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Theoretical study on the effect of intramolecular amino groups on C-NO$_2$ bond
— Amino and nitro substitutes of alkane, ethene and 1,3-butadiene —

Zhang Chaoyang[†], Shu Yuanjie, Huang Yigang,
Zhao Xiaodong, Wang Xinfeng, and Dong Haishan

Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), 621900, Mianyang, Sichuan, P R CHINA
[†]corresponding author: zcy19710915@yahoo.com.cn

Abstract

For the first time, the population of nitro group is defined as the ability to attract electrons (τ) and a criterion for measuring sensitivity of nitro compounds in this paper. The larger τ is, the less sensitivity will be. The effects of amino groups of different positions and quantity on C-NO$_2$ bonds are studied systematically at B3LYP/6-31G(d, p) level. The results indicate that: (1) For amino and nitro substitutes of alkanes, the effects of amino groups on C-NO$_2$ bond are inductive effects and spatial effects, and these effects will be very weak when the amino group and nitro groups are separated by more than 2 carbon atoms. (2) For amino and nitro substitutes of ethylene, amino group on No.1 position weakens C-NO$_2$ bond, on No.2 position strengthens it: the more amino groups, the shorter C-NO$_2$ bond, the stronger electro negativity on carbon atom of C-NO$_2$ bond, the longer the bond length of C=C, the more τ. That is to say, amino group is a very strong donor of electron and in the whole molecule the configuration effect is very large. (3) For amino and nitro substitutes of 1,3-butadiene, effects on C-NO$_2$ bond occurred by amino groups are kin to orientation effect on benzene ring when hydrogen bonds are not formed by H atoms in amino groups and O atoms in nitro groups; but the effects above will be weakened if hydrogen bonds formed (the stronger hydrogen bonds, the weaker C-NO$_2$ bond).

1. Introduction

In designing and evaluating new energetic materials, the objective is the somewhat contradictory one of maximizing energetic performance while minimizing sensitivity. The explosives which have high energies and low sensitivities are called insensitive high explosives (IHE). Usually, people need IHE for the purposes of both power and security. Now, the relationship between the sensitivity and molecular structure of IHE has become an important subject. The "trigger linkage" is an important and common concept,

which considers that a bond rupture is the key step in detonation initiation. Many researchers believe that C-NO$_2$, N-NO$_2$ and O-NO$_2$ bond are trigger spots in nitro compounds. Depluech and Cherville [1)-3)] propose that shock wave and thermal sensitivities in nitro compounds can be related to the electronic structure of molecule and properties of C-NO$_2$, N-NO$_2$ and O-NO$_2$ bonds such as electrostatic potential, length, strength etc. Xiao [4)] suggests that the stronger these bonds are, the more stable molecules are. Bates [5)] thinks that the sensitivity of tetrazole is related to the
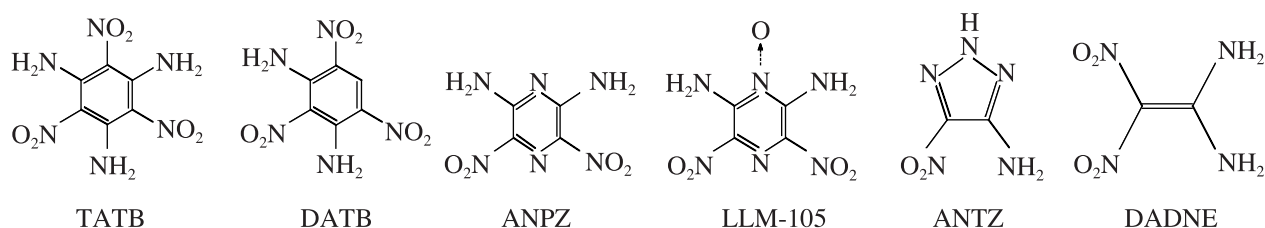

Fig. 1 Some IHE contain amino and nitro groups.

Table 1 τ and impact sensitivity of some typical nitroaniline explosives.

Explosive	Pent-nitroaniline	2,3,4,6-tetra-nitroaniline	TNA	DATB	TATB
τ	22.57	22.79	22.93	23.05	23.19
Impact sensitivity $h_{50\%}$(m)	0.15	0.41	1.77	3.20	»3.20

Note: τ is calculated from the feeblest C-NO$_2$ bond in explosives.

ability of substitution groups to attract electrons: the stronger the ability is, the more sensitive the compound is. But this criterion often meets "abnormal" cases. Kamlet and Adolph [6] draw a conclusion that the impact sensitivity of some nitro compounds can increase by their oxygen equilibriums enhance. Politzer concludes that sensitivity must be related to the molecular surface electrostatic potential, and more detailed overviews are presented on his paper [7].

