 \cdots Mg^{2+}$ and all the HF complexes are C_1 symmetry. From Table 1, for $NM \cdots Na^+$, $NA \cdots Na^+$ and $MN \cdots Na^+$, the $O6 \cdots Na7$ distances are within the range of 2.338–2.461 Å at MP2(full)/aug-cc-pVTZ level. Furthermore, the N5–O6 bond length in complex increases in comparison with that in the isolated monomer (see [Supplementary Material](#)). These results suggest that a molecule-cation interaction between Na^+ and the nitro group might be formed. In $C_2H_2N_2O_4 \cdots Mg^{2+}$, the distance $Mg7 \cdots \pi$ is found to be 2.751 Å at the MP2(full)/aug-cc-pVTZ level, suggesting the formation of a $Mg^{2+} \cdots \pi$ interaction between Mg^{2+} and the C=C double bond. For $NM \cdots HF$, $NA \cdots HF$ and $MN \cdots HF$, at the MP2(full)/aug-cc-pVTZ level, the values of the $O6 \cdots H7$ distance just fall into the common accepted distances of the $O \cdots H$ hydrogen bond. The increment of the N5–O6 bond length upon complex formation is 0.005, 0.004 and 0.003 Å, respectively. Furthermore, the H7–F8 bond length in complex also increases in comparison with that in the monomer. These results suggest that intermolecular hydrogen-bonding interaction might be formed.

Interestingly, as shown in Table 1, except for $C_2H_2N_2O_4 \cdots Mg^{2+}$, the bond length of the X–NO₂ trigger-bond decreases in complex in comparison with that in the isolated monomer at three levels of theory (see [Supplementary Material](#)). Furthermore, the values of the decrease in the molecule-cation interaction complexes are larger than those in the corresponding HF systems. For example, the decrease of the C1–N5, N1–N5 and O1–N5 bond lengths in the HF complexes is 0.003, 0.015 and

