

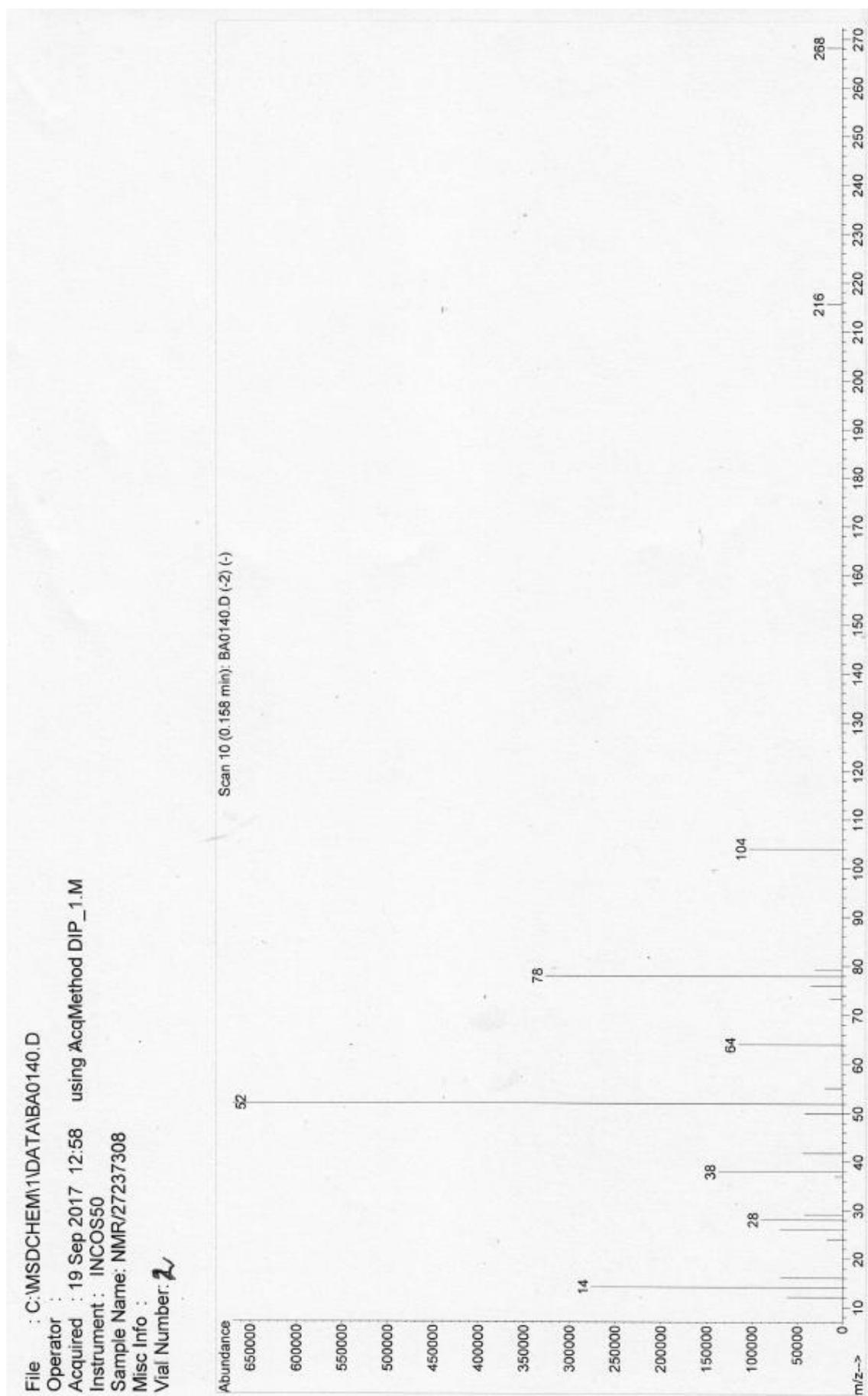
Electron impact generation of tetraazidocyclobutadiene radical cation from tetraazidopyridine-2-carbonitrile

Sergei V. Chapyshev and Evgeny N. Ushakov

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I. Experimental electron impact mass spectrum of tetraazidopyridine-2-carbonitrile



II. Details of DFT and CCSD(T) calculations

DFT calculations were performed using the Gaussian 09 program package [S1]. Molecular geometries were optimized in the gas phase using the M06-2X functional [S2] in combination with the 6-311+G(d) basis set. The geometry optimizations were followed by analytical frequency calculations at the same level of theory to verify the nature of stationary points and to compute zero point vibrational energies. The latter values were obtained using a scale factor of 0.97 for harmonic frequencies [S3].

