

Theoretical investigation of azido group dissociation in aromatic azides

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Abstract

MNDO-PM3 level calculations and ab initio calculations at the UHF/6-31G* level were performed for the neutral molecules (S_0 state), the lowest excited states (T_0 and S_1) and the radical anions (D_0 and D_1 states) of *p*-nitrophenyl, *p*-acetylphenyl and phenyl azides, 4-azidopyridine and HN_3 . Consideration of the nature of the frontier molecular orbitals, changes of the bond orders and the values of the activation barriers shows that decomposition of the azido group is facilitated on (or by) the excitation of the azide into the lowest excited states and formation of the radical anion. © 1997 Elsevier Science B.V.

Keywords: MNDO-PM3; Ab initio; Aromatic azide; Radical anion; Azido group dissociation

1. Introduction

The photochemical properties of organic azides have been investigated extensively [1–5]. However, there are only a restricted number of theoretical publications on this subject. The first excited singlet state S_1 and the lowest triplet state T_0 are the most interesting from the point of view of photochemistry, so these states are examined in the present paper in comparison with the ground state S_0 . Electron transfer to the azide, as well as excitation, is known to lead to the decomposition of the azido group [6,7], the radical anions of the azides being necessary intermediates in these reactions. Therefore, another subject for discussion in the present paper is the two states of the radical anions, D_0 and D_1 .

The structures of the azides and their radical anions were calculated with full optimization of geometrical

parameters using the semiempirical method MNDO-PM3 [8] (program package MOPAC 7.0). Energy parameters were improved by ab initio RHF, UHF methods with the basis 6-31G*. The correlation energy was calculated using the second and third order of Moller–Plesset perturbation theory (MP2 and MP3); the GAUSSIAN-94 code was used [9]. Excited states were calculated using CIS and CASSCF levels of theory in GAUSSIAN-94 and EXCITED and C.I. operators in MOPAC 7.0.

Fig. 1 shows the coordinate system used and the structures of the aromatic azides investigated: *p*-nitrophenyl azide (NPA), *p*-acetylphenyl azide (APA), 4-azidopyridine (AP), phenyl azide (PA), and, for comparison, the simplest azide HN_3 .

2. Results

2.1. Molecular orbitals and electron levels

Conventionally, we define the molecular orbital

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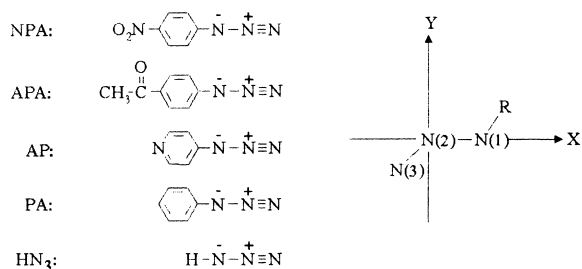


Fig. 1. Structures of the azides investigated and the coordinate system used.

(MO) lying in the plane of the aromatic ring as a σ -type MO, and that lying in the perpendicular plane as a π -type MO. Fig. 2 shows the structures of the frontier MOs: the highest occupied MO (HOMO), the lowest unoccupied MO (LUMO) and the second lowest unoccupied MO (SLUMO) of neutral aromatic azides in the region of the azido group using NPA as an example.

In accordance with our definition, HOMO and LUMO are π -type orbitals, and SLUMO is σ -type orbital. All three MOs are antibonding on the N(2)–N(3) bond; at the same time, in the region of the N(1)–N(2) bond HOMO is slightly bonding, LUMO is non-bonding, and SLUMO is antibonding.

Fig. 3 shows the changes of the electron levels of the neutral molecules in the series NPA–APA–AP–PA–HN₃. In this series, the electron level of the σ -type SLUMO changes slightly, but the electron level of the π -type LUMO increases, so that in passing from PA to HN₃ a change of order of these levels is observed.