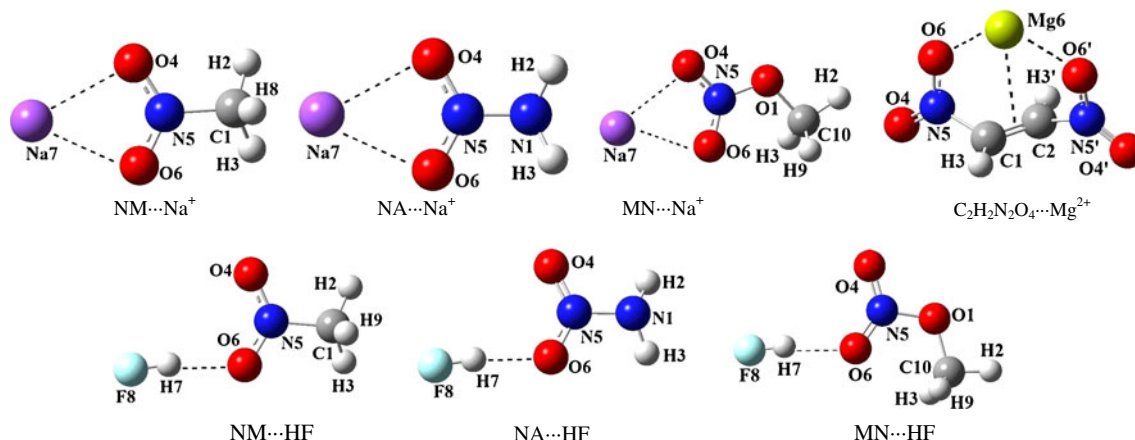


Fig. 1 Molecular structures of complexes at MP2(full)/aug-cc-pVTZ level

Table 1 Selected bond length (Å), charges (e) of nitro group in complexes

Parameter	NM \cdots Na $^+$	NA \cdots Na $^+$	MN \cdots Na $^+$	C ₂ H ₂ N ₂ O ₄ \cdots Mg $^{2+}$	NM \cdots HF	NA \cdots HF	MN \cdots HF
O6/ π \cdots Na7/Mg7/H7	2.437 ^a	2.407	2.504	2.775 ^b 2.023 ^b	1.799	1.801	1.840
	2.464 ^c	2.437	2.523	2.698 2.003	1.837	1.841	1.870
	2.440 ^d	2.388	2.461	2.751 2.048	1.780	1.790	1.823
H7–F8 ^e					0.936 ^a	0.935	0.932
					0.927 ^c	0.926	0.924
					0.932 ^d	0.931	0.929
C1/N1/O1–N5	1.494 ^a	1.324	1.339	1.495	1.500	1.376	1.398
	1.485 ^c	1.339	1.333	1.490	1.488	1.385	1.389
	1.473 ^d	1.321	1.326	1.481	1.475	1.369	1.379
N5–O6	1.229 ^a	1.239	1.227	1.295	1.232	1.233	1.221
	1.235 ^c	1.237	1.230	1.294	1.234	1.230	1.221
	1.230 ^d	1.232	1.225	1.276	1.229	1.227	1.217
Q_{NO_2}	-0.217 ^f	-0.054	-0.400	0.277	-0.219	-0.109	-0.272
	-0.261 ^g	-0.043	-0.407	0.334	-0.249	-0.073	-0.263
	-0.372 ^h	-0.056	-0.140	0.008	-0.355	-0.012	-0.073
	-0.349 ⁱ	-0.283	-0.076	-0.198	-0.316	-0.179	0.009
	-0.279 ^l	0.054	0.117		-0.282	0.058	0.188

^a At B3LYP/6-311++G** level^b The first means the Mg7 \cdots π distance and the second is the distance of O6 \cdots Mg7^c At MP2(full)/6-311++G** level^d At MP2(full)/aug-cc-pVTZ level^e The H–F bond length in monomer is 0.922, 0.916 and 0.920 Å at the B3LYP/6-311++G**, MP2(full)/6-311++G** and MP2(full)/aug-cc-pVTZ levels, respectively^f Mulliken charge at B3LYP/6-311++G** level^g Mulliken charge at MP2(full)/6-311++G** level^h Mulliken charge at MP2(full)/aug-cc-pVTZ levelⁱ Natural charge at MP2(full)/6-311++G** level^l APT charge at B3LYP/6-311++G** level

0.023 Å, while that in the corresponding Na $^+$ systems is up to 0.005, 0.063 and 0.076 Å at MP2(full)/aug-cc-pVTZ level, respectively. In most cases, shortening of a bond length might lead to strengthening of the bond [28]. Therefore, the X–NO₂ bond become stronger upon complex formation. Furthermore, the X–NO₂ bond in the molecule-cation interaction complex might become stronger than that in the corresponding hydrogen-bonded system. These results suggest that the explosive sensitivity in the molecule-cation interaction complex might be lower than that in the corresponding hydrogen-bonded system, and that introducing cations into the structure of explosives might be more efficacious at reducing sensitivity.

In C₂H₂N₂O₄ \cdots Mg $^{2+}$, the C1–N5 bond is elongated in comparison with that in C₂H₂N₂O₄ at three levels of theory (see [Supplementary Material](#)), suggesting that the strength of the C1–N5 bond is weakened upon complex formation. The NO₂ group is in the C1–C2–H3 plane in the isolated C₂H₂N₂O₄ molecule, while in C₂H₂N₂O₄ \cdots Mg $^{2+}$ the angle

by which the NO₂ group is rotated out of the C1–C2–H3 plane is 73.17° at MP2(full)/aug-cc-pVTZ level. Thus, the “ π - π_3^4 ” delocalization system of the –CH=CH–NO₂ moiety might be destroyed due to the rotation of the NO₂ group and the π -electron rearrangement upon complex formation, leading to an elongation of the C1–N5 bond.