High-level CCSD(T) calculations were carried out using the Priroda 17 program [S4]. The geometries of $C_4N_4^{++}$ and $C_3N_3^+$ were first optimized using the Laikov's L1 basis set (significantly improved analogue of the cc-pVDZ basis set) [5]; these optimizations were followed by numerical frequency calculations. The final CCSD(T) geometries were obtained using the L2 basis set (improved analogue of the cc-pVTZ basis set) [S5].

References

- [S1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford CT, 2013.
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- [S3] Database of frequency scale factors for electronic model chemistries. <http://comp.chem.umn.edu/freqscale/version3b2.htm>
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- [S5] D. N. Laikov, A new class of atomic basis functions for accurate electronic structure calculations of molecules, *Chem. Phys. Lett.*, 2005, **416**, 116. doi: 10.1016/j.cplett.2005.09.046

III. DFT data for the molecular ion of tetraazidopyridine-2-carbonitrile

1. Bond lengths and atomic charges

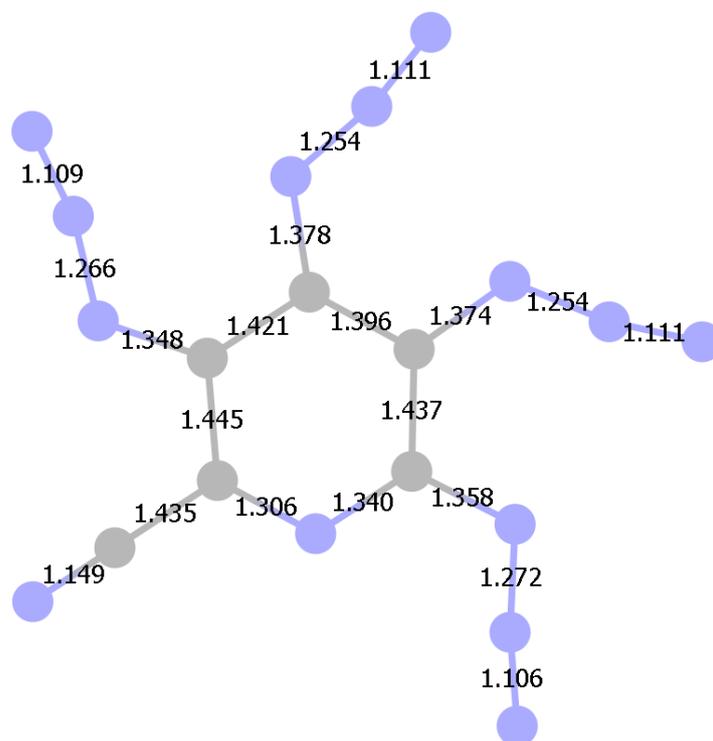


Figure S1. Bond lengths in the molecular ion $[1]^{*+}$.

