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Molecular structures of mononitroanilines and their thermal decomposition products

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Abstract. The molecular structures of 2-nitro, 3-nitro, and 4-nitroaniline and their internal rotational isomers were calculated by an *ab-initio* method using HF/6-31G* basis set. The geometries were influenced by the nitro group's position. The perturbation of the amino group on the nitro group was observed in a 2-nitroaniline isomer having a molecular structure distinct from that of the other two isomers. Among them, 4-nitroaniline is the most stable one. Internal rotation tests of either the nitro or amino group of 3-nitro and 4-nitroaniline indicate that no significant deformations of the phenyl ring occurred after internal rotation; however, the internal rotational isomers of 2-nitroaniline differed from its original structure. Relatively easier internal rotation of the nitro group than the amino group and different C–NO_2 and C–NH_2 bonds indicate the bond-breaking message of nitroanilines. As products of explosives induced by thermal or shock are of interest, five products of 2-nitroaniline were selected to assess their geometries and energies. The above calculations revealed that these products are thermodynamically unfavorable.

Key words: Nitroaniline – Internal rotation – Molecular orbital – Molecular structure – Intramolecular transfer

1 Introduction

Interest in the chemistry of certain nitro-containing molecules originates from using these compounds as energetic materials. Nitroanilines are one class of these materials, which are classified as secondary explosives [1, 2]. More thorough understanding the molecular structure of explosives is essential because the molecular structure is related to a chemical reaction having occurred [3, 4]. Moreover, an accelerated effort has been made to develop and to understand the relationship between the molecular structures of energetic compounds and their sensitivities to specific stimuli, e.g., impact or shock [5]. Experimental techniques such as X-ray diffraction or microwave spectroscopy, although capable of providing valuable information regarding the various molecular structures, provide incomplete geometrical information. Hence, a theoretical means to calculate explosives' molecular structure is necessary. Through this calculation, a molecule's geometry can be completely derived. Some molecular structures of explosives [6–10] were calculated by *ab-initio* methods; those results were similar to experimental data. Based on those precise calculations, we believe that the *ab-initio* approach can be applied to examine other explosives. In this work, three nitro compounds, 2-nitroaniline, 3-nitroaniline, and 4-nitroaniline, were selected. Through a better *ab-initio* method, their geometries were derived. According to this calculation, the substituent effects on the phenyl ring could be more thoroughly understood.

Internal rotation of either the nitro or amino group is also critical to clearly understand explosives. Since the rotational axis of these groups is the C–N bond, this bond's barrier may provide the message of bond rupture. A circumstance is discussed later in which the breaking of C–NO_2 bond is the early events of thermal decomposition of nitroanilines. Conventionally, the nitro group is coplanar with the benzene ring, the amino group is pyramidal with the phenyl ring, and the dihedral angle between the amino plane and the benzene plane is about 38° [11]. However, the amino group is a strong donor and the nitro group is a strong acceptor. In addition to the phenyl ring, the conjugation effects are found in all nitroanilines. Such effects may affect both the amino and nitro groups which tend to be coplanar with the phenyl ring. Hence, in this study, internal rotations of either the nitro or amino group at 90° of each molecule are calculated, respectively; the subsequent geometries are compared with those of the original molecules.

During the last two decades, structure-sensitivity relationships in energetic compounds are increasingly relevant topics so as to develop less-sensitive munitions [5, 12, 13]. Hence, an increasing use of molecular orbital methods allow one to explore not only the possible unimolecular mechanisms, but also the intermolecular mechanisms that may be important under high-pressure conditions occurring in explosions of energetic materials [14–18]. The geometry and energetics of species involved in possible reaction pathways can be evaluated by such methods. Experimental and theoretical works on 2,4,6-trinitrotoluene indicated the products to be consistent with the rupturing of the methyl C–H bond during early stages of decomposition [9, 19–22]; in addition, the products are derived primarily from the intramolecular shifts of hydrogen or oxygen [23–27]. Opposite to 2,4,6-trinitrotoluene, thermal decomposition of 2,4,6-trinitroaniline is dominated by the rupturing of the C–NO_2 bond [12, 13]. This bond is extremely strong because of the conjugation effects among the donor, acceptor, and the phenyl ring [28]. Based on these effects, 2,4,6-trinitroaniline is extremely less sensitive than 2,4,6-trinitrotoluene.