Interaction energies and BDEs in the X–NO₂ bond

From Table 2, the values of the interaction energies calculated using the B3LYP method are larger than those obtained from the MP2(full) method. Since the interaction energy given by the MP2(full) method with the high quality basis set is usually close to the experimental result, the values at MP2(full)/aug-cc-pVTZ level were used to elucidate trends in interaction energies. At the MP2(full)/aug-cc-pVTZ level, the intermolecular H-bonding interaction energies in the HF complexes are within the range of 20.48–27.19 kJ mol $^{-1}$, and the molecule-cation interaction energies

Table 2 Interaction energy [$-E_{\text{int}}(\text{kJ mol}^{-1})$] and bond dissociation energy [BDE (kJ mol^{-1})] in complex. Values in the parenthesis are BSSE-corrected [$-E_{\text{int}}(\text{BSSE})$] results

Parameter	NM \cdots Na $^+$	NA \cdots Na $^+$	MN \cdots Na $^+$	C ₂ H ₂ N ₂ O ₄ \cdots Mg $^{2+}$	NM \cdots HF	NA \cdots HF	MN \cdots HF
$-E_{\text{int}}$	122.12 ^b	135.97	109.46	567.75	28.91	28.08	21.33
	(120.21) ^b	(133.58)	(107.39)	(563.23)	(26.44)	(25.26)	(18.76)
	117.28 ^{a,b}	132.03 ^a	104.27 ^a	553.50 ^a	18.90 ^a	18.01 ^a	11.98 ^a
	110.93 ^c	118.45	98.06	553.60	23.82	22.55	16.67
	(102.22) ^c	(108.66)	(89.30)	(550.82)	(17.39)	(15.79)	(9.64)
	99.30 ^c	105.97	85.39	541.37	13.27	12.89	5.30
	114.60 ^d	122.96	102.75	475.76	24.79	23.56	17.57
	(108.11) ^d	(115.92)	(95.93)	(458.74)	(19.67)	(18.21)	(12.33)
	113.11 ^e	124.07	114.48	499.35	27.19	26.31	20.48
BDE _{C1/N1/O1-N5}	(99.32) ^e	(108.54)	(109.23)	(484.20)	(22.00)	(21.11)	(15.16)
	399.2 ^b	370.5	262.1	493.1	307.9	259.4	179.9
	(388.8) ^b	(358.7)	(253.4)	(483.5)	(302.4)	(250.0)	(177.3)
	415.0 ^c	376.1	265.9	510.4	345.3	287.5	199.2
	(390.1) ^c	(340.3)	(230.3)	(506.0)	(320.2)	(254.8)	(166.6)
	419.6 ^d	382.4	288.7	548.8	351.8	294.5	222.5
	(400.1) ^d	(356.1)	(261.8)	(511.7)	(332.6)	(270.8)	(197.8)
	417.6 ^e	413.3		593.8	367.5	322.4	
	(398.4) ^e	(361.9)		(566.9)	(347.6)	(301.2)	

^a Results with BSSE and ZPE [$-E_{\text{int}}(\text{BSSE-ZPE})$] correction^b At B3LYP/6-311++G** level^c At MP2(full)/6-311++G** level^d At MP2(full)/6-311++G(2d,p) level^e At MP2(full)/aug-cc-pVTZ level

in the corresponding Na $^+$ systems are up to the range of 113.11–124.07 kJ mol $^{-1}$. For C₂H₂N₂O₄ \cdots Mg $^{2+}$, the interaction energy can be up to 499.35 kJ mol $^{-1}$, i.e., four times larger than that in the Na $^+$ system. It should be noted that, except for

the Mg $^{2+}\cdots\pi$ interaction, the molecule-cation interaction between Mg $^{2+}$ and the nitro group might also be formed in C₂H₂N₂O₄ \cdots Mg $^{2+}$, accompanied by a short O6 \cdots Mg7 distance [2.048 Å at the MP2(full)/aug-cc-pVTZ level].