Fig. 4 shows the filling of the electron levels in

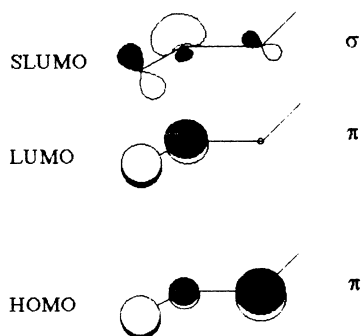


Fig. 2. Frontier orbitals of NPA in the region of the azido group.

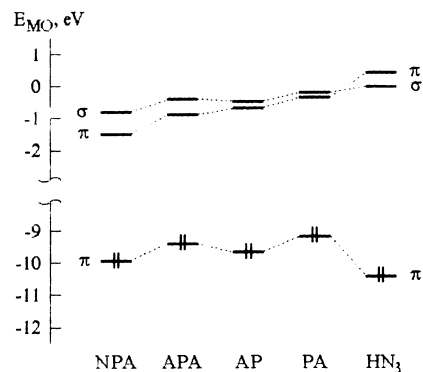


Fig. 3. PM3 calculated changes of the electron levels of neutral azides.

different states for the example of APA and its radical anion. One can see that the excited states S_1 and T_0 are similar to the D_0 state of the radical anion from the nature of the highest singly occupied MOs, which are σ -type MOs. In the S_0 and D_1 states, the highest occupied MOs are π -type MOs.

2.2. Geometry and charge distribution

Geometrical parameters are shown in Table 1, and bond orders (PM3 calculated), Mulliken density populations (RHF/6-31G* calculated) and effective atomic charges are shown in Table 2. The example of the HN₃, PA and NPA molecules shows that the geometrical parameters, calculated by the PM3 method, are in good accordance (within 0.02–0.03 Å for the bond lengths and 1–5° for the valence angles) with more

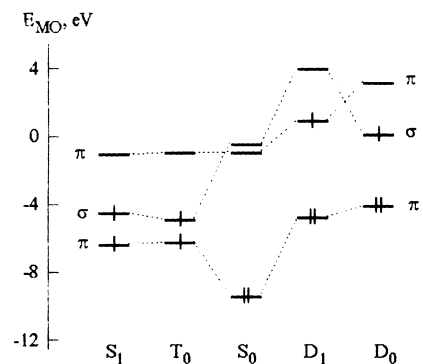


Fig. 4. Filling of the electron levels in different states of APA and its radical anion (PM3 calculation).

Table 1
Geometry of the XNNN fragment (X=H, C) in aryl azides and HN₃

Molecule	State	$r_{\text{X-N}(1)}$ (Å)	$r_{\text{N}(1)-\text{N}(2)}$ (Å)	$r_{\text{N}(2)-\text{N}(3)}$ (Å)	$\angle\text{NNN}$ (deg)	Method
HN ₃	S ₀	1.00	1.25	1.13	169.8	PM3
		1.02	1.28	1.11	171.1	RHF/3-21G
		1.01	1.24	1.10	173.8	RHF/6-31G*
		1.02	1.24	1.13	171.3	MCSCF/Huz ^a
		1.02	1.24	1.13	171.3	CASSCF(14,10)/Huz ^a
		1.02	1.25	1.16	171.1	MP2(FC)/6-31G*
		1.02	1.24	1.13	171.3	MCSCF + SDCl/Huz ^a
		1.02	1.24	1.13	171.3	Exp. ^b
	T ₀	0.99	1.38	1.16	127.6	PM3
		1.01	1.39	1.17	117.9	ROHF/6-31G*
HN ₃ ⁻	S ₁	0.99	1.37	1.16	129.8	PM3
		1.03	1.40	1.21	123.5	ROHF/3-21G
	D ₀	1.01	1.32	1.21	123.8	ROHF/6-31G*
		1.03	1.36	1.18	133.6	MP2(FC)/6-31G*
		1.00	1.34	1.17	173.3	PM3
PA	S ₀	1.44	1.26	1.13	169.6	PM3
		1.42	1.23	1.10	174.6	RHF/6-31G*
	T ₀	1.36	1.40	1.16	127.5	PM3
PA ⁻	S ₁	1.40	1.34	1.16	135.8	PM3
	D ₀	1.38	1.36	1.17	130.4	PM3
AP	S ₀	1.43	1.27	1.13	169.4	PM3
		1.37	1.39	1.16	127.3	PM3
	T ₀	1.41	1.37	1.16	134.0	PM3
AP ⁻	D ₀	1.37	1.37	1.17	130.2	PM3
	D ₁	1.38	1.30	1.16	170.1	PM3
APA	S ₀	1.43	1.27	1.13	169.3	PM3
		1.36	1.40	1.16	127.5	PM3
	T ₀	1.40	1.34	1.15	135.0	PM3
APA ⁻	D ₀	1.37	1.37	1.17	129.9	PM3
	D ₁	1.42	1.25	1.15	169.0	PM3
NPA	S ₀	1.42	1.27	1.13	169.2	PM3
		1.417	1.270	1.127	173.4	Exp. ^c
	T ₀	1.36	1.40	1.16	127.3	PM3
	S ₁	1.40	1.35	1.16	133.5	PM3
NPA ⁻	D ₀	1.35	1.38	1.16	129.6	PM3
	D ₁	1.43	1.25	1.14	169.1	PM3