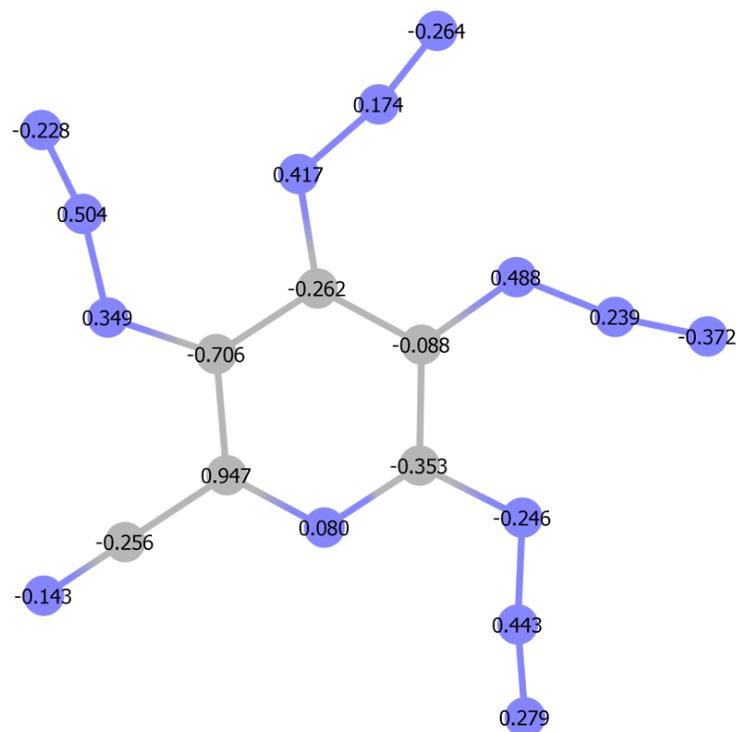
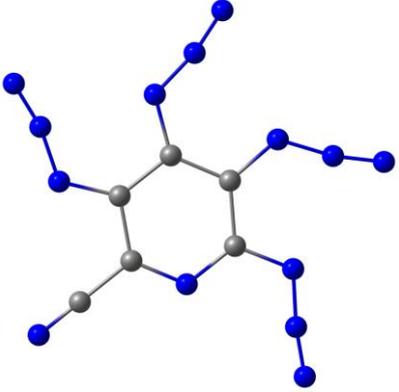


Figure S2. Mulliken atomic charges in the molecular ion $[1]^{*+}$.

2. Cartesian coordinates, DFT energy, and zero-point corrected energy

Table S1. Data from the M06-2X/6-311+G(d) calculations of [1]⁺.



Tetraazidopyridine-2-carbonitrile radical cation

Cartesian coordinates (Å)			
C	0.788947000	-0.568932000	0.000000000
C	-0.598256000	-0.722310000	-0.000001000
C	-1.400614000	0.470068000	0.000000000
N	-0.903060000	1.714386000	0.000002000
C	0.394449000	1.861253000	0.000002000
C	1.318316000	0.749783000	0.000001000
C	0.920993000	3.196227000	0.000004000
N	1.341102000	4.265597000	0.000005000
N	2.613261000	1.123362000	0.000002000
N	3.558734000	0.281042000	0.000001000
N	4.526726000	-0.259288000	0.000001000
N	1.747788000	-1.558996000	-0.000001000
N	1.447577000	-2.776765000	-0.000002000
N	1.384049000	-3.885843000	-0.000003000
N	-1.054825000	-2.018113000	-0.000002000
N	-2.277656000	-2.294530000	-0.000003000
N	-3.301601000	-2.725780000	-0.000003000
N	-2.745978000	0.286377000	0.000000000
N	-3.427566000	1.360166000	0.000001000
N	-4.128836000	2.214864000	0.000001000

DFT energy = -994.456037 a.u.
Zero-point correction = +0.096802 a.u.
Total energy = -994.359235 a.u.

IV. DFT data for the fragmented ions $C_4N_{12}^{*+}$, $C_4N_4^{*+}$, and $C_3N_3^+$

Table S2. Data from the M06-2X/6-311+G(d) calculations of $C_4N_{12}^{*+}$.

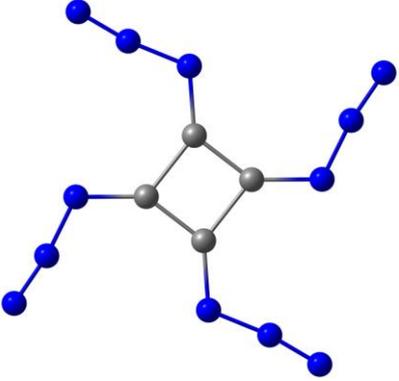
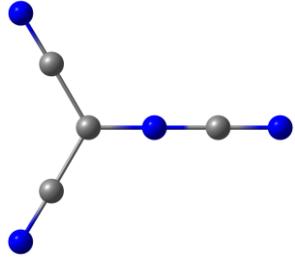
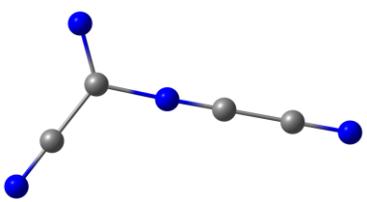
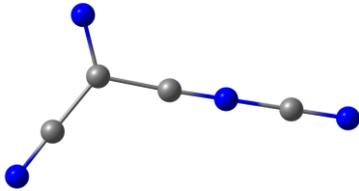
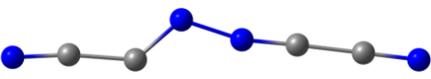
			