The decomposition of 2,4,6-trinitroaniline has been extensively studied employing a variety of experimental techniques. Those products are derived primarily from the intramolecular shifts of hydrogen or oxygen [29–31]. 2-nitroaniline and two of its thermal decomposition products were studied by a low-level *ab-initio* method [32]; however, the results were incomplete to adequately understand the nitroanilines. Moreover, not all the hydrogen or oxygen transfer products of 2-nitroaniline were listed. Hence, further examining the thermal decomposition products is necessary. In this work, we investigate intramolecular hydrogen transfer products of four kinds and an oxygen transfer compound of 2-nitroaniline. These products resemble those of 2,4,6-trinitroaniline. The energetics of reactions relating to these molecules at the HF level are also listed to assess the different kinds of reactions that are thermally favorable.

2 Calculation method

The Gaussian 92 package [33] was selected as the calculation tool, with *ab-initio* HF/6-31G* approach. Through the Z-matrix input of the bond lengths, bond angles, and dihedral angles and geometry optimizations of all variables, the most stable molecular structure of each molecule was obtained. Second derivatives were calculated by verifying the vibrational frequencies so that a local minimum could be found for each molecule. Internal rotations of the nitroanilines were examined on rotation of either the nitro or amino group by 90° from its optimized structure. These internal rotational isomers are discussed and compared with their original structures.

3 Results and discussion

3.1. Geometries of nitroanilines

Figure 1 and Tables 1–3 display the molecular structures of 2-nitroaniline, 3-nitroaniline, and 4-nitroaniline. Tables 1–3 summarize the experimental data of

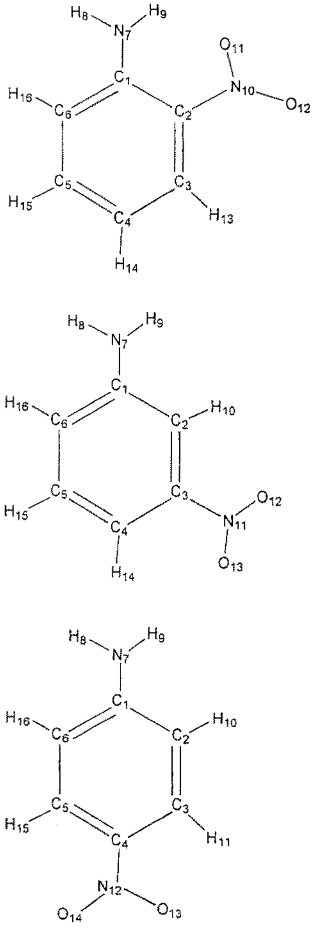


Fig. 1. Molecular structures of mononitroanilines

Table 1. The molecular structure of 2-nitroaniline and its internal rotational isomers

Bond	I	II	III	IV [13]	V [13]
C1–C2	1.4063	1.3927	1.3897	1.355	1.421
C2–C3	1.4009	1.3819	1.3797	1.435	1.441
C3–C4	1.3661	1.3823	1.3795	1.371	1.372
C4–C5	1.3998	1.3851	1.3896	1.380	1.365
C5–C6	1.3664	1.3847	1.3782	1.358	1.389
C1–C6	1.4136	1.3903	1.3996	1.415	1.398
C1–N7	1.3489	1.4007	1.3649	1.371	1.350
N7–H8	0.9921	0.9913	0.9916	0.94	1.04
N7–H9	0.9909	0.9916	0.9923	0.78	0.89
C2–N10	1.4422	1.4601	1.4649	1.490	1.429
N10–O11	1.2034	1.1902	1.1932	1.223	1.248
N10–O12	1.1940	1.1960	1.1932	1.216	1.223
C3–H13	1.0704	1.0728	1.0746	0.93	0.82
C4–H14	1.0732	1.0742	1.0733	0.97	0.99
C5–H15	1.0755	1.0749	1.0752	0.93	0.96
C6–H16	1.0753	1.0740	1.0755	1.05	1.20
H9–O11	1.9878	3.3630	2.8824	2.64	2.67
O12–H13	2.2888	2.6038	3.1609	—	—
C1–C2–C3	121.40	122.87	123.27	121.3	120.2
C2–C3–C4	121.04	119.13	119.53	122.7	118.8
C3–C4–C5	118.39	119.57	118.59	113.6	121.6
C4–C5–C6	121.27	120.32	121.38	125.9	120.1
C1–C6–C5	121.81	121.52	120.97	120.1	122.1
C2–C1–C6	116.09	116.59	116.27	116.4	116.9
C2–C1–N7	125.56	122.44	122.49	127.4	122.6
C6–C1–N7	118.35	120.95	121.24	116.2	120.1
C1–N7–H8	119.36	120.92	120.25	113	126
C1–N7–H9	121.08	120.89	122.51	101	109
C1–C2–N10	121.88	120.61	118.57	124.2	123.9
C3–C2–N10	116.72	116.52	118.17	114.5	115.9
C2–N10–O11	118.77	118.16	117.47	114.2	118.4
C2–N10–O12	118.32	116.77	117.46	120.0	121
C2–C3–H13	118.04	119.58	119.73	122	114
C3–C4–H14	120.68	119.88	120.46	123	118
C4–C5–H15	119.78	120.00	119.35	122	124
C5–C6–H16	120.13	120.63	120.15	121	124