^a Calculated using the Huzinaga basis (10s6p1d)_N, (6s2p)_H [10].

^b See Ref. [11].

^c Crystallographic data [12].

precise ab initio calculations and with experimental data. From Table 2 one can see the same trend of changes of the bond orders, density populations and charges in the azides investigated for both semi- and non-empirical calculations.

In the neutral azides, the azido group has near linear geometry: the valence angle NNN is 169–170°, the N(2)–N(3) bond length is 1.12–1.13 Å (bond order

$p_{23} = 2.48\text{--}2.55$), the N(1)–N(2) bond length is 1.26–1.27 Å (bond order $p_{12} = 1.33\text{--}1.35$) for NPA–APA–AP–PA and 1.25 Å ($p_{12} = 1.43$) for HN₃.

The excitation of an electron in aryl azides from the highest occupied π -MO to the lowest unoccupied σ -MO, which is antibonding on the N(1)–N(2) bond, results in a lengthening of this bond by 0.07–0.10 Å in the S₁ state. On the transition from the S₁ to the T₀

Table 2

Bond orders (PM3 calculated), Mulliken density populations (RHF/6-31G* calculated) and effective atomic charges in the XNNN fragment (X=H, C) in aryl azides and HN₃

Molecule	State	$p_{X-N(1)}$	$p_{N(1)-N(2)}$	$p_{N(2)-N(3)}$	q_X	$q_{N(1)}$	$q_{N(2)}$	$q_{N(3)}$	Method	
HN ₃	S ₀	0.93	1.43	2.48	0.13	-0.47	0.72	-0.37	PM3	
		0.62	0.60	1.22	0.39	-0.57	0.35	-0.17	RHF/6-31G*/PM3	
		0.62	0.58	1.32	0.38	-0.57	0.39	-0.20	RHF/6-31G*/6-31G*	
	T ₀	1.04	1.12	2.24	0.09	-0.06	0.14	-0.17	PM3	
		0.56	0.27	0.76	0.38	-0.31	-0.03	-0.05	ROHF/6-31G*/PM3	
		0.56	0.27	0.76	0.37	-0.29	-0.05	-0.03	ROHF/6-31G*/6-31G*	
HN ₃ ⁻	S ₁	1.04	1.14	2.27	0.09	-0.09	0.16	-0.16	PM3	
	D ₀	1.00	1.20	2.06	0.02	-0.64	0.26	-0.64	PM3	
		0.57	0.49	0.76	0.23	-0.75	-0.05	-0.43	ROHF/6-31G*/PM3	
	D ₁	0.96	1.05	2.05	0.03	-0.63	0.25	-0.66	PM3	
	PA	S ₀	1.01	1.37	2.51	0.04	-0.42	0.73	-0.34	PM3
			0.61	0.42	1.23	0.27	-0.52	0.39	-0.16	RHF/6-31G*/PM3
0.63			0.48	1.31	0.27	-0.51	0.44	-0.20	RHF/6-31G*/6-31G*	
T ₀	1.48	0.91	2.30	0.01	-0.14	0.16	-0.21	PM3		
S ₁	1.35	1.05	2.29	-0.01	-0.17	0.24	-0.19	PM3		
