Supporting information for:

Five Bonds to Carbon through Tri-Coordination in $Al_3C_3^{-/0}$

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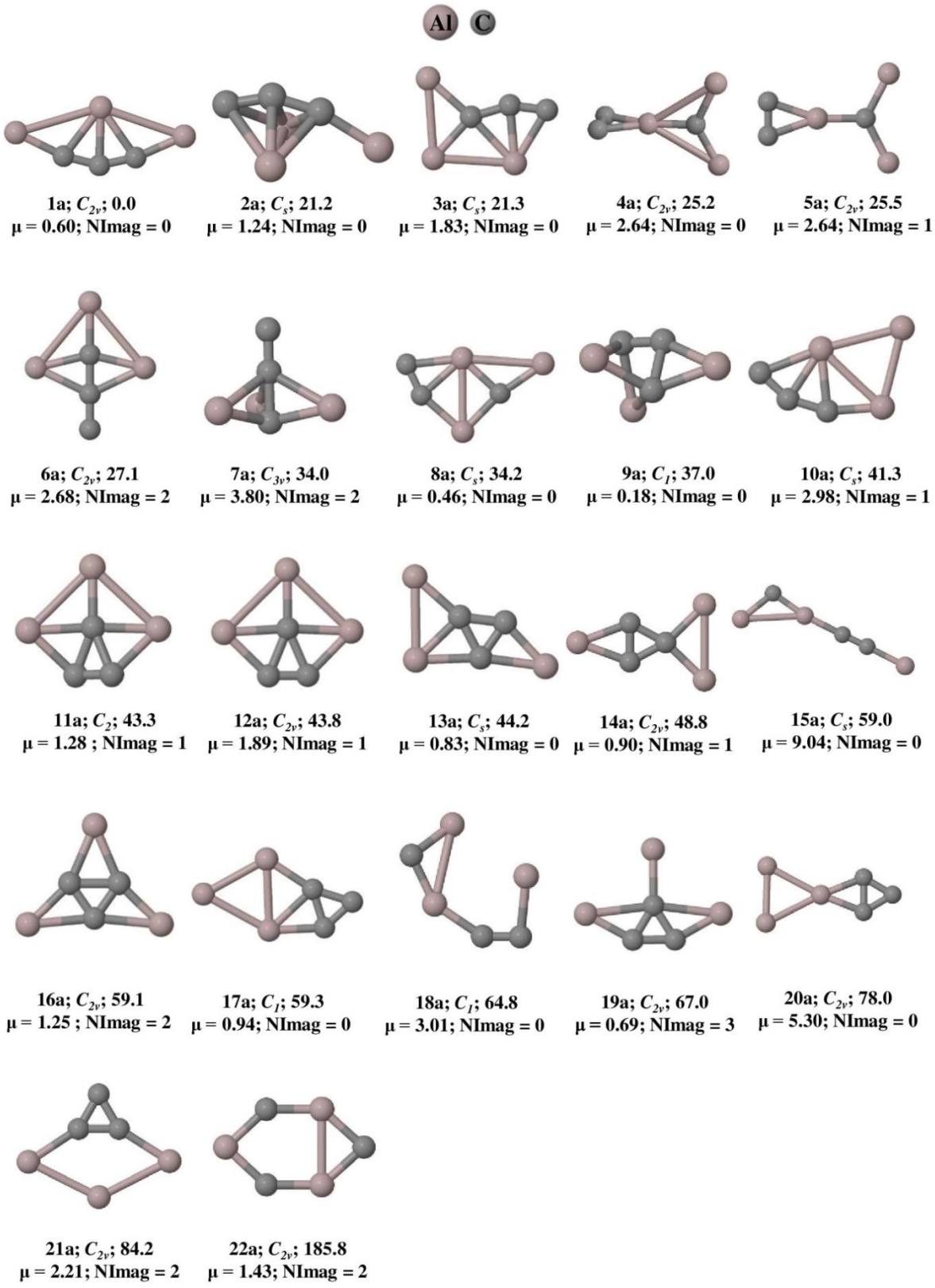

Figure S1. Isomers of $Al_3C_3^-$ with ZPVE-corrected relative energies (in kcal mol^{-1}), dipole moments (in Debye), and the number of imaginary frequencies (NImag) obtained at PBE0-D3/def2-TZVP level.