Table 3 Selected bond critical point (BCP) properties (in a.u.) in complexes at MP2(full)/aug-cc-pVTZ level

Parameter	NM \cdots Na $^+$	NA \cdots Na $^+$	MN \cdots Na $^+$	C ₂ H ₂ N ₂ O ₄ \cdots Mg $^{2+}$	NM \cdots HF	NA \cdots HF	MN \cdots HF
$\rho_{\text{BCP(O6}/\pi\cdots\text{Na7/Mg7/H7)}$	0.0144	0.0152	0.0158	0.0123 0.0388	0.0255	0.0250	0.0227
$\nabla^2\rho_{\text{BCP(O6}/\pi\cdots\text{Na7/Mg7/H7)}$	0.0886	0.0962	0.1004	0.0458 0.2993	0.1197	0.1193	0.1115
$\varepsilon_{\text{BCP(O6}/\pi\cdots\text{Na7/Mg7/H7)}$	0.0576	0.0436	0.0021	NA 0.0766	0.0546	0.0585	0.0595
$\rho_{\text{BCP(C1/N1/O1-N5)}}$ ^a	0.2296	0.3963	0.4079	0.2548	0.2408	0.3628	0.3582
$\nabla^2\rho_{\text{BCP(C1/N1/O1-N5)}}$ ^a	-0.0216	-1.0287	-0.8598	-0.5585	-0.2501	-0.8782	-0.6466
$\varepsilon_{\text{BCP(C1/N1/O1-N5)}}$ ^a	0.0754	0.3454	0.1650	0.1509	0.0744	0.2544	0.1472
$\rho_{\text{BCP(N5-O6)}}$ ^b	0.5062	0.5042	0.5180	0.4572	0.5056	0.5107	0.5200
$\nabla^2\rho_{\text{BCP(N5-O6)}}$ ^b	-1.2789	-1.1809	-1.2455	-1.0707	-1.2731	-1.2345	-1.2698
$\varepsilon_{\text{BCP(N5-O6)}}$ ^b	0.1339	0.1301	0.1427	0.1056	0.1312	0.1324	0.1260

^a The values of $\rho_{\text{BCP(C1/N1/O1-N5)}}$ of the trigger bonds C1–N5, N1–N5 and O1–N5 in the monomers NM, NA and MN are 0.2436, 0.3528 and 0.3391 a.u. at MP2(full)/aug-cc-pVTZ level, those of $\nabla^2\rho_{\text{BCP(C1/N1/O1-N5)}}$ are -0.3453, -0.8316 and -0.5620 a.u., and those of $\varepsilon_{\text{BCP(C1/N1/O1-N5)}}$ are 0.0731, 0.2327 and 0.1413 a.u.. In C₂H₂N₂O₄, $\rho_{\text{BCP(C1-N5)}}$, $\nabla^2\rho_{\text{BCP(C1-N5)}}$ and $\varepsilon_{\text{BCP(C1-N5)}}$ is 0.2585, -0.4493 and 0.0516 a.u., respectively

^b The values of $\rho_{\text{BCP(N5-O6)}}$ in the monomers NM, NA, MN and C₂H₂N₂O₄ are 0.5117, 0.5199, 0.5306 and 0.5071 a.u. at MP2(full)/aug-cc-pVTZ level, those of $\nabla^2\rho_{\text{BCP(N5-O6)}}$ are -1.2833, -1.2622, -1.3049 and -1.2500 a.u., and those of $\varepsilon_{\text{BCP(N5-O6)}}$ are 0.1336, 0.1333, 0.1251 and 0.1306 a.u., respectively

Table 2 also gives both uncorrected and corrected BDEs in the X–NO₂ bond after correction of the BSSE by means of the counterpoise method [26, 27]. For each level of theory, the proportion of corrected BDEs in the HF or Na⁺ complexes to their total BDEs, defined as $[BDE - BDE_{(BSSE)}] / BDE$, is no more than 10.00 %, indicating that the BSSE correction for BDE is not notable. In fact, in general, the BSSE corrections are not negligible. Only in case of the complete basis set, is the correction for BSSE not needed [27].