Some explosives such as TATB, DATB, ANPZ, LLM-105, ANTA and DADNE contain amino and nitro groups are regarded as IHE [8] (showed in Fig. 1). There is a simple explanation on the co-existing of amino and nitro groups in many insensitive explosives: nitro group offers energy and amino group enhances stability of explosives. But there are not further studies and explanations on it. i.e., the effects of amino group(s) on C-NO$_2$ bond(s) which is taken as trigger point mentioned above in molecule are still not clear. In process of "IHE molecules design", the following problems should be considered: in what molecule, amino group can strengthen C-NO$_2$ bond? How does amino group at different positions and of different quantity affect the stability of C-NO$_2$ bond and entire molecule and consequently the sensitivity of explosives? To answer these questions will have important realistic and theoretical meanings.

2. Method and calculation details

We take Mulliken population [9] of nitro group as its ability of attracting electrons (τ) and a criterion for evaluating sensitivity of nitro compounds (*C-NO$_2$ bond must be the weakest bond in molecule*) for the first time—the bigger τ is, the less sensitive the compound is. The main reason for this is that C-NO$_2$ bond is the feeblest bond in molecule and is the

"trigger point" of explosive decomposition. Nitro group is a strong attracting-electron one. The quantity of distributed electrons reflects the saturation of attracting electrons. That is to say, if more electrons have already been distributed to the nitro group, it can't attract more electrons. This can make C-NO$_2$ bond more stable and consequently make molecule more insensitive. τ can be expressed as following:

$$\tau = \sum_{N,O,O} P + \frac{1}{2} \sum_{N,O,O} Pi \qquad (1)$$

on the right of the above equation, the first item is the total population of N and O atoms in nitro group, the second one is the half of the sum of overlapping population of N and O atoms in nitro. In order to verify this criterion, the geometries of some explosives are fully optimized without symmetry constrains by energy gradient method. All optimized geometries are obtained using the Beck 3LYP hybrid density functional with 6-31G (d, p) basis set. Calculation results has demonstrated that the criterion is reliable (shown in Table 1)—the more τ, the less sensitive.

Amino and nitro substitutes of simple alkanes, ethylene and 1,3-butadiene are taken as the studying objects. *Ab initio* calculations at B3LYP/6-31G (d, p) level are carried out with GAUSSIAN-98 program package [10].

3. Results and discussion
3.1 Amino and nitro substitutes of simple alkanes

For amino and (or) nitro substitutes of alkanes containing carbon atoms form 1 to 6, their geometries are optimized and populations are analyzed (*the partial results were only listed in Table 2 due to limitation of paper space*). From Table 2 it can be seen that for Molecule 2 (M2), the repulsion force

Table 2 The calculation results of amino and nitro substitutes of alkane (B3LYP/6-31G (d, p) level).

Molecule	1	2	3	4	5	6
	NO$_2$	NO$_2$ / NH$_2$	NO$_2$	NO$_2$ / NH$_2$	NO$_2$ NH$_2$	NH$_2$ / NO$_2$ / NH$_2$
$R_{C\text{-}NO_2}$ (Å)	1.499	1.562	1.517	1.508	1.518	1.524
$P_{C\text{-}NO2}$	0.254	0.172	0.235	0.204	0.228	0.212
Q_C (e)	-0.334	-0.082	0.222	0.242	-0.187	0.012
Q_N (e)	0.453	0.438	0.455	0.450	0.454	0.447
τ	22.79	22.81	22.79	22.81	22.80	22.75

Note: $R_{C\text{-}NO2}$ — C-NO$_2$ bond length, $P_{C\text{-}NO2}$ — population of C-NO$_2$ bond length,
Q_C — net charge of C atom, Q_N — net charge of N atom, the same as following tables.

Table 3 The calculation results of amino and nitro substitutes of ethane (B3LYP/6-31G (d, p) level).

