Electronic Supplementary Material (ESI) for RSC Advances

Theoretical prediction of the nitrogen-rich CN_3^- and related salts $M^+[CN_3]^-$ (M=Li, Na, K)

Supporting Information

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Table S1. Total energies (a.u.) and relative energies in parentheses (kcal/mol) of the triplet isomers 1, 2, 3, 7, 8, the transition states Ts1/2, Ts1/3 and Ts3/8, Ts1/8 the dissociation products P1, P2, P3, P4 at four levels.

Species	B3LYP/6-311+G(d)	CCSD(T)/6-311+G(d)//B3LYP/6-311+G(d)	CASPT2(12,12)/6-311+G(d)//CASSCF(12,12)/6-311+G(d)	CASPT2(12,12)/aug-cc-pVTZ//CASSCF(12,12)/aug-cc-pVTZ
CN_3^- ^{3}**1**	-202.3577111 (0.0)	-201.8484426 (0.0)	-201.70674254 (0.0)	-201.94196493 (0.0)
^{3}**2**	-202.3071487 (31.7)	-201.8032282 (28.4)	-201.70693933 (-0.1)	-201.89706673 (28.2)
^{3}**3**	-202.28352 (45.6)	-201.7767851 (45.0)	——	-201.86950544 (45.5)
^{3}**7**	-202.2299192 (80.2)	-201.7396822 (68.2)		-201.84192110 (62.8)
^{3}**8**		-201.7398872 (68.1)	-201.70402663 (68.5)	−201.83430543 (67.6)
^{3}**Ts1/2**	-202.3054796 (32.8)	-201.801874 (29.2)	−201.76190156 (32.6)	-201.89191438 (31.4)
^{3}**Ts1/3**	202.2604472 (61.0)	-201.770036 (49.2)	——	——
^{3}**Ts3/8**	-202.2244546 (83.6)	-201.722656 (78.9)	——	——
^{3}**Ts1/8**	-202.231014 (79.5)	-201.7341205 (71.7)	——	——
$^1CN^-+N_2$ **P1**	-202.4481637 (-133.7)	-201.9669039 (-136.8)	——	——
$^3CN^-+N_2$ **P2**	-202.2459741 (-6.8)	-201.7421784 (4.2)	——	——
$^1CN^-+^3N_2$ **P3**	-202.1781228 (35.8)	-201.6882559 (38.0)	——	——
$^3CN^-+^3N_2$	-201.9759332	-201.4635304	——	——

P4	(162.6)	(179.1)		

To obtained more accurate values, we further calculated the energies of 1, 2, 3, 7, and 8 at the CASPT2(12,12)/6-311+G(d)//CASSCF(12,12)/6-311+G(d) and CASPT2(12,12)/ aug-cc-pVTZ//CASSCF(12,12)/aug-cc-pVTZ level. The symbol "——"indicates that the values are not calculated.

Table S2. Total energies (a.u.) and relative energies in parentheses (kcal/mol) of the singlet isomers 4, 5, 6, the transition states Ts6/P1, Ts2/P1, Ts5/6 and Ts2/3, the dissociation products P1, P2, P3, P4 at four levels.

Species	B3LYP/6-311+G(d)	CCSD(T)/6-311+G(d)//B3LYP/6-311+G(d)	CASPT2(12,12)/6-311+G(d)//CASSCF(12,12)/6-311+G(d)	CASPT2(12,12)/aug-cc-pVTZ//CASSCF(12,12)/aug-cc-pVTZ	CASPT2(12,12)/6-311+G(d)//CASSCF(12,12)/6-311+G(d)+ΔG
CN_3^- ^{1}6	-202.2351120 (76.9)	-201.7488716 (62.5)	-201.81312390 (66.7)	-201.83967532 (64.2)	-201.71832924 (0.0)
^{1}4	-202.2391007 (74.4)	-201.7536941 (59.5)	-201.76930063 (66.6)	-201.83430498 (67.6)	——
^{1}5	-202.2389 (74.6)	-201.74967 (62.0)	-201.74088059 (79.1)	-201.81522404 (79.5)	——
^{1}Ts6/P1	-202.1743479 (115.1)	-201.6843834 (102.9)	-201.64515505 (105.4)	-201.77237323 (106.4)	-201.65904204 (37.2)
^{1}Ts4/P1	-202.2251786 (83.2)	-201.7472513 (63.5)	-201.70484807 (67.9)	-201.77237323 (68.1)	——
^{1}Ts5/6	-202.1804205 (111.3)	-201.6825231 (104.1)	-201.70484807 (111.7)	-201.76807884 (109.1)	——
^{1}Ts5/P1	-202.231014 (79.5)	-201.7397128 (68.2)	——	——	——
^{1}Ts4/5	-202.2360363 (76.4)	-201.7470932 (63.6)	——	——	——

To obtained more accurate values, we further calculated the energies of 4, 5, 6, Ts6/P1, Ts4/P1, Ts5/P1, Ts4/5 and Ts5/6 at the CASPT2(12,12)/6-311+G(d)//CASSCF(12,12)/6-311+G(d) and CASPT2(12,12)/aug-cc-pVTZ//CASSCF(12,12)/aug-cc-pVTZ level. The symbol "——"indicates that the values are not calculated.

Table S3. Calculated geometrical parameters and total energies (a.u.) of the ^{3}**1** and conical intersections between singlet and triplet at CASSCF(8,8)/6-311+G(d) level.

species	^{3}1	Conical intersection for process $NCNN^{-}$ $(C_s)\rightarrow CN+N_2$
C1–N2	1.171	1.191
C1–N3	1.311	1.256
N3–N4	1.311	1.367
N2–C1–N3	176.4	179.8
C1–N3–N4	116.2	120.2
N2–C1–N3–N4	180.0	180.0
energy	-201.80968178	-201.77688152

Bond lengths are in angstroms and angles in degrees.

Table S4. Calculated geometrical parameters and total energies (a.u.) of the Ts6/P1 and conical intersections between singlet and triplet at CASSCF(12,12)/6-311+G(d) level.

species	Ts6/P1	Conical intersection for process CN_3^{-} $(C_s)\rightarrow CN+N_2$
C1–N2	1.361	1.381
C1–N3	1.586	1.581
C1–N4	1.586	1.581
N3–N4	1.292	1.293
N2–C1–N4	80.2	80.4
N2–C1–N3	80.2	80.4
N3–C1–N4	48.1	48.2
C1–N2–N3–N4	75.4	75.1
N2–C1–N4–N3	85.6	85.7
energy	-201.64515960	-201.64302416

Bond lengths are in angstroms and angles in degrees.

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