Note: Symbol I is the original structure, II is the internal rotation structure of amino group, III is the internal rotation structure of nitro group, and IV and V are experimental values. The unit of the bond angle is degree, and the unit of bond length is Å

2-nitroaniline [34] and 4-nitroaniline [35]. Although there are two crystal forms in 2-nitroaniline, Dhaneshwar et al. [34] pointed out that the differences between them are usually too insignificant in light of the rather large e.s.d.s. Calculated bond distances and bond angles of nitroanilines are similar to their experimental values. Similar to the experimental observations, 2-nitroaniline and 3-nitroaniline have the C_s symmetry, and 4-nitroaniline has the C_{2v} symmetry. The planar configurations are observed in all nitroanilines. The planar amino group is attributed to the strong electron-withdrawing power of the neighboring nitro group

Table 2. The molecular structure of 3-nitroaniline and its internal rotational isomers

Bond	I	II	III
C1–C2	1.3928	1.3884	1.3953
C2–C3	1.3801	1.3829	1.3753
C3–C4	1.3798	1.3828	1.3755
C4–C5	1.3854	1.3826	1.3874
C5–C6	1.3808	1.3862	1.3796
C1–C6	1.3973	1.3916	1.4019
C1–N7	1.3699	1.4078	1.3670
N7–H8	0.9914	0.9915	0.9916
N7–H9	0.9917	0.9915	0.9917
C2–H10	1.0712	1.0706	1.0745
C3–N11	1.4636	1.4590	1.4645
N11–O12	1.1941	1.1938	1.1916
N11–O13	1.1931	1.1942	1.1916
C4–H14	1.0698	1.0708	1.0728
C5–H15	1.0747	1.0743	1.0748
C6–H16	1.0759	1.0746	1.0756
H10–O12	2.3568	2.3892	3.1560
O13–H14	2.3921	2.3847	3.1924
C1–C2–C3	119.04	119.35	118.66
C2–C3–C4	123.38	122.40	124.08
C3–C4–C5	117.01	118.14	116.64
C4–C5–C6	121.26	120.24	121.36
C1–C6–C5	120.85	121.26	120.50
C2–C1–C6	118.46	118.62	118.86
C2–C1–N7	120.59	120.49	120.24
C6–C1–N7	120.95	120.89	120.90
C1–N7–H8	121.17	121.11	121.08
C1–N7–H9	117.98	121.08	121.31
C1–C2–H10	121.04	120.19	120.90
C2–C3–N11	117.98	118.76	119.43
C4–C3–N11	118.64	118.84	116.49
C3–N11–O12	117.85	117.79	117.14
C3–N11–O13	117.66	117.68	117.14
C3–C4–H14	120.90	120.21	121.33
C4–C5–H15	119.47	119.72	119.43
C5–C6–H16	119.77	120.21	119.87

Note: Symbol I is the original structure, II is the internal rotation structure of amino group, and III is the internal rotation structure of nitro group. The unit of the bond angle is degree, and the unit of bond length is Å

and the conjugation effects, despite the fact that the amino group in aniline was experimentally and theoretically found [36–40] to be pyramidal. The nitro groups of aromatic explosives generally tend to be coplanar with the aromatic ring if the steric crowding and intermolecular packing forces can be averted. This calculation reveals that all nitro groups are coplanar with the phenyl ring. For 2-nitroaniline, a strong intramolecular hydrogen bond is observed between the amino and nitro

Table 3. The molecular structure of 4-nitroaniline and its internal rotational isomers