Item / Molecule	R_{C-NO2} (Å)	P_{C-NO2}	P_{H-bond}	Q_C (e)	Q_N (e)	E(hart.)	Dipole (D)	$R_{C=C}$ (Å)	τ
1	1.466	0.273	-	0.066	0.440	-283.088	3.915	1.327	22.81
2	1.490	0.236	0.035	0.507	0.416	-338.445	3.893	1.339	22.88
3	1.429	0.294	0	-0.044	0.438	-338.453	7.176	1.353	22.92
4	1.393	0.313	0.069	-0.081	0.420	-393.819	8.201	1.392	22.99
5	1.475	0.179	-	0.482	0.395	-487.564	3.951	1.326	22.86
6	1.426	0.209	0.047	0.424	0.384	-542.829	6.463	1.375	22.98
7	1.405 / 1.432	0.196 / 0.227	0.065	0.371	0.395	-598.191	7.626	1.418	23.00
8	1.464	0.205	-	0.039	0.445	-487.574	0	1.327	22.27
9	1.500 / 1.421	0.199 / 0.243	0.033	0.536	0.420	-542.950	3.051	1.361	22.77
10	1.455	0.216	0.037	0.485	0.395	-598.302	0.005	1.388	22.99

Note: P_{H-bond} — maximum population of hydrogen bond , E — total energy, $R_{C=C}$ — C=C bond length, the same as the following table, M7, 9 have two different nitro groups.

between the amino and nitro groups makes $C-NO_2$ bond length larger (compared with M1) to 1.562Å (the largest in the similar compounds) owing to very large electron density, although the two groups are very close; for Molecules 4 and 5, the distance between amino and nitro groups in M4 is shorter than that in M5, $C-NO_2$ bond length in M4 is also shorter than that in M5. The reason is that $C-NO_2$ bond length does not change obviously when the two groups are separated by more than two carbons, in that inductive effect descends as their distance increased. M4 has shorter $C-NO_2$ bond length than that in M3 due to being added an amino group. However the $C-NO_2$ bond in M6 is not strengthened (compared with M4 and M5) in spite of more amino groups. In a word, effects of position and quantity of amino groups on $C-NO_2$ bond rely on inductive effects and spatial effects between amino groups and nitro groups, it will not have any effects on $C-NO_2$ bond when amino and nitro groups were separated by more than 2 carbon atoms.

3.2 Amino and nitro substitutes of ethylene

Compounds listed in Table 3 can be divided into 3 sorts according to the quantity and positions of nitro groups.

The first sort is substitutes of nitro-ethylene, including M1, 2, 3 and 4. Carbon atom connected with nitro group is numbered 1, carbon atom connected with No.1 carbon atom is numbered 2. In M2 an amino group is added, $C-NO_2$ and C=C bond length increase due to repulsion caused by great electron density, but τ of M2 does not decrease, this can be explained by hydrogen bond formation between H atom in amino group and N atom in nitro groups. For M3, whose amino group is connected with No.2 carbon atom (*note, on reverse orientation to nitro group*), $C-NO_2$ bond length decreases, and C=C bond length, electro-negativity of carbon atom on $C-NO_2$ and τ increase. It demonstrates that amino group connected with No.2 carbon atom strengthens $C-NO_2$ bond through conjugation effect. This can be validated by molecular orbital analysis. The LUMO of compound No.3 is

composed of 2Pz and 3Pz of C, N and O atoms in C-NO$_2$ bond and N atom in amino group, and very similar to that of TATB. If another amino group is added to No.2 carbon atom (M4), the effect mentioned above becomes even stronger.

M5, 6 and 7 belong to the second type (substitutes of 1, 1-dinitro-ethylene). When one or two amino groups are introduced to No.2 carbon atom, the rule mentioned above is still going.

M8, 9 and 10 belong to the third sort. When one (M9) or two amino (M10) groups are added to M8, the rule is still running.

M10, is the isomer of M7 (DADNE, FOX-7). They both have large value τ and are less sensitive. But M10 has a higher symmetry and lower total energy. Its dipole moment is close to zero and it has smaller distortion ability. This demonstrates that M10 may be more stable than FOX-7.

3.3 Amino and nitro substitutes of 1,3-butadiene

Compounds listed in Table 4 can be also divided into 3 groups to discuss.

M1, 2, 3 and 4 belong to the first group. Carbon atom

Table 4 The calculation results of amino and nitro substitutes of 1,3-butadiene(B3LYP/6-31G (d, p) level).