	1.28	0.99	2.19	0.14	-0.48	0.26	-0.49	PM3		
PA ⁻	D ₀	0.87	0.36	0.85	0.33	-0.61	-0.02	-0.29	ROHF/6-31G*/PM3	
		1.02	1.35	2.53	0.07	-0.42	0.73	-0.32	PM3	
		0.64	0.40	1.25	0.33	-0.52	0.39	-0.14	RHF/6-31G*/PM3	
	T ₀	1.40	0.91	2.23	0.01	-0.101	0.16	-0.19	PM3	
		1.35	0.98	2.26	0.01	-0.11	0.19	-0.20	PM3	
		1.33	0.97	2.21	0.17	-0.46	0.25	-0.47	PM3	
AP ⁻	D ₀	0.91	0.34	0.86	0.38	-0.60	-0.02	-0.27	ROHF/6-31G*/PM3	
		1.22	1.28	2.20	-0.07	-0.31	0.44	-0.53	PM3	
		1.02	1.35	2.53	0.07	-0.42	0.73	-0.32	PM3	
	S ₀	0.63	0.40	1.24	0.29	-0.52	0.39	-0.14	RHF/6-31G*/PM3	
		1.48	0.88	2.25	0.02	-0.12	0.16	-0.20	PM3	
		1.38	1.00	2.24	0.01	-0.13	0.20	-0.22	PM3	
APA ⁻	D ₀	1.37	0.95	2.22	0.17	-0.44	0.24	-0.45	PM3	
		0.90	0.28	0.85	0.34	-0.59	-0.04	-0.23	ROHF/6-31G*/PM3	
		1.07	1.45	2.27	-0.15	-0.33	0.62	-0.55	PM3	
	D ₁	1.04	1.33	2.55	0.10	-0.42	0.72	-0.30	PM3	
		0.64	0.40	1.25	0.31	-0.52	0.39	-0.12	RHF/6-31G*/PM3	
		1.47	0.89	2.25	0.02	-0.09	0.15	-0.17	PM3	
NPA ⁻	S ₁	1.38	0.98	2.22	0.02	-0.09	0.18	-0.20	PM3	
		1.46	0.92	2.24	0.19	-0.40	0.23	-0.41	PM3	
		0.93	0.26	0.85	0.35	-0.57	-0.04	-0.20	ROHF/6-31G*/PM3	
	D ₁	1.06	1.46	2.31	-0.14	-0.34	0.64	-0.50	PM3	

state, a further lengthening takes place, the bond order being reduced to $p_{12} = 0.88-0.91$.

In the radical anions (D₀ state) the azido group has trans-bent geometry: the valence angle NNN is 130–132°, the N(2)–N(3) bond length is 1.16–1.18 Å (bond order $p_{23} = 2.19-2.24$), and the N(1)–N(2) bond length is 1.36–1.38 Å (bond order $p_{12} = 0.92-0.99$) for the aryl azides and 1.31 Å ($p_{12} = 1.20$) for HN₃. One can see that from the geometrical parameters,

the D₀ state is similar to the S₁ state as a result of the similar nature of the singly occupied MOs (σ -type MOs).

The D₁ state differs from the D₀ state mainly by the values of the valence angle NNN and the bond length r_{12} . For aryl azides, according to the geometrical parameters, the D₁ state is similar to the S₀ state as a result of the similar nature of the highest occupied MOs (π -type MOs).