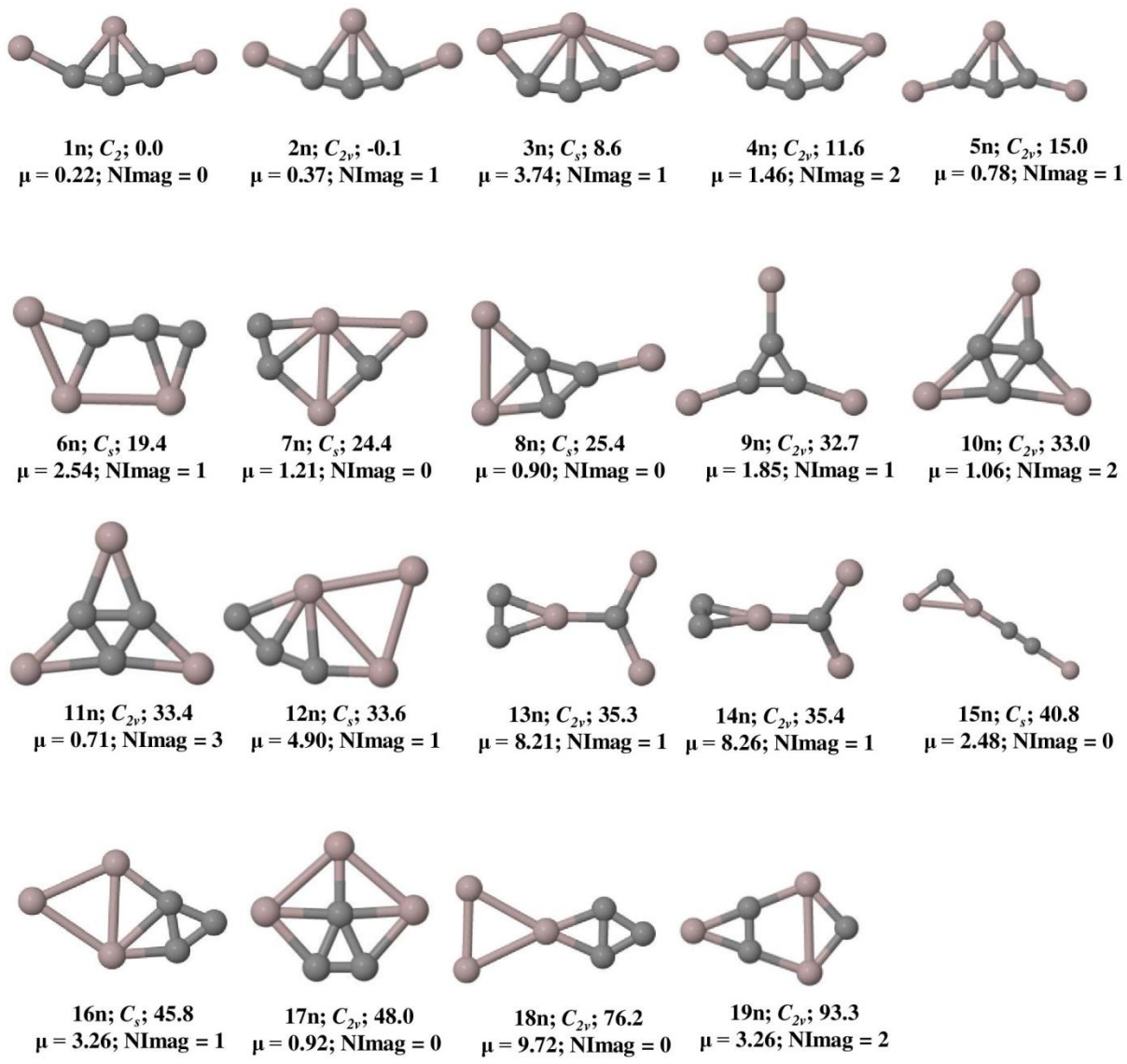

Figure S2. Isomers of Al_3C_3 with ZPVE-corrected relative energies (in kcal mol^{-1}), dipole moments (in Debye), and the number of imaginary frequencies (NImag) obtained at PBE0-D3/def2-TZVP level.