From Table 2, for the BDE in the X–NO₂ bond, the values calculated using the B3LYP method are all lower than those obtained by the MP2(full) method. This might be due to the fact that the dispersion interaction is not accounted for using the B3LYP method but is given by the MP2 method. The MP2(full) method is thus better suited to elucidate the trends in the calculated BDEs than the B3LYP method. However, some theoretical investigations have shown that the B3LYP method correctly describes BDE values while, due to the serious spin contamination, the MP2 method cannot be used to adequately describe BDEs [29–32]. In this work, the value of $\langle S^2 \rangle$ was up to 1.1 for $\cdot\text{CH}_3$, $\cdot\text{NH}_2$, $\cdot\text{OCH}_3$ and $\cdot\text{C}_2\text{H}_2\text{NO}_2$ radicals with the MP2 method while the spin contamination was negligible for the B3LYP method ($\langle S^2 \rangle = 0.75$). According to previous investigations [19, 20], the B3LYP/6-311++G** method was selected to elucidate trends in the calculated BDEs.

From Table 2, the BDEs of the X–NO₂ bond in the NM, NA and MN complexes are larger than those in the corresponding isolated monomers (see Supplementary Material), suggesting that the strength of the X–NO₂ bond is enhanced upon complex formation. In most cases, the stronger the X–NO₂ trigger bond in nitro explosives, the lower the explosive sensitivity [18, 33]. Therefore, it is possible that explosive sensitivity is reduced upon complex formation. This is in accordance with previous many experimental and theoretical results [17, 34–44].

As can be seen from Table 2, at four levels, the BDEs of the X–NO₂ bonds in the HF complexes are far weaker than those in the systems with Na⁺. For example, at the B3LYP/6-311++G** level, the BDE of the C–NO₂ bond in NM \cdots HF is only 307.9 kJ mol⁻¹ while it becomes 399.2 kJ mol⁻¹ in NM \cdots Na⁺. This result suggests that, in comparison with that of the isolated monomer, the increment of the BDE (ΔBDE) of the X–NO₂ bond in the Na⁺ complex is far greater than that in the corresponding HF complex. For instance, for the NM complex with HF, the increment of the BDE in the C–NO₂ bond is 24.1 kJ mol⁻¹ at B3LYP/6-311++G** level, while in the molecule-cation interaction complex NM \cdots Na⁺, it is up to 115.4 kJ mol⁻¹. The ΔBDE in molecule-cation interaction complex is four times larger than that in the corresponding hydrogen-bonded system. Furthermore, at B3LYP/6-311++G** level, the proportion of the increment of the BDE to the corresponding

BDE in monomer (see Supplementary Material), defined as $\Delta\text{BDE} / \text{BDE}_{\text{mono}}$, falls within the ranges of 40.67 % – 61.01 % and 8.48 % – 11.35 % for the molecule-cation interaction complexes and hydrogen-bonded systems, respectively. These results again indicate that, upon complex formation in molecule-cation interaction, ΔBDE is more notable. The molecule-cation interaction complex needs far more energy to counteract the increment of the bond dissociation energy in X–NO₂ bond in the process of detonation than the corresponding hydrogen-bonded system. Thus, the explosive sensitivity in the former might be far lower than that in the latter. Therefore, it is possible that introducing cations into the structure of explosives might be more efficacious at reducing explosive sensitivity than the formation of the intermolecular hydrogen-bonded complex, in accordance with the analysis of structure.

It should be noted that breaking of the X–NO₂ bond is not the only mechanism for initiating detonation. There might be many others for nitro explosive molecules, such as formation of nitrosoaromatic intermediates, reactions of the –NO₂ group with an ortho substituent, etc. [45–48]. Additionally, many factors are involved in sensitivity [33]. Therefore, the strengthened X–NO₂ bond does not lead in all cases to reduced sensitivity. It should also be noted that, in some cases, introducing cation into the structure of explosive might increase explosive sensitivity [33, 49].