Table 3

Heats of formation (H_f , PM3 calculated) and total energies (E , ab initio calculated) of aryl azides and HN_3 (S_0 state) and their radical anions (D_0 state), the first singlet vertical excitation energies (E_v) and electron affinities (EA)

Molecule	State	H_f (kcal mol ⁻¹)	E (a.u.)	E_v^a (eV)	EA (eV)	Method
HN_3	S_0	75.3	–	–(4.70)	1.02	PM3
			–162.8764	–	–1.07	RHF/3-21G//3-21G
			–163.8338	4.78	–0.99	RHF/6-31G**/PM3
			–163.8387	4.78	–1.03	RHF/6-31G**/6-31G*
			–163.8387	–	–0.79	UHF/6-31G**/6-31G*
			–164.3322	–	–1.78	MP2(FC)/6-31G**/6-31G*
			–164.3411	–	–1.67	MP2(FC)//6-31G**/MP2/6-31G*
			–164.3215	–	–1.22	MP3(FC)/6-31G**/6-31G*
HN_3^-	D_0	51.8	–	–	–	PM3
			–162.8372	–	–	ROHF/3-21G//3-21G
			–163.7974	–	–	ROHF/6-31G**/PM3
			–163.8008	–	–	ROHF/6-31G**/6-31G*
			–163.8096	–	–	UHF/6-31G**/6-31G*
			–164.2666	–	–	MP2(FC)/6-31G**/6-31G*
			–164.2798	–	–	UMP2(FC)/6-31G**/UMP2(FC)/6-31G*
			–164.2766	–	–	UMP3(FC)/6-31G**/6-31G*
PA	S_0	100.7	–	4.64(4.35)	1.79	PM3
			–393.3769	4.38	–0.02	RHF/6-31G**/PM3
			–393.3862	–	–	RHF/6-31G**/6-31G*
PA^-	D_0	59.4	–	–	–	PM3
			–393.3761	–	–	ROHF/6-31G**/PM3
AP	S_0	107.6	–	4.73(4.59)	2.09	PM3
			–409.3674	4.56	0.44	RHF/6-31G**/PM3
AP^-	D_0	59.4	–	–	–	PM3
			–409.3835	–	–	ROHF/6-31G**/PM3
APA	S_0	59.4	–	4.57(4.43)	2.15	PM3
			–545.1486	4.48	0.51	RHF/6-31G**/PM3
			–545.1486	–	0.75	UHF/6-31G**/PM3
APA^-	D_0	9.8	–	–	–	PM3
			–545.1673	–	–	ROHF/6-31G**/PM3
			–545.1761	–	–	UHF/6-31G**/PM3
NPA	S_0	91.7	–	4.51(3.94)	2.64	PM3
			–596.8427	4.59	0.95	RHF/6-31G**/PM3
			–596.8427	–	1.20	UHF/6-31G**/PM3
NPA^-	D_0	30.7	–	–	–	PM3
			–596.8778	–	–	ROHF/6-31G**/PM3
			–596.8869	–	–	UHF/6-31G**/PM3

^a Experimental values are given in parentheses.

Thus, the analysis of changes in the bond orders, N(1)–N(2) bond lengths and the nature of the occupied MOs shows that removal of an N_2 molecule from the T_0 , S_1 and D_0 states will occur more easily than from the S_0 state.

In all the azides under consideration, the terminal atoms N(1) and N(3) of the azido group are more negatively charged than the central nitrogen atom N(2).

Calculations show that in the aryl azides about 0.08–0.12 e moves through the π -system from the N(1) and N(3) atoms to the benzene ring, which results in an alteration of the charges on the carbon atoms in the ring. It is noteworthy that the quantity of electron density that moves to the ring through the π -system decreases in the order NPA–AP–APA–PA.

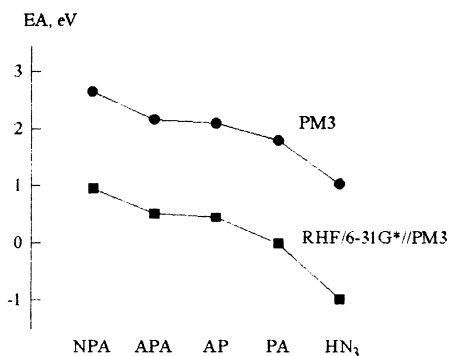


Fig. 5. Changes of the electron affinities of the azides calculated by different methods.