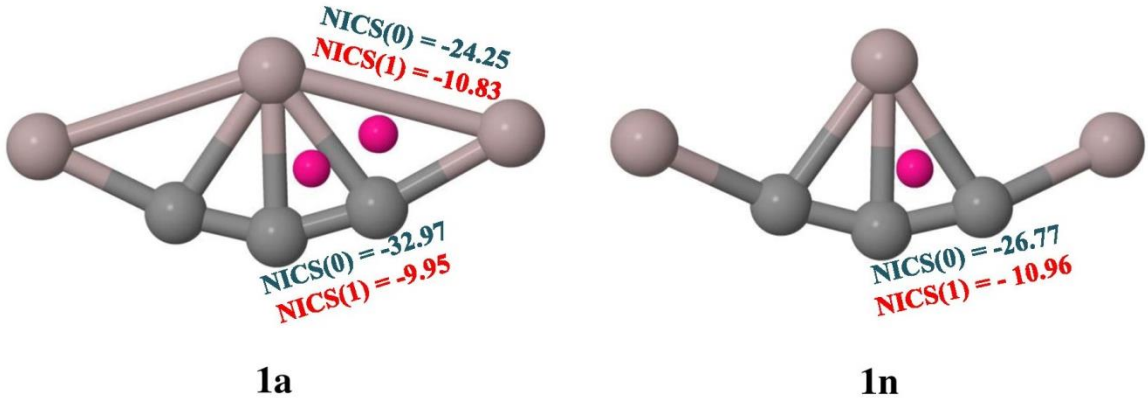

Figure S3. Nucleus-independent chemical shifts (NICSs; in ppm) for the isomers 1a and 1n. The values in the red color indicate the NICS (1) values at 1 Å above the central C atom of the ring.