Bond	I	II	III	IV [14]
C1–C2	1.4017	1.3934	1.3979	1.415
C2–C3	1.3745	1.3834	1.3796	1.373
C3–C4	1.3867	1.3846	1.3781	1.395
C4–C5	1.3867	1.3846	1.3781	1.390
C5–C6	1.3745	1.3834	1.3796	1.377
C1–C6	1.4017	1.3935	1.3979	1.408
C1–N7	1.3597	1.4128	1.3672	1.371
N7–H8	0.9921	0.9899	0.9917	0.96
N7–H9	0.9921	0.9899	0.9917	0.75
C2–H10	1.0751	1.0712	1.0753	0.83
C3–H11	1.0715	1.0693	1.0745	0.83
C4–N12	1.4427	1.4473	1.4620	1.460
N12–O13	1.1968	1.2266	1.1929	1.247
N12–O14	1.1768	1.2267	1.1929	1.246
C5–H15	1.0715	1.0693	1.0745	0.81
C6–H16	1.0751	1.0714	1.0752	0.95
H11–O13	2.3960	2.3923	3.2017	2.40
O14–H15	2.3960	2.3924	2.3924	2.45
C1–C2–C3	120.50	120.79	120.63	120.1
C2–C3–C4	119.72	118.69	119.33	119.8
C3–C4–C5	120.70	121.89	121.41	121.2
C4–C5–C6	119.72	118.69	119.32	119.2
C1–C6–C5	120.50	120.79	120.63	120.8
C2–C1–C6	118.85	119.15	118.69	118.9
C2–C1–N7	120.57	120.43	120.65	119.9
C6–C1–N7	120.57	120.43	120.66	121.2
C1–N7–H8	121.20	120.43	121.20	—
C1–N7–H9	121.20	120.88	121.20	—
C1–C2–H10	119.66	118.93	119.75	—
C2–C3–H11	120.57	121.36	120.26	—
C3–C4–N12	119.65	119.05	119.30	118.4
C5–C4–N12	119.65	119.06	119.30	120.4
C4–N12–O13	117.93	118.32	117.40	119.0
C4–N12–O14	117.93	118.32	117.39	117.7
C4–C5–H15	119.71	119.96	119.42	—
C5–C6–H16	119.84	120.28	119.62	—

Note: Symbol I is the original structure, II is the internal rotation structure of amino group, III is the internal rotation structure of nitro group, and IV is experimental value. The unit of the bond angle is degree, and the unit of bond length is Å

groups (bond 011–H9). Because of this strong hydrogen bonding effect, localization in a nitro group tends to occur and Mulliken population analyses of 2-nitroaniline demonstrate that 011 atom (− 0.524 e.s.u.) has more of a negative atomic charge than 012 atom (− 0.474 e.s.u.). However, delocalization exists in 3-nitroaniline and 4-nitroaniline where N–O bond lengths and atomic charge of O atoms of each nitro group are similar. Tilting of the amino or nitro group is affected by its neighboring group. For 2-nitroaniline tilts of C1–N7 and C2–N10 bonds are obvious, hence different tilt angles of C2–C1–N7 and C6–C1–N7 and C1–C2–N10 and C3–C2–N10 are observed. Tilting of the amino or nitro group in 3-nitroaniline and 4-nitroaniline is insignificant, probably owing to the weak perturbation between the amino and nitro groups. Those results are the same as found in nitrotoluenes [9].

The substituted groups affect deformations of the phenyl ring. The interior bond angle at the carbon to which an amino group is attached is invariably smaller than that normally adopted as the interior bond angle of the benzene ring [41], whereas the interior angle at the carbon to which a nitro group is invariably attached exceeds the nominal 120°. Those results exhibit the same trends as in the molecular geometries of substituted benzene derivatives by Domenicano et al. [42, 43]. Hofmann and Birner [44] assessed the factors affecting the conformation of the aromatic nitro group; the ring bonds adjacent to a nitro group tend to be shorter than those in unsubstituted benzene. According to our calculation, this trend is unobvious, likely affected by another substituent, the amino group. The same trend was also observed by the substituent of the methyl group [9].