2.3. Energy parameters and electron affinities

Heats of formation (PM3 calculated), total energies (ab initio calculated), the first singlet vertical excitation energies and electron affinities of the azides are shown in Table 3. The example of HN₃ and PA shows that total energies, calculated on the RHF/6-31G**/PM3 and RHF/6-31G**/6-31G* levels, differ by 0.0045 a.u. and 0.0093 a.u., correspondingly. In all cases, the PM3 and HF/6-31G* calculated E_v values are in good agreement with the experimental values (within 0.14–0.29 eV for PM3 and 0.03–0.08 eV for HF/6-31G*). The case of NPA is an exception and should be discussed separately.

The example of HN₃ shows that the electron affinity changes significantly by going from the PM3

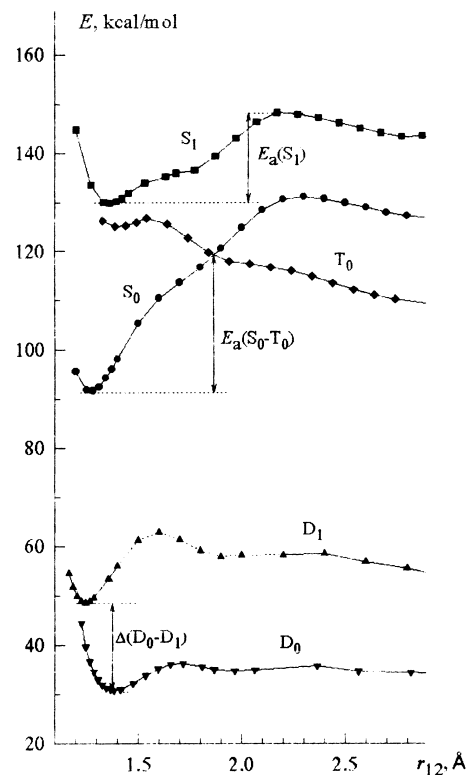


Fig. 7. Minimal energy paths of azido group dissociation in the ground (S_0) and excited (T_0 , S_1) states and in the radical anions (D_0 and D_1 states) of NPA. Examples of E_a and Δ calculations are shown.

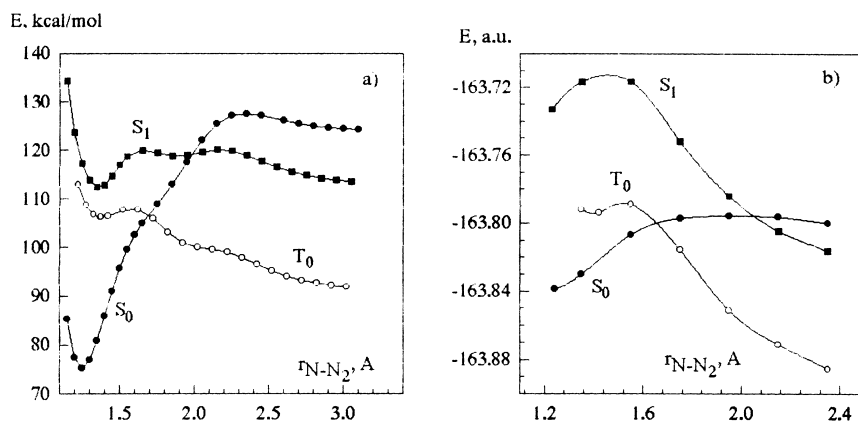


Fig. 6. Minimal energy path of azido group dissociation in the ground (S_0) and excited (T_0 , S_1) states of HN₃: (a) PM3 calculated; (b) calculated at the HF/6-31G* level (in accordance with Tables 3 and 4).