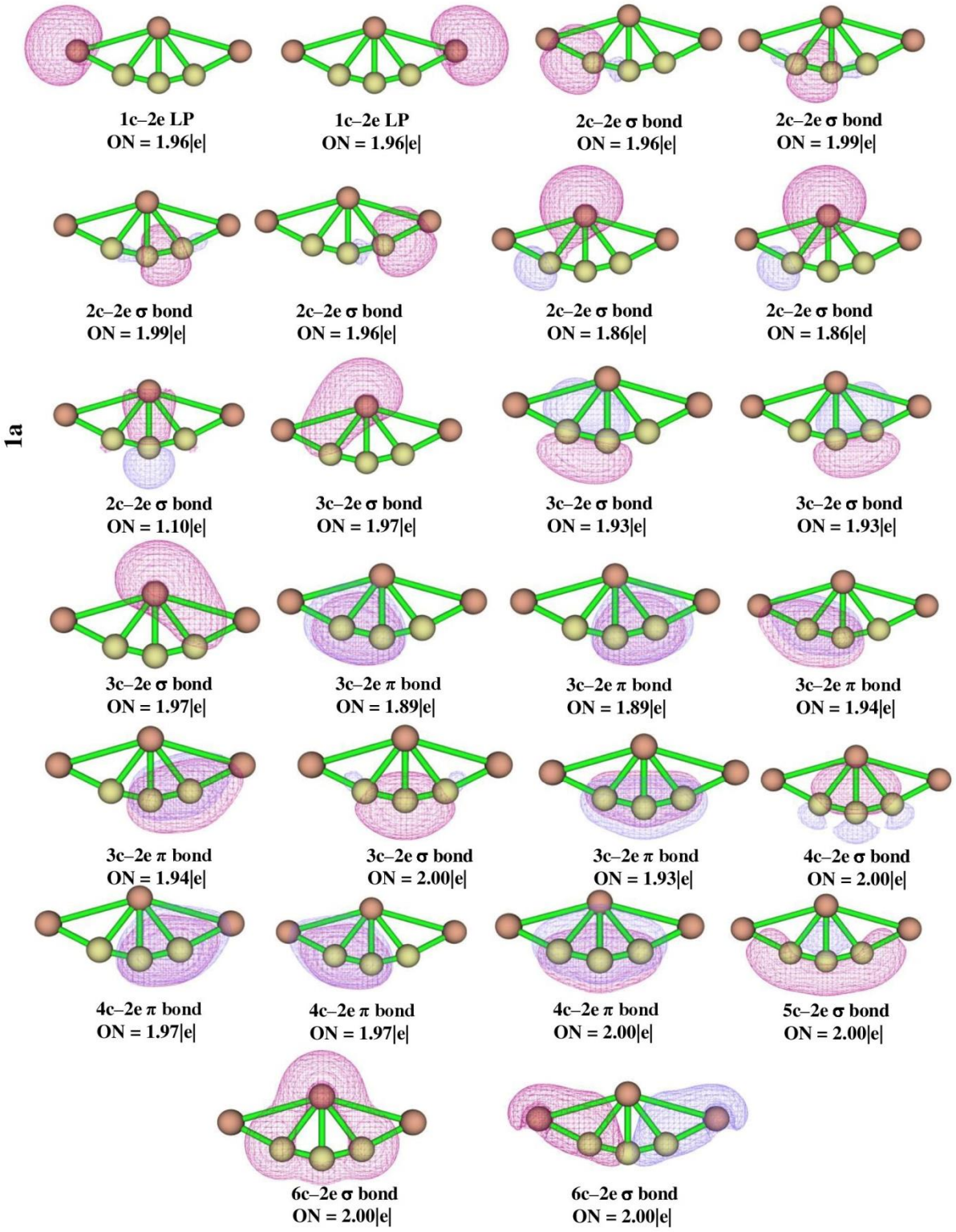

Figure S4. AdNDP bonding patterns with occupation numbers (ONs) for isomers 1a.

