

Supporting Information for Unexpected Reversal of Stability in Strained Systems Containing One-Electron Bonds

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Contents

1	Methods	2
1.1	Experiments	2
1.2	Computational Details	3
1.2.1	Enthalpy Calculations	3
1.2.2	The GPF-EP Method	3
2	Cartesian Coordinates	5
2.1	Open-chain isomers	5
2.2	Cyclic isomers	13
3	Thermochemical Analysis	21
4	Interference Energy Analysis	22
5	One-Electron Ring Stabilization Energy (1e-RSE)	23

1 Methods

1.1 Experiments

The experimental setup is composed of a pulsed electron gun (Kimball ELG-2 electron gun), a reflectron time of flight mass spectrometer (Mini-TOF-MS by Kore Technologies, Ltd), and a gas cell. The components were mounted as close as possible to another. A pair of Helmholtz coils was used to compensate the Earth's magnetic field for active focusing along the beam axis. The electron beam of 100 ns width, driven by a source current around 80 nA, set at 50 kHz repetition rate, was collected by a Faraday cup after traversing the gas cell with 4 mm wide entrance and exit apertures. During the experiments, the beam current was monitored by a picoammeter (Keithley) and recorded in time by software. The beam was focussed optimized with the help a YAG-crystal screen placed close to the gas cell exit and of the Faraday cup with entrance collimator. The two extraction electrodes of the mass spectrometer were enclosed within the gas cell and a 1 ms long voltage pulse of 350 V was applied to the isolated extraction electrode to start the time-of-flight recording. The delay between the extraction pulse and the pulsed electron beam was set as short as possible not to lose fast fragments. The extracted ions were focused by an electrostatic lens, accelerated to 2 kV and deflected into an array of electrodes, where the applied voltage increases from -2 kV to 0 V to reflect the ions towards a discrete dynode electron multiplier detector (ETP AF824 by Scientific Instrument Services, Inc.). The detector gain was adjusted for highest efficiency for large masses. The spectrometer chamber was differentially pumped to guarantee a high-vacuum environment for the detector at 10^{-8} mbar when the experimental chamber was operated with the sample gas at 10^{-6} mbar. An absolute capacitive manometer attached to the gas inlet monitored the gas pressure amounting to 0.007 mbar on average and the pressure recorded in time by software.

Cyclohexane, C_6H_{12} , is liquid at room temperature. The liquid sample, purchased from Sigma-Aldrich with purity greater than 99.5%, was placed in a glass vial, containing molecular sieves. It was degassed by several freeze-pump-thaw cycles before admission into the ultra high vacuum chamber. Since the vapor pressure of C_6H_{12} reaches around 120 Torr at room temperature, it was not necessary to heat the sample to vaporize the liquid. To avoid contamination of water, the glass vial was cooled down to temperatures around $-5^{\circ}C$ in a water-ice-salt-alcohol mixture, during the experiments. The injection line was pre-heated at $60^{\circ}C$ before the injection of cyclohexane to avoid water along the line.

The increase of the total ionization cross section above the ground state ionization energy is determined by the additional ionization channels opening up as the electron impact energy increases. As reported by Jiao *et al.* the

absolute total ionization cross section gets steeper from threshold of the ground state ionization up to the peaking of the cross section of $16.1 \times 10^{-16} \text{ cm}^2$ at 60 eV. From this electron impact energy upwards a steadily decaying cross section as function of the energy sets in and at 200 eV the cross section decreases to $13.3 \times 10^{-16} \text{ cm}^2$. No structures were observed in the absolute total cross section. Due to the cross section dependence with the electron impact energy smaller energy step between 5 eV and 10 eV were chosen up to the electron impact energy of 100 eV, then wider steps of 100 to 250 eV were selected. The measurements were carried out at electron impact energies in the range of 12 eV up to 2000 eV.

1.2 Computational Details

1.2.1 Enthalpy Calculations

The enthalpy values at 298 K (H_{298}) were calculated by the following equation:

$$\begin{aligned} H_{298} &= H^{CCSD(T)} = E^{CCSD(T)} + ZPE^{DFT} + H_{corr}^{DFT} \\ &= E^{CCSD(T)} + H^{DFT} \end{aligned} \quad (1)$$

in which $E^{CCSD(T)}$ is the electronic energy value at the CCSD(T) level, ZPE^{DFT} is the zero-point energy obtained at the DFT level and H_{corr}^{DFT} are the thermal corrections to the enthalpy at 298 K, also estimated by DFT. The H^{DFT} term, on the other hand, includes both the ZPE^{DFT} and H_{corr}^{DFT} . The H_{298} values are shown relative to the global minimum-energy structure for $\text{C}_6\text{H}_{12}^{+\bullet}$ (**1**, $\Delta H_{298} = 0.0 \text{ kcal.mol}^{-1}$). The calculations were performed using the softwares Jaguar 7.9¹ and Gaussian 16.²