Table 4
Calculated energy differences (Δ) between different states of the azides and radical anions (for definition, see Fig. 7)

Molecule	State	Δ (kcal mol ⁻¹)	Method
HN ₃	S ₀ -T ₀	31	PM3
		26	ROHF/6-31G**/PM3
		26	ROHF/6-31G**/6-31G*
	S ₀ -S ₁	50	MP3(FC)/6-31G**/6-31G*
		37	PM3
HN ₃ ⁻	D ₀ -D ₁	66	CIS/6-31G**/6-31G*
		21	PM3
		51	CIS/6-31G**/6-31G*
PA	S ₀ -T ₀	29	PM3
	S ₀ -S ₁	35	PM3
PA ⁻	D ₀ -D ₁	(22) ^a	PM3
AP	S ₀ -T ₀	32	PM3
	S ₀ -S ₁	36	PM3
AP ⁻	D ₀ -D ₁	25	PM3
APA	S ₀ -T ₀	31	PM3
	S ₀ -S ₁	36	PM3
APA ⁻	D ₀ -D ₁	22	PM3
NPA	S ₀ -T ₀	33	PM3
	S ₀ -S ₁	38	PM3
NPA ⁻	D ₀ -D ₁	18	PM3

^a Estimated value.

semiempirical calculation to the ab initio RHF/6-31G**/PM3 level; however, it changes only slightly during geometry optimization on the 6-31G* level. By going from RHF to UHF, the electron affinity changes by 0.2 eV. Electron correlation on the MP3(FC)/6-31G**/6-31G* level results also in a minor (0.2 eV) change of the electron affinity value.

For the aromatic azides investigated, the RHF/6-31G**/PM3 calculated electron affinities differ from the semiempirical values less than for HN₃ (by 1.7 eV), and by going from RHF to UHF, the changes are the same, as in the case of HN₃. Therefore, calculations on the RHF/6-31G**/PM3 level are sufficient for revealing a qualitative picture of electron affinity changes in the set of azides under investigation. Calculations show that in the series NPA-APA-AP-PA-HN₃ the electron affinity decreases monotonically (Fig. 5), and, as a result, for the last members of the series the formation of radical anions becomes thermodynamically unfavourable.

Fig. 6 shows the PM3 and HF/6-31G* level calculated minimal energy path of azido group dissociation for the S₀, T₀ and S₁ states of HN₃. One can see

that the semiempirical and ab initio methods give a qualitatively similar picture of the HN₃ dissociation process.

Fig. 7 shows the relative position of the states under discussion and the minimal energy paths of azido group dissociation in aryl azides for the example of NPA. Fig. 7 demonstrates the principle of the calculation of the energy differences (Δ) between the different states of the azides and radical anions, and activation barriers (E_a) for the azido group dissociation reaction (the value of $E_a(S_0-T_0)$ was approximately estimated as a cross-over point of two curves). Calculated Δ values for all the discussed states of the azides are shown in Table 4, and E_a values are given in Table 5.

The difference in the heats of formation (or total molecular energies) in the S₀ and T₀ states of HN₃ ($\Delta(S_0-T_0)$; Table 4) shows that the ROHF/6-31G**/6-31G* and ROHF/6-31G**/PM3 calculated values are similar, and less than the PM3 calculated value by 5 kcal mol⁻¹. The MP3(FC)/6-31G**/6-31G* calculated value exceeds the PM3 calculated value by 19 kcal mol⁻¹.

Table 5

Calculated activation energy (E_a) of the azido group dissociation reaction in different states of the azides and their radical anions (for definition, see Fig. 7)