Item / Molecule	R_{C-NO2} (Å)	P_{C-NO2}	P_{H-bond}	Q_C (e)	Q_N (e)	E (hartr.)	Dipole (D)	τ
1 H$_2$C⟍⟋NO$_2$	1.449	0.270	-	0.004	0.430	-360.492	4.665	22.76
2 H$_2$C⟍ NO$_2$ / NH$_2$	1.423	0.281	0.000	-0.080	0.424	-415.850	6.665	22.91
3 H$_2$N / H$_2$C⟍NO$_2$	1.451	0.243	0.000	-0.005	0.438	-415.848	5.547	22.84
4 H$_2$N⟍⟋NO$_2$	1.434	0.265	0.000	-0.030	0.428	-415.859	9.459	22.89
5 NO$_2$ CH$_2$ / H$_2$C	1.490	0.202	-	0.350	0.374	-360.486	3.648	22.92
6 NO$_2$ CH$_2$ / NH$_2$	1.451	0.217	0.000	0.270	0.367	-415.851	6.809	23.00
7 NO$_2$ CH$_2$ / H$_2$C NH$_2$	1.486	0.205	0.000	0.272	0.272	-415.836	4.105	22.91
8 NO$_2$ / H$_2$C NH$_2$	1.492	0.202	0.000	0.367	0.372	-415.846	4.961	22.76
9 H$_2$N NO$_2$ CH$_2$ / NH$_2$	1.467	0.195	0.042	0.260	0.364	-471.213	1.963	22.97
10 NO$_2$ CH$_2$ / NH$_2$ NH$_2$	1.449	0.238	0.000	0.176	0.381	-471.207	6.726	22.90
11 NO$_2$ NH$_2$ / NH$_2$	1.451	0.236	0.000	0.268	0.372	-471.208	6.076	23.09
12 H$_2$N NO$_2$ CH$_2$ / NH$_2$ NH$_2$	1.419	0.244	0.065	0.163	0.359	-526.572	6.576	23.10
13 NO$_2$ NH$_2$ / H$_2$N NH$_2$	1.413	0.246	0.070	0.251	0.340	-526.571	6.373	23.18
14 NH$_2$ NH$_2$ / NO$_2$ NH$_2$	1.389	0.250	0.015	0.339	0.319	-526.433	5.957	23.27

connected with nitro group directly is numbered as No.1, the neighbor carbon atom is numbered as No.2, other carbon atoms are numbered as No.3, 4···by analogy. Effect of amino group at No.1 carbon atom on C-NO$_2$ bond is similar to that in section 2.2 and need not to be discussed here any more. Calculation results show that the order of strengthening C-NO$_2$ bond by amino group at different positions (M2,3,4) is: No.2 >No.4 >No.3. Electro-negativity of carbon atom on C-NO$_2$ bond and τ increase in the same order. The results can be explained as follows: for M2, amino group at position No.2 affects nitro group in two ways: inductive effects and conjugation effects. For M3 and 4, there only exists conjugation effect. We find these molecules are similar to *ortho*-(No.2) or *para*-(No.4) nitroaminobenzene by molecular orbital analyses. Certainly, position of amino group has also effects on the molecular properties, for instance, the dipole moment of molecule increases as the distance between amino groups and nitro groups increases. In addition, M4 has lower energy than M2, though the latter has stronger C-NO$_2$ bond.

M5, 6, 7 and 8 belong to the second group. They are analogs of amino-2-nitro-1,3-butadiene. Carbon atom connected with nitro group is numbered as No.2, carbon atom at the end of double bond and connected with carbon atom No.2 is numbered as No.1, the other side carbon atom connected with No.2 is taken as No.3 and the forth carbon atom is numbered as No.4. The order of strengthening C-NO$_2$ bond by amino group is as following: No.1 >No.3 >No.4. And negative electrons and τ of carbon atoms on C-NO$_2$ bond increase in the same order. This may be due to the inductive and conjugated effect on No1. and No.3. But amino group on No.4 weakens C-NO$_2$ bond as amino group does in *meta*- nitro-aminobenzene.

The third sort is of multi-amino-2-nitro-1, 3-butadiend including M9, 10, 11, 12, 13 and14. We need not discuss this sort any more, for it is very close to the first group. On the basis of molecules of the second group, adding one or two amino groups will strengthen C-NO$_2$ bond—the more

amino groups, the stronger C-NO$_2$ bond. The "*ortho*- or *meta*- orientation effect" mentioned above do not come forth when an amino is added at No.1 or No.3 or No.4 in M6. This may be related to formation of hydrogen bond. For example, M9 has the strongest hydrogen bond but the feeblest C-NO$_2$ bond among M9, 10 and 11. Effect of hydrogen bond mentioned above still exists in substitutes of triamino-2-nitro-1, 3-butadiene, M14 has the feeblest hydrogen bond but strongest C-NO$_2$ bond.