1.2.2 The GPF-EP Method

The general form of a GPF wave function, as defined by McWeeny,³ is given by:

$$\Psi_{GPF} = \hat{A}\{\Psi_1\Psi_2\cdots\Psi_N\} \quad (2)$$

where \hat{A} is the antisymmetrizer operator, and the indexes $1, 2, \dots, N$ represent different orthogonal wave functions, or groups. In this approach, the electrons are blocked into distinct groups and described by different wave functions. In our calculations, all core electrons were inserted into one group, and treated at the Restricted Hartree-Fock (RHF)

level. Each electron bonding pair was placed into distinct two-electron groups described by Generalized Valence Bond⁴⁻⁶ wave functions in the Perfect-Pairing approximation (GVB-PP).⁷ The extra electron, which is associated to the elongated bond, was inserted into a one-electron group and described by the Spin-Coupled Valence Bond theory for N Electrons in M Orbitals, SCVB(N,M).⁸ In this case, the group is composed of one electron and two non-orthogonal and self-consistently optimized orbitals with occupancy numbers of ~ 0.5 , which are localized in the atoms that are involved in the elongated bond.

The group partitioning and the strong orthogonality condition that is imposed for each group assure that the interference effects promoted by each distinct chemical bond can be obtained separately. In the GPF-EP formalism, the partitioning of the electron density into intragroup and intergroup terms is obtained from the first- and second-order reduced density matrices (RDMs) of the GPF wave function (see Cardozo & Nascimento 2009 for details).⁹ For a system composed of two electrons described by a normalized one-group GPF wave function containing two singly-occupied orbitals, ϕ_1 and ϕ_2 , the total electronic density can be partitioned as follows:

$$\begin{aligned}\rho^{TOT}(1,2) &= N(\phi_1 + \phi_2)^2 \\ &= N(\phi_1^2 + \phi_2^2) + 2N\phi_1\phi_2 \\ &= \rho^{QC}(1,2) + \rho^{INT}(1,2)\end{aligned}\tag{3}$$

The electronic energy is also fully described by the first- and second-order RDMs. By properly collecting the various energy terms that arise from the density partitioning into quasi-classical and interference contributions, it is possible to obtain a general expression for the total electronic energy:

$$\begin{aligned}E[TOT] &= E[ref] + E[x] + E[I] + E[II] \\ &= E[ref + x] + E[I + II] \\ &= E[QC] + E[INT]\end{aligned}\tag{4}$$

where $E[ref]$ is the total reference energy, $E[I]$ and $E[II]$ are the first- and second-order interference energies, and $E[x]$ is the total intergroup exchange energy, merely a symmetry correction to the reference energy due to the separation of the total wave function into different groups. In Eq. 4, the sum $E[ref] + E[x]$ (or $E[ref + x]$) corresponds to the quasi-classical contribution, $E[QC]$, and $E[I] + E[II]$ (or $E[I + II]$) is the total interference contribution, $E[INT]$. The $E[ref]$ and $E[I]$ terms can be separated into kinetic ($T[ref]$ and $T[I]$), electron-electron potential ($V_{ee}[ref]$ and

$V_{ee}[I]$) and electron-nuclei ($V_{en}[ref]$ and $V_{en}[I]$) energies. On the other hand, the $E[II]$ term consists entirely of electron-electron repulsion terms, and can be equivalently referred to as $V_{ee}[II]$. Since the group that describes the elongated bond contains only one electron, the $E[II]$ (or $V_{ee}[II]$) term is zero, and $E[I] = E[INT]$. The GPF-EP program is incorporated into the VB2000 code,¹⁰ which is released as part of the GAMESS program.¹¹ All GVB (or SCVB) calculations were done with cc-pVDZ basis set.