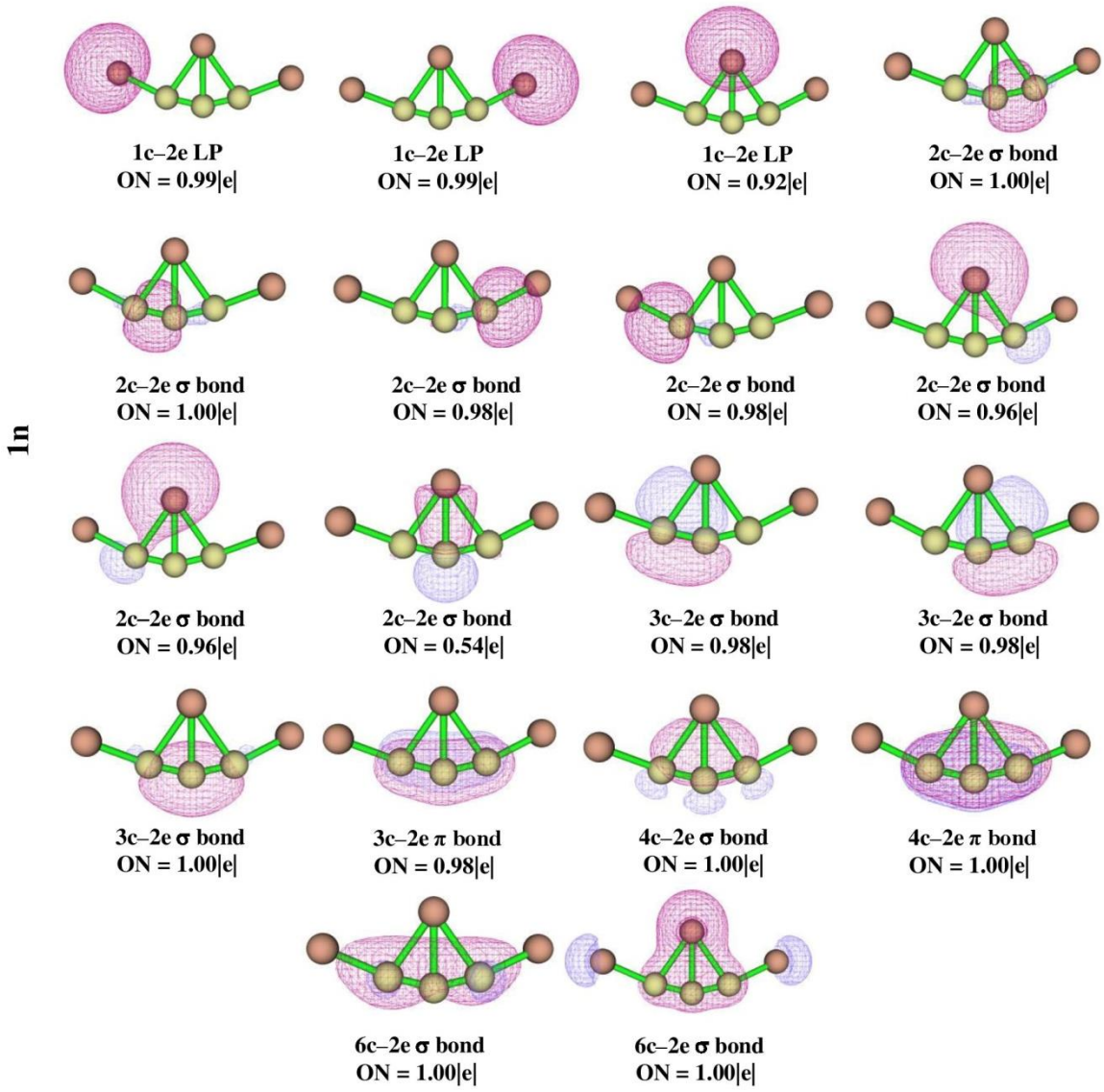

Figure S5. AdNDP bonding patterns with occupation numbers (ONs) for isomers 1n.

Table S1. Total energy (in a.u)**,** zero-point vibrational energy (ZPVE; in a.u), ZPVE corrected total energy (E+ZPVE; in a.u), relative energy (ΔE + ZPVE; in kcal mol^{-1}), dipole moment (in Debye) and the number of imaginary frequencies (NImag) of $Al_3C_3^-$ isomers calculated at PBE0-D3/def2-TZVP level.

PBE0-D3/def2-TZVP						
Isomer	**Energy (a.u)**	**ZPVE (a.u)**	**E+ZPVE (a.u)**	**ΔE+ZPVE (kcal mol^{-1})**	**Dipole moment (Debye)**	**NImag**
1a	-841.153071	0.015352	-841.137719	0.0	0.60	0
2a	-841.11786	0.01388	-841.10398	21.2	1.24	0
3a	-841.118464	0.014719	-841.103745	21.3	1.83	0
4a	-841.110815	0.013243	-841.097572	25.2	2.78	0
5a	-841.110302	0.013205	-841.097096	25.5	2.64	1
6a	-841.107948	0.013404	-841.094544	27.1	2.68	2
7a	-841.0965	0.01289	-841.08361	34.0	3.80	2
8a	-841.097186	0.01389	-841.083296	34.2	0.46	0
9a	-841.092188	0.013351	-841.078837	37.0	0.19	0
10a	-841.086422	0.014574	-841.071848	41.3	2.98	1
11a	-841.08176	0.012979	-841.068781	43.3	1.28	1
12a	-841.080602	0.012746	-841.067856	43.8	1.89	1
13a	-841.081189	0.013952	-841.067237	44.2	0.83	0
14a	-841.073452	0.013515	-841.059936	48.8	0.90	1
15a	-841.056934	0.013268	-841.043665	59.0	9.04	0
16a	-841.054536	0.011037	-841.043498	59.1	1.25	2
17a	-841.057039	0.013887	-841.043152	59.3	0.94	0
18a	-841.047314	0.012821	-841.034493	64.8	3.01	0
19a	-841.042885	0.011906	-841.030978	67.0	0.69	3
20a	-841.027162	0.013749	-841.013413	78.0	5.30	0
21a	-841.015738	0.012115	-841.003622	84.2	2.22	2
22a	-840.85352	0.011839	-840.841681	186.0	1.43	2

Table S2. Total energy (in a.u)**,** zero-point vibrational energy (ZPVE; in a.u), ZPVE corrected total energy (E+ZPVE; in a.u), relative energy (ΔE + ZPVE; in kcal mol^{-1}), dipole moment (in Debye) and the number of imaginary frequencies (NImag) of Al_3C_3 isomers calculated at PBE0-D3/def2-TZVP level.

PBE0-D3/def2-TZVP						
Isomer	**Energy (a.u)**	**ZPVE (a.u)**	**E+ZPVE (a.u)**	**ΔE+ZPVE (kcal mol^{-1})**	**Dipole moment (Debye)**	**NImag**
1n	-841.05269	0.013707	-841.03898	0.0	0.22	0
2n	-841.05264	0.013435	-841.03921	-0.1	0.37	1
3n	-841.04023	0.014982	-841.02525	8.6	3.74	1
4n	-841.0351	0.014613	-841.02049	11.6	1.46	2
5n	-841.0287	0.013676	-841.01503	15.0	0.78	0
6n	-841.02274	0.014651	-841.00809	19.4	2.54	1
7n	-841.01467	0.014636	-841.00004	24.4	1.21	0
8n	-841.01154	0.013065	-840.99847	25.4	0.90	0
9n	-840.99878	0.0119	-840.98689	32.7	1.85	1
10n	-840.99759	0.011212	-840.98638	33.0	1.06	2
11n	-840.99607	0.010323	-840.98574	33.4	0.71	3
12n	-840.99911	0.013738	-840.98538	33.6	4.90	1
13n	-840.99573	0.013021	-840.98271	35.3	8.21	1
14n	-840.99557	0.012979	-840.98259	35.4	8.26	1
15n	-840.98742	0.013445	-840.97398	40.8	2.48	0
16n	-840.97943	0.013483	-840.96594	45.8	3.26	1
17n	-840.9771	0.014542	-840.96256	48.0	0.92	0
18n	-840.93079	0.013172	-840.91761	76.2	9.72	0
19n	-840.90324	0.01292	-840.89032	93.3	3.26	2