From Table 2, for C₂H₂N₂O₄ \cdots Mg²⁺, the BDE in the C–NO₂ bond obtained from Eq. (2) is 493.1 kJ mol⁻¹ at the B3LYP/6-311++G** level. It is worth mentioning that, in C₂H₂N₂O₄ \cdots Mg²⁺, there is one Mg²⁺ \cdots π interaction and two Mg²⁺ \cdots O molecule-cation interactions between Mg²⁺ and the nitro group (see Fig. 1). Therefore, the result of the BDE calculated according to Eq. (2) should be close to the sum of one Mg²⁺ \cdots π interaction, one molecule-cation interaction and the “real” BDE of the C1–N5 bond. To estimate the “real” BDE of the C1–N5 bond in C₂H₂N₂O₄ \cdots Mg²⁺, we carried out the calculations on the Mg²⁺ \cdots π interaction in the reference system Mg²⁺ \cdots CH₂=CH₂ ($R_{\text{Mg}^{2+}\cdots\pi} = 2.775$ Å) and the Mg²⁺ \cdots O molecule-cation interaction in the Mg²⁺ complex involving the nitro group of the reference molecule CH₂=CH–NO₂ ($R_{\text{Mg}^{2+}\cdots\text{O}} = 2.023$ Å). At the B3LYP/6-311++G** level, the BDEs are ~100 and ~250 kJ mol⁻¹, respectively. Thus, the “real” BDE of the C1–N5 bond in C₂H₂N₂O₄ \cdots Mg²⁺ might be close to ~150 kJ mol⁻¹, which is lower than that in the C₂H₂N₂O₄ monomer (287.3 kJ mol⁻¹). This result shows that the strength of the C1–N5 bond is weakened upon complex formation, in agreement with the analysis of the structure of C₂H₂N₂O₄ \cdots Mg²⁺. Note that, since the Mg²⁺ \cdots π and two Mg²⁺ \cdots O molecule-cation interactions are formed in the complex, in the process of detonation C₂H₂N₂O₄ \cdots Mg²⁺ needs energy to break not only the C–NO₂ trigger-bond but also the Mg²⁺ \cdots π and Mg²⁺ \cdots O molecule-cation interactions. According to the above analysis,

the energy used to break the C–NO₂ bond and the Mg²⁺⋯π and Mg²⁺⋯O molecule-cation interactions is just that obtained from Eq. (2) for C₂H₂N₂O₄⋯Mg²⁺. This energy is far larger than that in the isolated C₂H₂N₂O₄ molecule. Therefore, explosive sensitivity might also be reduced upon the formation of the C₂H₂N₂O₄⋯Mg²⁺ complex. In other words, although the “real” BDE of the trigger-bond C1–N5 in C₂H₂N₂O₄⋯Mg²⁺ is lower than that in C₂H₂N₂O₄, the explosive sensitivity might be reduced upon complex formation due to the formation of the additional strong Mg²⁺⋯π and Mg²⁺⋯O molecule-cation interactions.

AIM, NBO and charge analyses of nitro group

According to our AIM results, for each of the HF complexes, there is a bond path linking the H7 atom with the O6 atom of the nitro group accompanied by a bond critical point (BCP) (see Fig. 1). From Table 3, the values of electron density $\rho_{\text{BCP}(\text{O6}\cdots\text{H7})}$ fall into the common values for H-bonds (0.002–0.04 au) [21]. Furthermore, the values of their Laplacians $\nabla^2\rho_{\text{BCP}}$ are all positive, indicating a typical closed-shell type of interaction. These results are in accordance with the topological properties of normal hydrogen bonds [21]. Like HF complexes, for each of the Na⁺ systems, there is also a bond path linking the Na⁺ cation with the oxygen atom of the nitro group accompanied by a BCP. The values of $\rho_{\text{BCP}(\text{O6}\cdots\text{Na7})}$ are within the range of 0.0144–0.0158 a.u.. Moreover, their Laplacians $\nabla^2\rho_{\text{BCP}}$ are also positive. These are basically similar to the topological properties of the molecule-cation interaction. The Mg²⁺⋯π interaction is also suggested by the small $\rho_{\text{BCP}(\pi\cdots\text{Mg7})}$ and positive $\nabla^2\rho_{\text{BCP}(\pi\cdots\text{Mg7})}$ value.