Tetraazidocyclobuta-1,3-diene radical cation			
Cartesian coordinates (Å)			
C	0.764345000	-0.338499000	-0.563249000
C	-0.516183000	-1.007766000	-0.182318000
C	-1.210782000	0.158751000	-0.469012000
C	0.069746000	0.828019000	-0.849945000
N	-0.699409000	-2.269575000	0.248294000
N	-1.891515000	-2.607303000	0.510763000
N	2.071542000	-0.645787000	-0.632690000
N	2.391431000	-1.822125000	-0.294812000
N	-2.517979000	0.466038000	-0.399570000
N	-2.837873000	1.642374000	-0.737448000
N	0.252977000	2.089826000	-1.280559000
N	1.445086000	2.427543000	-1.543030000
N	2.430652000	2.861904000	-1.809868000
N	-3.269982000	2.631015000	-1.000353000
N	-2.877075000	-3.041678000	0.777598000
N	2.823534000	-2.810768000	-0.031906000
DFT energy = -808.718473 a.u.			
Zero-point correction = +0.074869 a.u.			
Total energy = -808.643604 a.u.			

Table S3. Data from the M06-2X/6-311+G(d) calculations of $C_3N_3^+$.

			
Cartesian coordinates (Å)			
C	-1.903683000	0.915032000	-0.000116000
N	-0.589885000	0.969337000	0.000024000
C	0.556280000	1.016677000	0.000087000
C	1.922047000	1.073146000	0.000120000
N	3.074540000	1.120803000	0.000166000
N	-3.054088000	0.867421000	-0.000170000
DFT energy = -278.067139097 a.u.			
Zero-point correction = +0.026076 a.u.			
Total energy = -278.041063097 a.u.			

Table S4. Data from the M06-2X/6-311+G(d) calculations of C₄N₄⁺.