3.2. *Internal rotation of the nitro or amino group*

The nitro and amino groups are essential to determine the characteristics of explosives. To more thoroughly understand the influence of the nitro or amino group on the geometry of nitroaniline explosives, internal rotations of the nitro and amino groups of each nitroaniline molecule at 90° were studied, respectively. Tables 1– 3 summarize those results. Deformations of the phenyl ring owing to internal rotation depend on the perturbation effect between the nitro and amino groups; for 2-nitroaniline, deformations of the phenyl ring are obvious. However, deformations of the benzene ring are insignificant in 4-nitro and 3-nitroaniline. Different values of C–NH_2 bond before and after internal rotation of the amino group indicate that this bond is significantly affected by the internal rotation of the amino group, regardless of what the nitroanilines are. However, no significant change of the C–NO_2 bond for each isomer was observed when examining the nitro group's internal rotation. Among 2-nitroaniline and its internal rotational isomers, a significant aspect is the tilting of the C–N bonds. Less-significant tilting of the C–N bonds is observed in 3-nitro and 4-nitroaniline and their internal rotational isomers. Comparing the tilting effects of C–NH_2 and C–NO_2 bonds reveals that tilting of C–NO_2 bond is less than C–NH_2 bond. Therefore, the nitro group's rotation – internal rotation coupling is weak.

3.3. *Stability of nitroanilines*

Table 4 displays the HF energies and two other physical parameters of all nitroanilines and their internal rotational isomers. Of all molecules, 4-nitroaniline is the most stable because it has the least HF energy. Because of a better conjugation effect of 2-nitroaniline than that of 3-nitroaniline, lower HF energy of 2-nitroaniline is observed. Internal rotation of the nitro or amino group yields a lower HF energy than the original one. Comparing the HF energies of internal rotation of amino and nitro groups reveals that for all nitroanilines, the nitro group's internal rotation is easier than that of the amino group. This finding can be accounted for by the different effects of the nitro or amino group. Similar internal rotational barriers were observed in 3-nitroaniline, either internal rotation of the

Table 4. HF energies and physical parameters of nitroanilines and their internal rotational isomers

	2-nitroaniline		
	I	II	III
Point group	C_S	C_1	C_1
HF energy	– 489.2047073	– 489.1819310	– 489.1886474
Dipole moment	5.3118	4.5913	4.2129
Ionization energy	0.3103	0.3571	0.3104
	3-nitroaniline		
Point group	C_S	C_1	C_1
HF energy	– 489.2006675	– 489.1899862	– 489.1901065
Dipole moment	6.1013	5.4509	5.8351
Ionization energy	0.3076	0.3573	0.3087
	4-nitroaniline		
Point group	C_{2V}	C_1	C_1
HF energy	– 489.2068600	– 489.9772183	– 489.1904060
Dipole moment	7.4924	6.5051	6.6027
Ionization energy	0.3155	0.3700	0.3095

Note: Symbol I is the original structure, II is the internal rotation structure of amino group, and III is the internal rotation structure of nitro group. The unit of HF energy and ionization energy is hartree. The unit of dipole moment is Debye

$C–NH_2$ or $C–NO_2$ bond, which is accounted by weak conjugation effects of this molecule. Double-bond characteristics are observed in $C–NH_2$ bond because of the migration of lone-pair electrons from the N atom to C atom. However, the $C–NO_2$ bond tends to have single-bond characteristics. Hence, for each nitroaniline isomer, $C–NO_2$ bond length is always longer than that of $C–NH_2$ bond. Consequently, easier bond rupturing of $C–NO_2$ bond can be analyzed from this calculation which is the same as that predicted by impact-sensitivity experiments [12, 13].

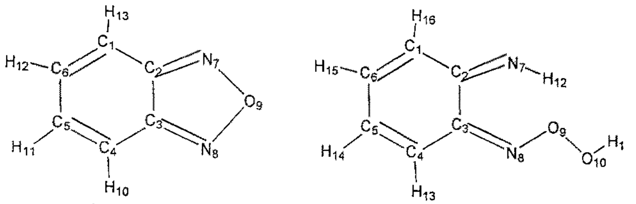
Data of dipole moments are useful in relation to solvent chemistry. According to a previous calculation of nitrotoluenes, the calculated values of dipole moment were overestimated but the errors were not large [9]. Hence, the same trends of nitroanilines can be expected, although no experimental values were observed. Table 4 lists the values of dipole moments. From this calculation, 2-nitroaniline has the lowest value and 4-nitroaniline has the largest value. As this table demonstrates, ionization energies estimated according to Koopmans' method reveal that 3-nitroaniline has the lowest value and 4-nitroaniline has the largest value. Data of ionization energies can provide valuable information regarding the stabilities of energetic molecules [45]. From those values, we can infer that 4-nitroaniline is the most stable molecule and 3-nitroaniline is the most unstable molecule among these three nitroanilines. Because of different interactions of $C–NO_2$ and $C–NH_2$ in nitroanilines, our results indicate that internal rotation of $C–NH_2$ group significantly alters the value of ionization energy. However, no obvious change in ionization energy is observed when internal rotation of $C–NO_2$ group occurs for each nitroaniline.