Table S3. Optimized geometries of $Al_3C_3^-$ isomers in Cartesian coordinates (in Angström units) obtained at PBE0-D3/def2-TZVP level.

1a				**2a**			
Al	-0.000000	0.000000	0.815526	C	0.660151	0.000000	0.301957
Al	-2.924850	-0.000000	1.662464	C	0.620106	0.000000	-1.067733
Al	2.924850	0.000000	1.662464	Al	-0.667735	1.535312	-0.502927
C	0.000000	0.000000	2.857555	Al	-0.667735	-1.535312	-0.502927
C	-1.274801	-0.000000	2.553730	C	-0.012397	0.000000	-2.201528
C	1.274801	0.000000	2.553730	Al	0.227432	-0.000000	2.116319
3a				**4a**			
Al	-0.765751	0.000000	0.290829	Al	-0.843153	-0.408535	-0.134128
Al	0.461785	0.000000	2.739373	Al	0.022287	0.351447	3.067599
C	1.106863	0.000000	0.930626	C	0.375251	-0.017341	1.251704
Al	3.106720	-0.000000	1.810121	C	3.950699	-0.581285	0.427584
C	2.179146	-0.000000	0.049762	Al	2.138253	0.007921	0.769103
C	3.410322	-0.000000	-0.294354	C	3.855750	0.647794	0.144495
5a				**6a**			
C	-0.000000	0.631669	2.860786	Al	0.041331	-0.000000	-0.282491
Al	0.000000	1.689297	-1.639073	C	0.304949	0.000000	2.658850
Al	-0.000000	-1.689297	-1.639073	C	1.059674	0.000000	1.634652
C	-0.000000	-0.631669	2.860786	Al	3.195639	0.000000	2.029714
C	0.000000	0.000000	-0.796140	C	1.895102	-0.000000	0.496818
Al	-0.000000	0.000000	1.031058	Al	3.002388	-0.000000	-1.011186
7a				**8a**			
C	0.161271	0.000000	0.261466	Al	-0.137540	-0.000000	1.066716
Al	1.801716	-0.000000	-1.240871	C	-2.183724	0.000000	1.287147
Al	-1.029717	1.678190	-0.572138	Al	2.799037	-0.000000	1.259897
Al	-1.029717	-1.678190	-0.572138	Al	-0.101800	0.000000	3.732648
C	-0.179894	-0.000000	-1.201763	C	-1.628521	0.000000	2.420720
C	0.443288	0.000000	1.499845	C	1.252548	-0.000000	2.338341
9a				**10a**			
C	-0.921671	0.187907	0.571214	Al	0.000000	1.077856	-0.000000
C	0.683048	-0.322281	-0.593669	C	1.982066	1.976682	-0.000000
C	-0.607739	0.660038	-0.623573	Al	-2.366430	-0.349016	0.000000
Al	-0.632294	-1.796274	-0.157823	C	1.315552	-0.520385	-0.000000
Al	0.547829	0.763134	-2.258339	C	1.952462	0.689785	-0.000000
Al	1.090646	0.507477	1.205350	Al	-0.056684	-1.719339	0.000000
11a				**12a**			
C	0.251493	0.597132	-1.587020	C	0.000000	0.639308	-1.611046
C	-0.000000	-0.000000	-0.092189	C	-0.000000	0.000000	-0.108435
Al	-0.074960	2.045679	-0.174347	Al	0.000000	2.057131	-0.132782