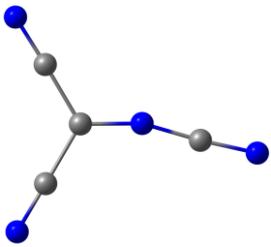
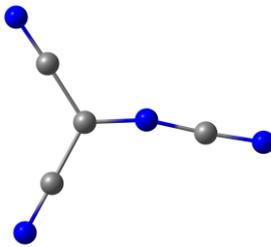
 <p>(Dicyanomethylene)cyanamide radical cation</p>	 <p>Valence isomer A Presumably, it is this isomer that forms in the gas phase reaction of NCCN with NCCN⁺ [M. J. McEwan, V. G. Anicich, <i>J. Phys. Chem.</i>, 1995, 99, 12204].</p>																																																																
<p>Cartesian coordinates (Å)</p> <table border="1"> <tbody> <tr><td>C</td><td>-1.689712000</td><td>0.839124000</td><td>-0.000020000</td></tr> <tr><td>N</td><td>-0.573644000</td><td>1.361413000</td><td>-0.000008000</td></tr> <tr><td>C</td><td>0.584077000</td><td>1.901633000</td><td>0.000005000</td></tr> <tr><td>C</td><td>1.753316000</td><td>1.085613000</td><td>0.000103000</td></tr> <tr><td>C</td><td>0.709729000</td><td>3.321933000</td><td>-0.000077000</td></tr> <tr><td>N</td><td>0.831557000</td><td>4.466587000</td><td>-0.000143000</td></tr> <tr><td>N</td><td>2.709050000</td><td>0.444014000</td><td>0.000182000</td></tr> <tr><td>N</td><td>-2.777619000</td><td>0.330437000</td><td>-0.000031000</td></tr> </tbody> </table>	C	-1.689712000	0.839124000	-0.000020000	N	-0.573644000	1.361413000	-0.000008000	C	0.584077000	1.901633000	0.000005000	C	1.753316000	1.085613000	0.000103000	C	0.709729000	3.321933000	-0.000077000	N	0.831557000	4.466587000	-0.000143000	N	2.709050000	0.444014000	0.000182000	N	-2.777619000	0.330437000	-0.000031000	<p>Cartesian coordinates (Å)</p> <table border="1"> <tbody> <tr><td>C</td><td>0.139313000</td><td>6.180995000</td><td>0.512078000</td></tr> <tr><td>C</td><td>-0.050527000</td><td>4.796628000</td><td>0.200706000</td></tr> <tr><td>C</td><td>-1.607044000</td><td>2.532401000</td><td>3.025882000</td></tr> <tr><td>C</td><td>-1.065226000</td><td>3.331124000</td><td>2.049562000</td></tr> <tr><td>N</td><td>-0.614645000</td><td>3.997346000</td><td>1.238092000</td></tr> <tr><td>N</td><td>0.289491000</td><td>7.290284000</td><td>0.767099000</td></tr> <tr><td>N</td><td>0.224525000</td><td>4.214374000</td><td>-0.880361000</td></tr> <tr><td>N</td><td>-2.061774000</td><td>1.861552000</td><td>3.844352000</td></tr> </tbody> </table>	C	0.139313000	6.180995000	0.512078000	C	-0.050527000	4.796628000	0.200706000	C	-1.607044000	2.532401000	3.025882000	C	-1.065226000	3.331124000	2.049562000	N	-0.614645000	3.997346000	1.238092000	N	0.289491000	7.290284000	0.767099000	N	0.224525000	4.214374000	-0.880361000	N	-2.061774000	1.861552000	3.844352000
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<p><i>DFT energy</i> = -370.849238436 a.u. <i>Zero-point correction</i> = +0.034134 a.u. <i>Total energy</i> = -370.815104 a.u.</p>	<p><i>DFT energy</i> = -370.850702037 a.u. <i>Zero-point correction</i> = +0.034776 a.u. <i>Total energy</i> = -370.815926 a.u.</p>																																																																
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<p>Cartesian coordinates (Å)</p> <table border="1"> <tbody> <tr><td>C</td><td>-2.009204000</td><td>1.168153000</td><td>0.137371000</td></tr> <tr><td>N</td><td>-0.712780000</td><td>0.967825000</td><td>0.002145000</td></tr> <tr><td>C</td><td>0.413212000</td><td>0.793471000</td><td>-0.115790000</td></tr> <tr><td>C</td><td>1.852233000</td><td>0.620719000</td><td>-0.239795000</td></tr> <tr><td>N</td><td>2.546838000</td><td>1.561660000</td><td>0.247002000</td></tr> <tr><td>N</td><td>-3.140046000</td><td>1.342492000</td><td>0.255070000</td></tr> <tr><td>C</td><td>2.341971000</td><td>-0.564778000</td><td>-0.883387000</td></tr> <tr><td>N</td><td>2.711796000</td><td>-1.520410000</td><td>-1.401649000</td></tr> </tbody> </table>	C	-2.009204000	1.168153000	0.137371000	N	-0.712780000	0.967825000	0.002145000	C	0.413212000	0.793471000	-0.115790000	C	1.852233000	0.620719000	-0.239795000	N	2.546838000	1.561660000	0.247002000	N	-3.140046000	1.342492000	0.255070000	C	2.341971000	-0.564778000	-0.883387000	N	2.711796000	-1.520410000	-1.401649000	<p>Cartesian coordinates (Å)</p> <table border="1"> <tbody> <tr><td>C</td><td>-0.629396000</td><td>2.956945000</td><td>0.466486000</td></tr> <tr><td>C</td><td>0.316923000</td><td>-2.965793000</td><td>-0.446920000</td></tr> <tr><td>C</td><td>-0.006783000</td><td>-1.645628000</td><td>-0.234273000</td></tr> <tr><td>C</td><td>-0.247206000</td><td>1.657492000</td><td>0.251053000</td></tr> <tr><td>N</td><td>0.041794000</td><td>0.564312000</td><td>0.072700000</td></tr> <tr><td>N</td><td>-0.953878000</td><td>4.046919000</td><td>0.647651000</td></tr> <tr><td>N</td><td>0.452190000</td><td>-4.102798000</td><td>-0.617988000</td></tr> <tr><td>N</td><td>0.647835000</td><td>-0.580909000</td><td>-0.139344000</td></tr> </tbody> </table>	C	-0.629396000	2.956945000	0.466486000	C	0.316923000	-2.965793000	-0.446920000	C	-0.006783000	-1.645628000	-0.234273000	C	-0.247206000	1.657492000	0.251053000	N	0.041794000	0.564312000	0.072700000	N	-0.953878000	4.046919000	0.647651000	N	0.452190000	-4.102798000	-0.617988000	N	0.647835000	-0.580909000	-0.139344000
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<p><i>DFT energy</i> = -370.840171 a.u. <i>Zero-point correction</i> = +0.034630 a.u. <i>Total energy</i> = -370.805541 a.u.</p>	<p><i>DFT energy</i> = -370.826457 a.u. <i>Zero-point correction</i> = +0.034263 a.u. <i>Total energy</i> = -370.7922 a.u.</p>																																																																