As can also be seen from Table 3, the electron density ρ_{BCP} at the N1/O1–N5 trigger-bond in the complex is larger than that in monomer. Charge density at the BCP of a given bond can be used as an estimator of bond strength. The reason is that the energy difference between the radicals and initial molecule depends mainly on the strength of the bond

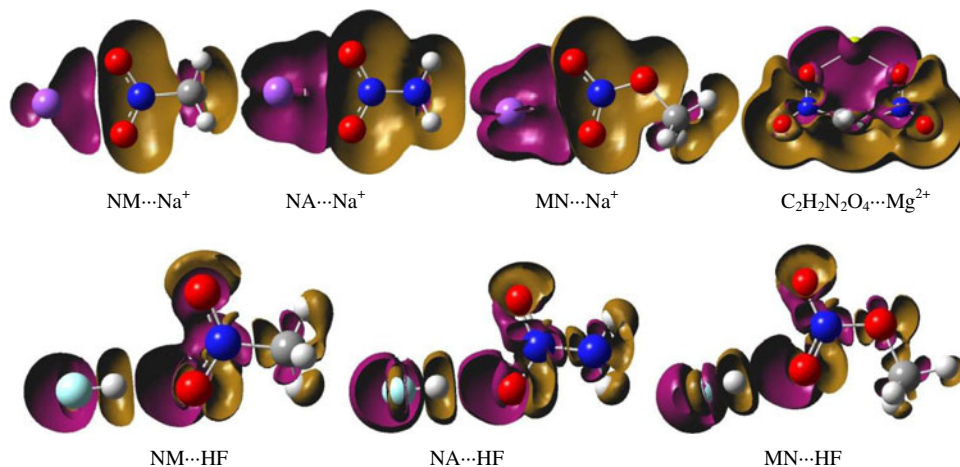
broken [50, 51]. Therefore, the strength of the N1/O1–N5 trigger-bond is increased and explosive sensitivity might be decreased upon complex formation.

Furthermore, except for NM⋯Na⁺, the value of $\rho_{\text{BCP}(\text{C1}/\text{N1}/\text{O1}-\text{N5})}$ in the molecule-cation complex is larger than that in the corresponding hydrogen-bonded system, suggesting that the increase of $\rho_{\text{BCP}(\text{C1}/\text{N1}/\text{O1}-\text{N5})}$ upon complex formation in the molecule-cation interaction complex is greater than that in the hydrogen-bonded system. In other words, introducing cations into the structure of the explosive is more efficacious at increasing electron density ρ_{BCP} at the X–NO₂ trigger bond, and thus more efficacious at reducing explosive sensitivity. These results are in agreement with the analyses of structure and energy.

In order to probe further into the origin of the change in electron density ρ_{BCP} at the X–NO₂ trigger bond, we carried out NBO analysis. A notable delocalization interaction was found between LP[O6(p)] and the trigger bond C1/N1/O1–N5 anti-bond orbitals. $E^{(2)}_{\text{LP}(\text{O6}(\text{p}))\rightarrow\sigma(\text{C1}/\text{N1}/\text{O1}-\text{N5})^*}$ is 56.54, 82.59 and 121.45 kJ mol^{−1} in NM⋯Na⁺, NA⋯Na⁺ and MN⋯Na⁺, respectively. In the corresponding hydrogen-bonded complexes, it is predicted to be 58.51, 93.51 and 144.61 kJ mol^{−1}, respectively. For C₂H₂N₂O₄⋯Mg²⁺, it is 81.97 kJ mol^{−1}. These results show that the electron density shifts from the oxygen atom of the nitro group toward the X–NO₂ trigger bond. As a result, the strength of the trigger bond C1/N1/O1–N5 is improved and the sensitivity might be reduced, which is in accordance with the analyses of structure, energy and AIM. This should be at least one of the reasons why the electron density ρ_{BCP} at the N1/O1–N5 trigger bond is increased upon complex formation.