2 Cartesian Coordinates

2.1 Open-chain isomers

Table 1 Isomer 1⁺

C	-2.589299585	0.256447551	0.512957809
C	-3.009987825	1.435262671	1.298213669
C	-2.164348477	0.388501388	-0.835626693
C	-2.391993638	1.639464665	-1.587835511
C	-2.622523223	-1.066184890	1.171473249
C	-1.481306126	-0.725021545	-1.526985584
H	-2.761379411	-1.892320219	0.479433348
H	-3.383185105	-1.088098488	1.949411006
H	-1.656211787	-1.212371856	1.675428153
H	-0.830833824	-0.348340085	-2.313573588
H	-2.252072472	-1.333652797	-2.021760845
H	-0.929516721	-1.377786820	-0.855697019
H	-4.100322765	1.532783085	1.194247579
H	-2.560130403	2.365265595	0.962273615
H	-2.814652925	1.277949032	2.357377159
H	-1.486508878	2.255656920	-1.491098902
H	-3.232807125	2.221744321	-1.222285673
H	-2.507148218	1.428955992	-2.649757546

Table 2 Isomer 2⁺

C	-6.171454986	0.316908793	2.512391399
C	-5.740711748	-0.443971178	1.323756835
C	-4.565439703	-0.083885511	0.619085567
C	-3.636674763	0.987509044	0.976428440
C	-2.167994553	0.613857487	0.720166412
C	-6.544861280	-1.589325367	0.873816207
H	-5.466501189	0.113014763	3.329165041
H	-7.166751934	0.030963813	2.837567359
H	-6.124309216	1.393232278	2.336092681
H	-7.527568242	-1.211472990	0.561175836
H	-2.016770308	0.314759012	-0.315164443
H	-3.896355852	1.821806068	0.300168587
H	-1.536004770	1.473333557	0.924274930
H	-4.344250747	-0.651115629	-0.280374588
H	-6.095422099	-2.149153890	0.060105935
H	-6.755062645	-2.246140635	1.723404715
H	-1.860023396	-0.201975289	1.369967142
H	-3.799849048	1.351291459	1.988750124

Table 3 Isomer 3⁺

C	-7.882055611	1.379084264	2.352056516
C	-6.743593749	0.496229834	2.092574119
C	-5.503308822	0.854763294	1.513082007
C	-4.557385436	-0.243107045	1.208303745
C	-3.331618790	0.094086783	0.377062116
C	-5.147358284	2.251419219	1.228909219
H	-8.814619806	0.863279781	2.115930238
H	-7.835872937	2.334265635	1.840364930
H	-7.926116662	1.560438858	3.436882183
H	-6.850461358	-0.545500166	2.379317864
H	-4.123206493	2.444654620	1.555424143
H	-3.610901693	0.502196739	-0.593254742
H	-2.683639378	0.809190101	0.880238184
H	-4.258721293	-0.635863046	2.196154169
H	-5.823082412	2.981529670	1.659157202
H	-2.753166650	-0.809252108	0.203852181
H	-5.126256478	-1.073084485	0.772858194
H	-5.123348595	2.379046341	0.137651784

Table 4 Isomer 4⁺

C	-6.481869365	-1.733005510	3.857081811
C	-7.562234687	-0.940461933	4.309830485
C	-5.838160742	-1.792216555	2.538364519
C	-5.972197215	-0.642930754	1.545970096
C	-8.443349331	-0.188430549	3.394415699
C	-7.843310745	-0.882329105	5.755799406
H	-6.084169374	-2.421722997	4.596730409
H	-7.898473395	0.693591959	3.035712715
H	-9.341999247	0.148197998	3.903048549
H	-7.080135086	-1.346183720	6.372386382
H	-6.966519646	-0.566518671	1.117073495
H	-5.708109222	0.307168896	2.007865166
H	-4.784187743	-2.021903523	2.724324672
H	-8.005486779	0.155161541	6.059142797
H	-8.805344533	-1.384772067	5.927682605
H	-8.702291129	-0.770862669	2.510791253
H	-6.210644857	-2.738942857	2.103018316
H	-5.277804432	-0.811879094	0.727075886

Table 5 Isomer 5⁺

C	-7.021747042	0.559324200	1.433756755
C	-5.671501518	-0.136503797	1.289389979
C	-4.620000093	0.719681979	0.768256833
C	-3.261601901	0.593191607	1.104950453
C	-2.209647559	1.491045240	0.638658962
C	-5.754630747	-1.262121656	0.182833356
H	-6.979948768	1.346142756	2.183820201
H	-7.772118971	-0.165908851	1.740069274
H	-7.336114048	0.994509178	0.485228154
H	-6.535095198	-1.943001104	0.520864498
H	-4.822560622	-1.812424479	0.081057315
H	-6.042133829	-0.839156716	-0.777407429
H	-5.357040651	-0.620284962	2.214330169
H	-4.889022025	1.465978019	0.024035528
H	-2.568392864	2.274048003	-0.021613525
H	-2.987901941	-0.221477482	1.769006740
H	-1.699690647	1.929116558	1.505624409
H	-1.431295983	0.897406356	0.141983167