3.4. Hydrogen bonding effects

The crystallographic analysis indicates the occurrence of both intra- and intermolecular hydrogen bonding in nitroanilines. In general, an O ... H separation less than the sum of oxygen and hydrogen van der Waals radii (1.4 and 1.2 Å, respectively) is interpreted as evidence of intramolecular hydrogen bonding. Tables 1–3 list all of the hydrogen bonds. Because of the strong conjugation effects, hydrogen bonding effect in nitroaniline is stronger than that of nitrotoluene [9]. Among all three nitroaniline isomers, the main hydrogen bond of 2-nitroaniline is C–NO ... HN–C type and is generally strong. However, for other isomers, main hydrogen bonds are C–NO ... H–C types and are generally weak. Internal rotation of amino or nitro group alters the resonance effect of each molecule; no hydrogen bonding effects are observed for all internal rotational isomers.

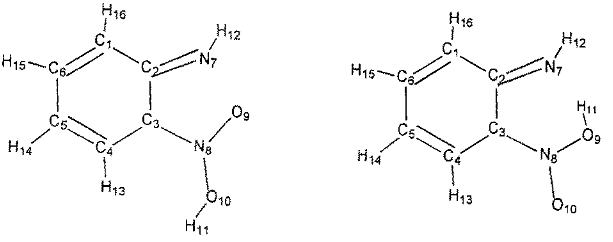
3.5. Thermal decomposition products of 2-nitroaniline

As the amino and nitro groups of 2-nitroaniline are adjacent to the benzene ring, some intramolecular transfer tautomers of hydrogen, oxygen, or cyclization reaction products were found after thermal decomposition of 2-nitroaniline [46, 47]. The possible products are furazan, a nitroaromatic compound, and aci-2-nitroaniline, as indicated in Fig.2. Previous *ab-initio* calculations of furazan and



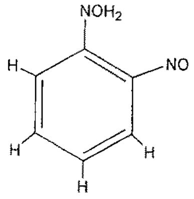
furazan

aci-2-nitroaniline I



aci-2-nitroaniline II

aci-2-nitroaniline III



nitrosoaromatic compound

Fig. 2. Thermal decomposition products of 2-nitroaniline

aci-2-nitroaniline at the HF/3-21G level [32] indicated that furazan is endothermically formed and, thus, unfavorable relative to 2-nitroaniline. However, aci-2-nitroaniline was calculated as an unstable molecule, despite the fact that aci-2-nitroaniline was observed when reaction of 2-nitroaniline occurred in the condensed phase. No calculation of the nitrosoaromatic compound was given; it is also an important thermal decomposition product. In this calculation, a better *ab-initio* approach was performed for furazan, aci-2-nitroaniline, and nitrosoaromatic compound of 2-nitroaniline using 6-31G* basis set. Table 5 presents the geometrical configuration of furazan. The lesser the aromatic character of the phenyl ring is owing to the formation of the five-membered ring. Hence, C1–C6, C1–C2, C2–C3, and C4–C5 bonds have the characteristics of a single bond, whereas C3–C4 and C5–C6 bonds still qualify as double bonds. In the five-membered ring, double bonds are found at C1–N7 and C2–N8. Planar structures are obtained for the phenyl ring and the five-membered ring.

Figure 2 depicts three types of aci-2-nitroaniline and Table 6 lists their geometries. As this figure reveals, aci-2-nitroaniline I is a transition state because the calculated vibrational frequencies yield one imaginary value. Local minimum is observed in both aci-2-nitroaniline II and III, implying that these two aci-tautomers are theoretically found. Although aci-2-nitroaniline II has been calculated by a SCF-3-21G method [32], no local minimum was found in that calculation. Our better HF/6-31G* calculation confirms that this molecule has a local minimum. The existence of aci-2-nitroaniline II from experiments [48–50] correlates with our calculation that this aci-tautomer is actually observed both experimentally and theoretically. Aci-2-nitroaniline II and III are *cis– trans* isomers and are both stable molecules. Since the aci-tautomers are predominant in intramolecular hydrogen transfer, the optimum migration of H atom from the amino group to nitro group should be observed to be similar to aci-2-nitroaniline III. HF energy calculations indicate that aci-2-nitroaniline III is more stable than aci-2-nitroaniline II. Hence, we can infer that aci-2-nitroaniline III is the most observed tautomer of aci-2-nitroaniline.

