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Supplementary Material

UNIFIED STATISTICAL RRKM APPROACH TO THE FRAGMENTATION AND AUTONEUTRALIZATION OF METASTABLE MOLECULAR NEGATIVE IONS OF HEXAAZATRINAPHTHYLENES

Rustem V. Khatymov[1], Pavel V. Shchukin[1], Mars V. Muftakhov[1], Igor K. Yakushchenko[2], Ol'ga V. Yarmolenko[2], Evgeniy Yu. Pankratyev[1]

[1]Institute of Molecule and Crystal Physics, Ufa Federal Research Centre of the Russian Academy of Sciences, Ufa 450075, Russia
[2]Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region 142432, Russia

Table S1.

Theoretical thermochemical characteristics of HATNA according to DFT calculations and those measured / estimated from experimental data

Thermochemical parameter [a]	**Value, eV**
Molecular adiabatic electron affinity, $EA_a(^2M^{\bullet -} \rightarrow {}^1M+e)$	2.76 ± 0.40[b] 1.45[c] 2.15[d] 2.21[e]
Adiabatic electron affinity of dehydrogenated molecule, $EA_a(^3[M–H]^- \rightarrow {}^2[M–H]^{\bullet} + e)$	2.28[e,f]
Bond dissociation energy in neutral molecule $BDE(^1M \rightarrow {}^2[M–H]^{\bullet} + {}^2H)$	4.72[e,f]
Bond dissociation energy in molecular anion $BDE(^2M^{\bullet -} \rightarrow {}^3[M–H]^- + {}^2H^{\bullet})$	4.66[e,f]
Threshold appearance energy of $[M–H]^-$ ions, $AE(^1M+e \rightarrow {}^3[M–H]^- + {}^2H^{\bullet})$	2.44[e,f] **> 5**[g]

[a] The schemes of the processes for calculating energy change are shown in parenthesis. Left superscript digit denotes a spin multiplicity of corresponding species found to be the lowest in energy according to quantum-chemical calculations.

[b] Solid state electron affinity measured by inverse photoelectron spectroscopy [S1, S2]

[c] Theoretical DFT B3LYP/6-31G** prediction for gas phase molecules [S2]

[d] Best fit result from the statistical RRKM model, this work (see Section 3.3)

[e] Result from DFT PBE/3ζ calculations (see Section 3.1).

[f] H-atom abstraction energies from the structural positions 1 and 2 (see Chart 1) coincide within ±0.04 eV; mean value is shown.

[g] Visual estimates from experimental EYC of $[M–H]^-$ ions in Fig. 2c

References

[S1] B. R. Kaafarani, T. Kondo, J. Yu, Q. Zhang, D. Dattilo, C. Risko, S. C. Jones, S. Barlow, B. Domercq, F. Amy, A. Kahn, J.-L. Brédas, B. Kippelen, S. R. Marder. High Charge-Carrier Mobility in an Amorphous Hexaazatrinaphthylene Derivative. *Journal of the American Chemical Society.* **2005**;*127*:16358-16359.

[S2] S. Barlow, Q. Zhang, B. R. Kaafarani, C. Risko, F. Amy, C. K. Chan, B. Domercq, Z. A. Starikova, M. Y. Antipin, T. V. Timofeeva, B. Kippelen, J.-L. Brédas, A. Kahn, S. R. Marder. Synthesis, Ionisation Potentials and Electron Affinities of Hexaazatrinaphthylene Derivatives. *Chemistry – A European Journal.* **2007**;*13*:3537-3547.

Table S2

Energy parameters predicted by theoretical DFT PBE /3ζ calculations for characterization of thermodynamic stability and fragmentation of HMHATA molecule/anion and those obtained from RRKM model

Energy parameter	DFT PBE /3ζ		Best fit result from RRKM model, eV
	Description*	Value, eV	
Molecule			
Molecular adiabatic electron affinity	structure **A** (see Chart 1) $EA_a(^2M^{\bullet -} \rightarrow {}^1M+e)$	1.748	1.875
	structure **B**	2.032	
Dehydrogenation			
Adiabatic electron affinity of dehydrogenated molecule	structure **A**, position 1(CH_3) $EA_a(^3[M–H]^- \rightarrow {}^2[M–H]^{\bullet} + e)$	1.940	–
	structure **A**, position 2 $EA_a(^3[M–H]^- \rightarrow {}^2[M–H]^{\bullet} + e)$	2.267	–
Bond dissociation energies for detachment of hydrogen atom	from neutral molecule's position 1(CH_3), $BDE(^1M \rightarrow {}^2[M–H]^{\bullet} + {}^2H^{\bullet})$	3.983	–
	from molecular anion's position 1(CH_3), $BDE(^2M^{\bullet -} \rightarrow {}^3[M–H]^- + {}^2H^{\bullet})$	4.023	–
Threshold appearance energy	$AE(^1M+e \rightarrow {}^3[M–H]^- + {}^2H^{\bullet})$	2.066	–
Demethylation			
Adiabatic electron affinity of demethylated molecule	structure **A** $EA_a(^1[M–CH_3]^- \rightarrow {}^2[M–CH_3]^{\bullet} + e)$	2.703	–
Bond dissociation energies for detachment of one methyl group	from neutral molecule, $BDE(^1M \rightarrow {}^2[M–CH_3]^{\bullet} + {}^2CH_3^{\bullet})$	2.287	–
	from molecular anion, $BDE(^2M^{\bullet -} \rightarrow {}^1[M–CH_3]^- + {}^2CH_3^{\bullet})$	1.509	1.709
Threshold appearance energy	$AE(^1M+e \rightarrow {}^1[M–CH_3]^- + {}^2CH_3^{\bullet})$	–0.448	–
Second stage demethylation			
Adiabatic electron affinity of doubly demethylated molecule	Structure **A**, demethylated positions 1 and 4, $EA_a(^2[M–2CH_3]^- \rightarrow {}^1[M–2CH_3]^{\bullet} + e)$	2.494	–
Bond dissociation energies for detachment of second methyl group	from fragment anion's position 4, $BDE(^1[M–CH_3]^- \rightarrow {}^2[M– 2CH_3]^- + {}^2CH_3^{\bullet})$	1.755	1.765
	from fragment anion's positions 7, 10, 13, or 16, $BDE(^1[M–CH_3]^- \rightarrow {}^2[M–2CH_3]^- + {}^2CH_3^{\bullet})$	2.158 – 2.235	–
Threshold appearance energy	$AE(^1M+e \rightarrow {}^2[M–2CH_3]^- + {}^2CH_3 + {}^2CH_3^{\bullet})$	1.307	–

Demethoxylation			
Adiabatic electron affinity of demethoxylated molecule	structure **A** $EA_a(^3[M–OCH_3]^- \rightarrow ^2[M–OCH_3]^{\bullet} + e)$	2.090	–
Bond dissociation energies for detachment of methoxyl group	from neutral molecule, $BDE(^1M \rightarrow ^2[M–OCH_3]^{\bullet} + ^2OCH_3^{\bullet})$	4.093	–
	from molecular anion, $BDE(^2M^{\bullet -} \rightarrow ^3[M–OCH_3]^- + ^2OCH_3^{\bullet})$	3.987	–
Threshold appearance energy	$AE(^1M+e \rightarrow ^3[M–OCH_3]^- + ^2OCH_3^{\bullet})$	2.030	–

* See Chart 1 for the structures **A** and **B**. Left superscript denotes a spin multiplicity of corresponding lowest-energy species.