V. CCSD(T) data for the most probable structures of $C_4N_4^{*+}$ and $C_3N_3^+$

Table S5. Data from the CCSD(T) calculations of NC–N=C⁺–CN.

CCSD(T)/L1 geometry				CCSD(T)/L2 geometry			
							
Cartesian coordinates (Å)				Cartesian coordinates (Å)			
C	0.000000000	0.000000000	1.914096630	C	0.000000000	0.000000000	1.911036300
N	0.000000010	0.000000010	0.595255420	N	0.000000010	0.000000010	0.595658940
C	0.000000010	0.000000010	-0.561084920	C	0.000000000	0.000000010	-0.560089280
C	0.000000010	0.000000010	-1.930248770	C	0.000000010	0.000000010	-1.927968010
N	-0.000000010	-0.000000020	-3.103030440	N	-0.000000010	-0.000000020	-3.098793930
N	-0.000000010	-0.000000010	3.085012070	N	-0.000000010	-0.000000010	3.080155980
Unscaled vibrational frequencies				<i>CCSD(T)/L2 energy = -277.672598 a.u.</i>			
Num.	Frequency, cm ⁻¹	Intensity					
1	103.25	12.849					
2	103.26	12.848					
3	231.42	1.416					
4	231.44	1.416					
5	416.2	1.101					
6	416.21	1.101					
7	498.35	8.313					
8	498.36	8.313					
9	616.76	1.095					
10	1142.24	9.987					
11	2166.04	2.376					
12	2248.79	399.852					
13	2393.98	117.163					
<i>CCSD(T)/L1 energy = -277.485943 a.u.</i>							
<i>Zero-point correction = +0.025211 a.u.</i>							
<i>Total energy = -277.460732 a.u.</i>							

Table S6. Data from the CCSD(T) calculations of $[(\text{NC})_2\text{C}=\text{N}-\text{CN}]^{+\bullet}$.

CCSD(T)/L1 geometry				CCSD(T)/L2 geometry			
							
(Dicyanomethylene)cyanamide radical cation							
Cartesian coordinates (Å)				Cartesian coordinates (Å)			
C	-0.078604040	-0.000003060	2.068070970	C	-0.072786470	0.000000890	2.069580360
N	0.188160590	0.000001630	0.847467060	N	0.165184420	-0.000007860	0.846279880
C	0.092210090	0.000005570	-0.420724610	C	0.082534550	-0.000014680	-0.421926360
C	-1.196095040	0.000001170	-1.050029660	C	-1.199971270	-0.000001090	-1.061404800
C	1.275532280	0.000005960	-1.227867410	C	1.272274620	-0.000015960	-1.217793570
N	2.218145970	-0.000007630	-1.906389100	N	2.218265360	0.000019470	-1.889121170
N	-2.235895330	-0.000002730	-1.567924780	N	-2.234176320	0.000009870	-1.587244490
N	-0.263454510	-0.000000900	3.257397530	N	-0.231324900	0.000009370	3.261630150
Unscaled vibrational frequencies				<i>CCSD(T)/L2 energy = -370.311285 a.u.</i>			
Num.	Frequency, cm ⁻¹	Intensity					
1	49.42	1.187					
2	101.98	8.43					
3	123.14	6.574					
4	219.57	6.957					
5	256.73	1.044					
6	305.31	0.022					
7	389.8	20.656					
8	473.43	9.284					
9	524.66	2.408					
10	566.41	1.067					
11	618.61	4.795					
12	684.64	8.119					
13	1118.95	26.458					
14	1212.12	124.215					
15	1764.94	376.865					
16	1980.12	53.441					
17	2347.54	217.204					
18	2352.6	302.416					
<i>CCSD(T)/L1 energy = -370.059131 a.u.</i> <i>Zero-point correction = +0.034377 a.u.</i> <i>Total energy = -370.024754 a.u.</i>							