Except for the migration of H atom, transfer of oxygen atom from the nitro group to the amino group is also possible. This kind of tautomer is the nitrosoaromatic compound as shown in Fig.2. Although kinetic measurement of formation and thermal decomposition of nitrosoaromatic compounds from nitroaromatic compounds are unavailable, Fields et al. [51] reported a reaction of this kind. Based on the successful calculation of a molecular structure of a nitrosoaromatic

Table 5. The molecular structure of furazan

C1–C2	1.4273	C3–H10	1.0729	C2–C1–N7	107.91
C2–C3	1.4406	C4–H11	1.0747	C1–C2–N8	107.89
C3–C4	1.3403	C5–H12	1.0747	C1–N7–O9	105.65
C4–C5	1.4608	C6–H13	1.0729	C2–N8–O9	105.67
C5–C6	1.3403	C1–C2–C3	120.91	N7–O9–N8	112.88
C1–C6	1.4406	C2–C3–C4	116.44	C2–C3–H10	120.67
C1–N7	1.2852	C3–C4–C5	122.66	C3–C4–H11	119.85
C2–N8	1.2851	C4–C5–C6	122.66	C4–C5–H12	117.49
N7–O9	1.3303	C1–C6–C5	116.44	C5–C6–H13	120.90
N8–O9	1.3304	C2–C1–C6	120.91		

Note: The unit of the bond length is Å, and the unit of the bond angle is degree

Table 6. The molecular structure of aci-2-nitroaniline I

C1–C2	1.5028	C3–H13	1.0733	C1–C2–N8	128.25
C2–C3	1.4715	C4–H14	1.0743	C2–N8–O9	116.78
C3–C4	1.3268	C5–H15	1.0753	N8–O9–O10	104.93
C4–C5	1.4638	C6–H16	1.0760	O9–O10–H11	99.61
C5–C6	1.3282	C1–C2–C3	118.22	C2–C3–H13	116.00
C1–C6	1.4776	C2–C3–C4	121.77	C3–C4–H14	120.76
C1–N7	1.2607	C3–C4–C5	120.53	C4–C5–H15	118.36
N7–H12	1.0063	C4–C5–C6	121.59	C5–C6–H16	121.01
C2–N8	1.2672	C1–C6–C5	122.43	C1–C2–N8–O9	0.00
N8–O9	1.3255	C2–C1–C6	115.44	C2–N8–O9–O10	0.00
O9–O10	1.3968	C2–C1–N7	120.89	N8–O9–O10–H11	180.00
O10–H11	0.9510	C1–N7–H12	110.68	C6–C1–N7–H12	180.00

Note: The unit of the bond length is Å, and the unit of the bond angle is degree

Table 6. The molecular structure of aci-2-nitroaniline II

C1–C2	1.4884	C3–H13	1.0696	C2–N8–O9	130.29
C2–C3	1.4601	C4–H14	1.0741	C2–N8–O10	115.83
C3–C4	1.3305	C5–H15	1.0752	C1–N7–H12	110.23
C4–C5	1.4576	C6–H16	1.0758	N8–O10–H11	101.97
C5–C6	1.3287	C1–C2–C3	120.01	C2–C3–H13	118.55
C1–C6	1.4775	C2–C3–C4	120.65	C3–C4–H14	120.14
C1–N7	1.2625	C3–C4–C5	120.90	C4–C5–H15	118.60
N7–H12	1.0057	C4–C5–C6	121.19	C5–C6–H16	120.91
N8–O9	1.2179	C1–C6–C5	122.90	C6–C1–C2–N7	180.00
C2–N8	1.2977	C2–C1–C6	114.35	C1–C2–C3–N8	180.00
O10–H11	0.9549	C6–C1–N7	123.31	C6–C1–N7–H12	0.00
N8–O10	1.3562	C1–C2–N8	120.47	C1–C2–N8–O9	0.00