Al	0.000000	0.000000	1.817416	Al	0.000000	-0.000000	1.815854
Al	0.074960	-2.045679	-0.174347	Al	-0.000000	-2.057131	-0.132782
C	-0.251493	-0.597132	-1.587020	C	-0.000000	-0.639308	-1.611046
13a				**14a**			
Al	-0.264169	0.000000	0.265499	C	0.495368	-0.000000	-0.000000
Al	-0.013260	0.000000	2.928784	C	-0.795376	-0.694519	-0.000000
C	1.300727	-0.000000	1.483323	C	-0.795376	0.694519	-0.000000
C	2.740513	-0.000000	1.142610	Al	1.880854	-1.349035	0.000000
C	1.834920	-0.000000	0.102522	Al	-2.666263	0.000000	-0.000000
Al	3.900353	-0.000000	-0.396381	Al	1.880854	1.349035	-0.000000
15a				**16a**			
C	-1.196043	-0.000000	0.736357	C	0.000000	0.000000	-0.822761
Al	-1.779864	-0.000000	2.512800	C	-0.000000	-0.812309	0.326508
Al	0.585504	-0.000000	0.830520	Al	-0.000000	-2.188927	-1.029471
Al	5.651669	0.000000	0.319840	Al	0.000000	2.188927	-1.029471
C	2.505092	0.000000	0.630703	Al	-0.000000	-0.000000	2.228771
C	3.732728	0.000000	0.496136	C	0.000000	0.812309	0.326508
17a				**18a**			
Al	0.030733	-0.018829	0.320625	Al	0.271323	0.017955	0.816129
Al	-0.837633	0.002915	2.770464	C	0.061232	-0.435830	2.536288
Al	1.794786	0.016267	2.172098	Al	1.622899	0.285536	3.258670
C	3.201710	0.010852	0.789891	C	2.637686	0.282254	-1.081007
C	1.980611	-0.007265	0.036454	C	1.453408	0.227589	-0.678256
C	3.328877	-0.003940	-0.563174	Al	3.452536	-0.377503	0.674532
19a				**20a**			
C	0.000000	0.739906	-1.287595	Al	-1.314405	-0.000000	0.785866
C	-0.000000	0.000000	-0.082397	Al	-0.423765	0.000000	3.027067
C	-0.000000	-0.739906	-1.287595	Al	1.277975	-0.000000	1.052183
Al	0.000000	2.375889	-0.361778	C	3.219479	-0.000000	1.048099
Al	0.000000	-0.000000	1.918965	C	2.669972	-0.000000	-0.302072
Al	-0.000000	-2.375889	-0.361778	C	4.069828	-0.000000	-0.084786
21a				**22a**			
Al	0.000000	-0.000000	-1.814050	C	2.319180	-0.000000	0.000000
C	0.000000	-0.710579	0.577903	Al	0.915676	-1.256166	-0.000000
Al	0.000000	-2.481757	-0.573234	C	-0.932410	-1.256519	-0.000000
Al	-0.000000	2.481757	-0.573234	Al	-2.285712	0.000000	0.000000
C	-0.000000	0.000000	1.804796	C	-0.932410	1.256519	0.000000
C	-0.000000	0.710579	0.577903	Al	0.915676	1.256166	0.000000

Table S4. Optimized geometries of Al_3C_3 isomers in Cartesian coordinates (in Angström units) obtained at PBE0-D3/def2-TZVP level.