VI. Geometry optimization of an acyclic form of the fragmented ion $C_4N_{12}^{*+}$

Program: Gaussian 09, Revision D.01

Keywords: nosym opt(calcall) m062x/6-311+G(d,p) int=ultrafine

The initial molecular structure for the geometry optimization was obtained by removing NCCN from the molecular ion $[1]^{*+}$.

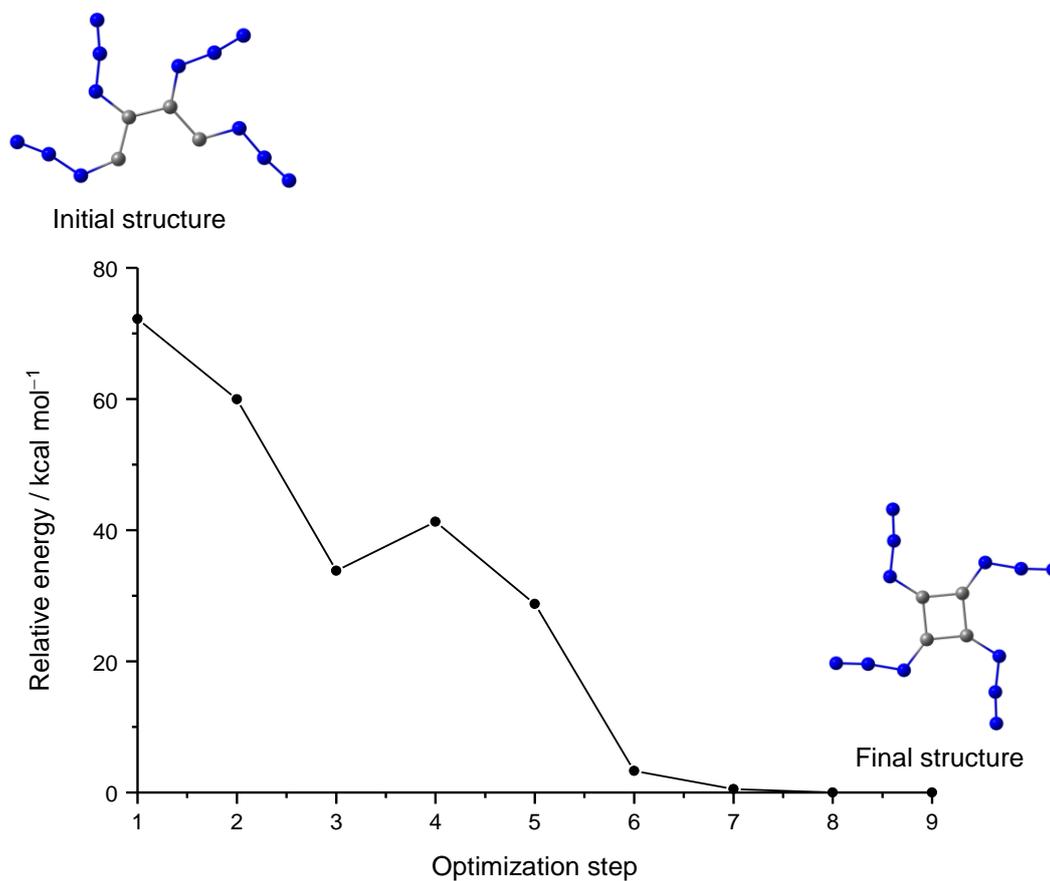


Figure S3. Optimization convergence.