3.4 Comparison of τ, C-NO$_2$ bond length and its population

To a certain extent, τ, C-NO$_2$ bond length and its population can explain the stability of explosives with C-NO$_2$ group. Figure 2 is drawn by using data from Table 2, 3 and 4 to find their relations (in view of convenience, we keep three sorts of data on a same number level by zooming out 10 times of C-NO$_2$ bond length, 100 times of its population). From Fig. 2, it can be concluded: (1) For all compounds of same group, τ and C-NO$_2$ bond length are very close, but C-NO$_2$ bond populations are quite different; (2) they don't follow the changing rule entirely—the shorter C-NO$_2$ bond length, the bigger its population and more τ. The main reason is that when hydrogen bond is formed, the electrons will be redistributed in molecules—when C-NO$_2$ bond length increases and its population reduces to some extent, τ may not reduce, even it may increase to make molecule more stable. So we can estimate the stability of molecules with τ. There is a limitation to do it when we only use C-NO$_2$ bond length or its population.

4. Conclusions

For the first time, population of nitro group is taken as its ability to attract electrons and a criterion for measuring sensitivity of nitro compounds—the more τ, the less sensitivity. C-NO$_2$ bond affected by intramolecular amino groups of different positions and quantity in amino and nitro substitutes of alkanes, ethylene and 1,3-butadiene
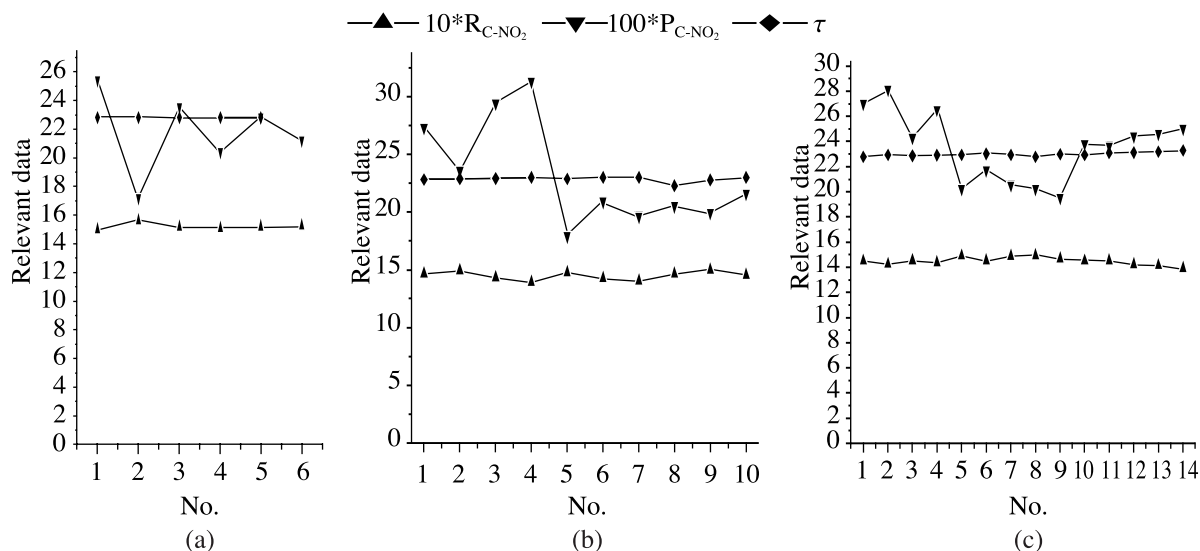

Fig. 2 τ, C-NO$_2$ bond lengths and population of different compounds: (a) from Table 2, (b) from Table 3, (c) from Table 4.

were studied systematically and the results show that:

(1) For amino and nitro substitutes of alkanes, effect of amino group position quantity of due to the inductive and spatial effect between amino and nitro groups, but it is very weak when these groups are separated more than 2 carbon atoms away.

(2) For amino and nitro substitutes of ethylene, amino group on No.1 weakens $C-NO_2$ bond and on No.2 strengthens it: the more amino groups, the shorter $C-NO_2$ bond, the more electronegativity on carbon atom of $C-NO_2$ bond, the longer $C=C$ bond, the more τ. That is, there are strong effects of donating electrons by amino groups and strong conjugated effect in entire molecule.

(3) For amino and nitro substitutes of 1,3-butadiend, effect of amino group on $C-NO_2$ bond is similar to orientation effect on benzene ring when hydrogen bonds were not formed by H atoms in amino group and O atoms in nitro group; but the effects would be weakened when hydrogen bonds formed (the stronger hydrogen bonds are, the weaker $C-NO_2$ bond).

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