Molecule	State	E_a (kcal mol ⁻¹)	Method
HN ₃	S ₀	52	PM3
		27	RHF/6-31G*/PM3
		27	RHF/6-31G**/6-31G*
		22	CASSCF(4,4)/6-31G**/6-31G*
		39	CASSCF(8,8)/6-31G**/6-31G*
		48	MP3(FC)/6-31G**/6-31G*
		53.6	Exp. ^a
	S ₀ -T ₀	32	PM3
		25	RHF/6-31G**/6-31G*
		39	CASSCF(14,10)/Huz ^b
		35	MCSCF + SDCl/Huz ^b
		36.2	Exp. ^a
	T ₀	2	PM3
		7	ROHF/6-31G**/6-31G*
		2	UHF/6-31G**/6-31G*
		1	PUHF/6-31G**/6-31G*
		2	MP3(FC)/6-31G**/6-31G*
	S ₁	8	PM3
		10	CIS/6-31G**/6-31G*
HN ₃ ⁻	D ₀	37	PM3
		19	ROHF/6-31G**/6-31G*
		13	UHF/6-31G**/6-31G*
		11	PUHF/6-31G**/6-31G*
		14	MP2(FC)/6-31G**/6-31G*
		12	PMP2(FC)/6-31G**/6-31G*
		14	MP3(FC)/6-31G**/6-31G*
	D ₁	17	PM3
		5	CIS/6-31G**/6-31G*
PA	S ₀	35	PM3
	T ₀	2	PM3
	S ₀ -T ₀	27	PM3
	S ₁	19	PM3
PA ⁻	D ₀	(10) ^c	PM3
AP	S ₀	40	PM3
	T ₀	2	PM3
	S ₀ -T ₀	27	PM3
	S ₁	16	PM3
AP ⁻	D ₀	8	PM3
APA	S ₀	36	PM3
	T ₀	2	PM3
	S ₀ -T ₀	27	PM3
	S ₁	18	PM3
APA ⁻	D ₀	7	PM3
NPA	S ₀	39	PM3
	T ₀	2	PM3
	S ₀ -T ₀	28	PM3
	S ₁	18	PM3
NPA ⁻	D ₀	6	PM3
	D ₁	14	PM3

^a See Ref. [13].

^b Calculated using the Huzinaga basis (10s6p1d)N, (6s2p)H [10].

^c Estimated value.

One can see that the values of $\Delta(S_0-T_0)$ and $\Delta(S_0-S_1)$ change slightly for all the azides under investigation and lie in the region of 29–33 kcal mol⁻¹ and 35–38 kcal mol⁻¹, respectively. A more significant change is observed for the difference $\Delta(D_0-D_1)$; this value is minimal for NPA (18 kcal mol⁻¹) and increases (to 25 kcal mol⁻¹) in the order NPA–APA–AP.

The PM3 calculated activation barrier, $E_a(S_0)$, for HN₃ coincides with experimental values (52 kcal mol⁻¹ and 53.6 kcal mol⁻¹, respectively; Table 5). The RHF/6-31G**/6-31G* and RHF/6-31G**/PM3 calculated values of $E_a(S_0)$ are similar and less than the PM3 calculated value by 25 kcal mol⁻¹; the correlation correction makes up 21 kcal mol⁻¹.

The value of $E_a(S_0-T_0)$ was estimated as the difference in the total energy (S_0) of the system at the minimal point and for the N(1)–N(2) bond length when the total energies in the S_0 and T_0 states coincide (Fig. 7). The PM3 calculated activation barrier $E_a(S_0-T_0)$ agrees with experimental values (32 kcal mol⁻¹ and 36.2 kcal mol⁻¹, respectively; Table 5). The RHF/6-31G**/6-31G* calculated value is equal to 25 kcal mol⁻¹; the correlation correction increases this value by 10 kcal mol⁻¹.

For the excited states (T_0, S_1), the PM3 and ab initio calculated activation barriers differ within 2–5 kcal mol⁻¹. Taking into account the above corrections, the PM3 method can be used for the qualitative estimation of the relative reactivity of aromatic azides in different states.

For all the azides under consideration, the activation barrier, both semi- and non-empirically calculated (Fig. 6, Fig. 7, Table 5) is the highest for the S_0 state and is comparatively small for the excited states (T_0, S_1) and for the radical anion (D_0 and D_1 states).

Comparison of the E_a values for the azides discussed above (Table 5) shows that the value of the activation barrier for every specific state does not practically depend on the nature of the azide and is mainly determined by the nature of the state.

Thus, the calculations show that decomposition of

the azido group is facilitated on (or by) excitation of the azide into the lowest excited states (T_0 or S_1) and formation of the radical anion (D_0 or D_1 state). This conclusion is in full accordance with the known experimental results [1–7].

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