In most cases, the more negative the charge carried by the nitro group, the lower the sensitivity shown by the explosives [15, 17]. From Table 1, the natural charge of the nitro group in complex is more negative than that in the monomer (see Supplementary Material), suggesting that a lot of negative charge concentrates on the nitro group, accompanied by possibly reduced explosive sensitivity. Furthermore, the

Fig. 2 Shifts in electron density as a result of the formation of the complex. Purple Gain, yellow loss



values of Mulliken charge (MP2(full)/aug-cc-pVTZ), natural charge (MP2(full)/6-311++G**) and APT charge (B3LYP/6-311++G**) of the nitro group in the molecule-cation interaction complex are all more negative than those in the hydrogen-bonded system. These results again show that the explosive sensitivity in the molecule-cation interaction complex might be lower than that in the hydrogen-bonded system, and that introducing cations into the structure of explosives might be more efficacious at reducing sensitivity.

Analysis of electron density shifts

In order to obtain deeper insight into the origin of the change in X–NO₂ bond strength, analysis of electron density shifts was carried out. For this purpose, the electron density shift was calculated by evaluating the difference between the total electron densities of complex and individual monomers.

$$\rho_{\text{shift}} = \rho_{(\text{RNO}_2 \cdots \text{Na}^+/\text{Mg}^{2+}/\text{HF})} - \rho_{\text{RNO}_2} - \rho_{\text{Na}^+/\text{Mg}^{2+}/\text{HF}}$$

The shifts in electron density are illustrated in Fig. 2.

Figure 2 shows the Na⁺ or Mg²⁺ cation to be filled with much purple area and the nitro group to be around the yellow region, suggesting that the electron density of the nitro group is lost toward Na⁺ or Mg²⁺ and that a molecule-cation interaction is formed. A Mg²⁺⋯π interaction is suggested by the yellow region below the xy-plane including the C=C double bond. H-bond formation is shown by the yellow region around the hydrogen atom of HF and the purple region surrounding the oxygen atom of the nitro group.

In each of the complexes, it is interesting to note the large purple area around the C and N atoms of the X–NO₂ trigger-bond or extending toward the X–NO₂ bond, showing that the electron density shifts toward the C and N atoms or the trigger-bond. It is well known that, the more intensive the electron between two atoms, the greater the chance that they overlap. As a result, the strength of the X–NO₂ bond is improved. Thus, we can draw the conclusion that the electron density shifts toward the X–NO₂ bond upon complex formation, leading to a strengthened X–NO₂ bond and possibly reduced explosive sensitivity. This might be the nature of the change in explosive sensitivity, which is in agreement with the above analyses.

Conclusions

We have presented a comparative theoretical investigation into the strength of the trigger-bond in the Na⁺, Mg²⁺ and HF complexes involving the nitro group of RNO₂ (R=–CH₃,

–NH₂, –OCH₃) or the C=C bond of (E)-O₂N–CH=CH–NO₂. Except for C₂H₂N₂O₄⋯Mg²⁺, the strength of the trigger-bond X–NO₂ was enhanced in complex in comparison with that in monomer. The increment of the BDE of the X–NO₂ bond in the Na⁺ complex was greater than that in the HF complex. It is possible that introducing cations into the structure of explosives might be more efficacious at reducing explosive sensitivity than the formation of intermolecular hydrogen-bonded complexes. The electron density shifted toward the X–NO₂ bond upon complex formation, leading to the strengthened X–NO₂ bond and possibly reduced explosive sensitivity.

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