1n				**2n**			
C	0.000000	0.000000	-1.035913	Al	0.000000	0.000000	0.699214
C	-0.000013	1.269254	-0.737076	Al	-3.082523	0.000000	1.775782
Al	0.000000	0.000000	1.075729	Al	3.082523	0.000000	1.775782
Al	-0.498436	2.988915	0.046358	C	0.000000	0.000000	2.815726
Al	0.498436	-2.988915	0.046358	C	-1.268641	0.000000	2.519483
C	0.000013	-1.269254	-0.737076	C	1.268641	0.000000	2.519483
3n				**4n**			
C	0.000000	0.061131	-1.129903	C	0.000000	0.000000	-1.225285
C	0.000000	1.364915	-1.054148	C	0.000000	1.272603	-0.905762
Al	0.000000	0.126200	0.906370	Al	0.000000	0.000000	0.790415
Al	0.000000	2.673380	0.206885	Al	0.000000	2.665673	0.305523
Al	0.000000	-2.916121	0.114009	Al	0.000000	-2.665673	0.305523
C	0.000000	-1.171919	-0.678367	C	0.000000	-1.272603	-0.905762
5n				**6n**			
C	0.000000	0.000000	-0.523117	Al	-0.992592	0.000000	0.484970
C	0.000000	1.257652	-0.160183	Al	0.587489	0.000000	2.529223
C	0.000000	-1.257652	-0.160183	C	0.912930	0.000000	0.592127
Al	0.000000	3.080401	-0.615118	Al	3.358730	0.000000	1.868010
Al	0.000000	-3.080401	-0.615118	C	2.183240	0.000000	0.105010
Al	0.000000	0.000000	1.632945	C	3.449287	0.000000	-0.052983
7n				**8n**			
Al	-0.051980	0.000000	1.080730	Al	-0.608469	0.000000	0.386135
C	-1.970375	0.000000	1.235694	Al	0.355849	0.000000	3.097894
Al	2.568575	0.000000	1.135743	C	1.347182	0.000000	1.328742
Al	-0.146569	0.000000	3.757778	C	2.557386	0.000000	0.486036
C	-1.664185	0.000000	2.445618	C	1.311150	0.000000	-0.090688
C	1.264533	0.000000	2.449905	Al	4.535986	0.000000	0.318238
9n				**10n**			
C	-0.574651	-0.331775	0.000000	C	0.753170	0.000000	0.000000
C	0.084007	0.892782	0.000000	C	-0.552527	-0.687354	0.000000
C	0.815175	-0.373639	0.000000	C	-0.552527	0.687354	0.000000
Al	-2.322085	-1.340657	0.000000	Al	1.443748	-1.906092	0.000000
Al	-0.296062	2.819372	0.000000	Al	-2.535550	0.000000	0.000000
Al	2.293617	-1.666083	0.000000	Al	1.443748	1.906092	0.000000
11n				**12n**			
C	0.000000	0.000000	-0.851757	Al	0.004190	1.218429	0.000000
C	0.000000	-0.761090	0.331882	C	1.956503	1.964934	0.000000
Al	0.000000	-2.228858	-1.075756	Al	-2.435842	-0.322767	0.000000
Al	0.000000	2.228858	-1.075756	C	1.354973	-0.538755	0.000000
Al	0.000000	0.000000	2.339587	C	1.934441	0.656475	0.000000
C	0.000000	0.761090	0.331882	Al	0.012701	-1.822733	0.000000
13n				**14n**			
C	0.000000	0.632293	2.843399	Al	0.000000	1.678609	-1.635361

Al	0.000000	1.676150	-1.626833	Al	0.000000	-1.678609	-1.635361
Al	0.000000	-1.676150	-1.626833	C	0.000000	0.000000	-0.830548
C	0.000000	-0.632293	2.843399	C	0.633579	0.000000	2.829277
C	0.000000	0.000000	-0.813226	Al	0.000000	0.000000	1.042427
Al	0.000000	0.000000	1.058436	C	-0.633579	0.000000	2.829277
15n				**16n**			
C	-1.220545	0.000000	0.683176	Al	-0.380350	1.402193	0.000000
Al	-1.666977	0.000000	2.457609	Al	-2.553104	-0.196967	0.000000
Al	0.586052	0.000000	0.908604	Al	0.070953	-1.274277	0.000000
Al	5.655906	0.000000	0.286699	C	1.935573	-0.736812	0.000000
C	2.461885	0.000000	0.660563	C	1.424886	0.586459	0.000000
C	3.682766	0.000000	0.529705	C	2.841627	0.299963	0.000000
17n				**18n**			
C	0.000000	0.644679	-1.592668	Al	0.000000	1.248428	-1.994639
C	0.000000	0.000000	-0.156529	Al	0.000000	-1.248428	-1.994639
Al	0.000000	2.008167	-0.066628	Al	0.000000	0.000000	0.420313
Al	0.000000	0.000000	1.694885	C	0.000000	-0.728225	2.179389
Al	0.000000	-2.008167	-0.066628	C	0.000000	0.728225	2.179389
C	0.000000	-0.644679	-1.592668	C	0.000000	0.000000	3.399850
19n							
C	2.244624	0.000000	0.000000				
Al	1.036418	-1.398395	0.000000				
C	-0.849444	-0.685495	0.000000				
Al	-2.618572	0.000000	0.000000				
C	-0.849444	0.685495	0.000000				
Al	1.036418	1.398395	0.000000				

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