Note: The unit of the bond length is Å, and the unit of the bond angle is degree

Table 6. The molecular structure of aci-2-nitroaniline III

C1–C2	1.4628	C3–H13	1.0710	C1–C2–N8	121.26
C2–C3	1.4424	C4–H14	1.0733	C2–N8–O9	120.30
C3–C4	1.3371	C5–H15	1.0756	C2–N8–O10	124.65
C4–C5	1.4472	C6–H16	1.0751	N8–O9–H11	108.23
C5–C6	1.3381	C1–C2–C3	121.16	C2–C3–H13	117.85
C1–C6	1.4591	C2–C3–C4	120.41	C3–C4–H14	120.90
C1–N7	1.2806	C3–C4–C5	119.64	C4–C5–H15	118.47
N7–H10	1.0007	C4–C5–C6	122.25	C5–C6–H16	121.21
C2–N8	1.3357	C1–C6–C5	121.73	C6–C1–N7–H12	0.00
N8–O9	1.3083	C2–C1–C6	114.81	C1–C2–N8–O9	0.00
N9–H11	1.0034	C2–C1–N7	120.67	C3–C2–N8–O10	0.00
N8–O10	1.1988	C1–N7–H12	114.22	C2–N8–O9–H11	0.00

Note: The unit of the bond length is Å, and the unit of the bond angle is degree

Table 7. Calculated HF/6-31G* energies of 2-nitroaniline and its thermal decomposition products

	Total energy [Hartree]	Relative energy [kcal/mol]
2-nitroaniline	– 489.2047073	0
Furazan	– 413.1813829	–
Furazan + H_20	– 489.1921357	7.89
aci-2-nitroaniline I	– 489.0992133	66.20
aci-2-nitroaniline II	– 489.1336002	44.62
aci-2-nitroaniline III	– 489.1523618	32.85

compound of 2-nitrotoluene [9], a nitrosoaromatic compound of 2-nitroaniline should be found. However, despite exhaustive computational efforts, an energy minimum corresponding to this compound was not found. This finding suggests no tendency arises for oxygen transfer in 2-nitroaniline molecule.

3.6. Energies of thermal decomposition molecules of 2-nitroaniline

Table 7 lists our total optimized energies at the HF/6-31G* level for the molecules of interest. Relative energies of each molecule are included in this tabulation. The reaction of 2-nitrotoluene to form anthranil and water is thermally favored [9]; however, the formation of furazan and water from 2-nitroaniline is thermally unfavored from this calculation. This difference can be accounted for by different thermal decomposition mechanisms [13].

Since the reaction of 2-nitroaniline to form furazan and water has a calculated ΔE value of + 7.89 kcal/mol, the formation of furazan is predicted to occur to a significant extent, but without any notable net change in energy. The formation of aci-2-nitroaniline III is also thermally unfavorable with a calculated ΔE value of + 32.85 kcal/mol. Matvee et al. [49] indicated that the activation energy for thermal decomposition of 2-nitroaniline to aci-tautomer is relatively large with a value of 57.5 kcal/mol. According to our calculations, aci-2-nitroaniline I is a transition state of the thermal decomposition of 2-nitroaniline and the activation energy is calculated with a value of 66.20 kcal/mol, i.e. markedly higher than the experimental value.

4 Conclusions

1. The molecular structures of three mono-substituted nitroanilines were calculated by an *ab-initio* self-consistent-field molecular-orbital approach with a 6-31G* basis set. The calculations indicated that 4-nitroaniline is the most stable compound. Because of the conjugation effect, C–NH_2 bond is shorter than C–NO_2 bond. From this calculation, we can infer that the C–NH_2 bond tends to have double-bond characteristics; however, C–NO_2 bond is still a single bond. Perturbations of the nitro and amino groups influence each isomer's geometry.

2. Internal rotation of the nitro or amino group of each mono-nitroaniline was assessed according to the geometries and energies. For 2-nitroaniline, after internal rotation, its geometry alters significantly. However, only a slightly change of the

structures was found for 3-nitro and 4-nitroaniline. That internal rotation of the C–NO_2 bond is easier than the C–NH_2 bond and that double-bond characteristics of C–NH_2 bond and single-bond characteristics of C–NO_2 bond indicate that bond rupture tends to C–NO_2 bond after thermal decomposition.

3. Five possible rearrangement products of 2-nitroaniline were tested, which are intramolecular transfer tautomers of hydrogen or cyclization reaction products. Second derivative calculations observed that furazan, and two aci-2-nitroanilines are stable molecules, aci-2-nitroaniline I is a transition state; a nitrosoaromatic compound does not exist. For those observed thermal decomposition products, HF energies show that they are thermally unfavorable.

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