Table 6 Isomer 6⁺

C	-7.750210235	-2.837615928	3.951291385
C	-7.515285280	-1.510807466	3.523991731
C	-6.160326517	-0.961133555	3.659300957
C	-5.818489733	0.196951269	2.735070785
C	-8.620063627	-0.702420814	2.995423093
C	-6.100845669	-0.516454500	5.167009334
H	-6.954196599	-3.420843035	4.394800952
H	-8.721629975	-3.296996408	3.830283822
H	-8.587925778	0.309033996	3.407264872
H	-9.596707658	-1.151172841	3.144281713
H	-5.094998669	-0.135380824	5.333264547
H	-5.912653665	-0.088415682	1.688027147
H	-6.453341101	1.062192795	2.921176097
H	-4.788595619	0.499723944	2.909454521
H	-5.436180977	-1.773005085	3.557646791
H	-6.819592000	0.278091806	5.357998712
H	-6.278718800	-1.340280109	5.854963133
H	-8.440072932	-0.572703132	1.918091432

Table 7 Isomer 7⁺

C	-9.410188416	-2.003949496	3.782525167
C	-8.291281701	-1.065260759	3.340239933
C	-7.181439599	-1.744536357	2.690833181
C	-6.347655054	-1.194120143	1.698646218
C	-7.583133607	-0.429258115	4.600451028
C	-6.380503164	0.186983800	1.222238275
H	-9.904230117	-2.457084880	2.925725896
H	-10.151477824	-1.442416400	4.346636335
H	-9.021941665	-2.795299631	4.423331401
H	-8.671776373	-0.245808426	2.732950974
H	-8.368485116	0.099054114	5.140093323
H	-6.801987706	0.275749874	4.326333509
H	-7.170463620	-1.203239687	5.244070325
H	-6.934063083	-2.742465269	3.043126643
H	-5.632216682	-1.865494326	1.236065583
H	-6.704933527	0.170577013	0.171285773
H	-5.362118658	0.584841114	1.184934697
H	-7.027733243	0.844841109	1.791315006

Table 8 Isomer 8⁺

C	-7.645277907	2.322055744	0.248505487
C	-6.375463726	1.528415920	-0.033752111
C	-5.242668787	2.538198454	-0.514102260
C	-4.090932765	1.710094387	-0.794403413
C	-3.049680349	1.488725006	0.122271688
C	-1.855906535	0.699541743	-0.163279555
H	-8.421043693	1.637095175	0.588284044
H	-8.000621873	2.824811848	-0.648623151
H	-7.482500447	3.065816684	1.025954273
H	-6.540643628	0.787796903	-0.814315682
H	-6.031639109	1.010051410	0.859952353
H	-5.066283576	3.259450583	0.281129031
H	-5.618296188	3.027827588	-1.411042938
H	-4.049312538	1.173819999	-1.737977352
H	-1.793785056	-0.116935499	0.569219254
H	-0.962692747	1.303734795	0.033516064
H	-3.143041824	1.947653500	1.102118038
H	-1.830452344	0.300001508	-1.172009090

2.2 Cyclic isomers

Table 9 Isomer 9⁺

C	-4.896586289	0.435592107	-0.004765895
C	-5.534037132	-0.158715106	1.196712470
C	-3.845742784	0.702969833	1.000055943
C	-6.454732273	0.662394868	2.015481587
C	-5.413724043	-1.604118212	1.487238217
C	-2.623420076	-0.100162996	1.153108920
H	-6.345774808	1.728805116	1.833902470
H	-6.358737789	0.443994245	3.078686345
H	-7.474577948	0.379682586	1.725244869
H	-6.398202278	-2.049882274	1.301474214
H	-4.689583554	-2.111209331	0.857442047
H	-5.192346053	-1.782031792	2.540763798
H	-1.798846445	0.512075788	0.763226272
H	-2.646731916	-1.028723759	0.590617769
H	-2.385276584	-0.287339560	2.200927265
H	-3.935236833	1.609794210	1.583576864
H	-5.399305347	1.323360341	-0.375762123
H	-4.607755241	-0.282375922	-0.764666100

Table 10 Isomer 10⁺

C	-6.478113663	0.720074063	2.058856161
C	-5.539024549	-0.026406701	1.209099389
C	-4.853050574	0.536166682	0.021203427
C	-3.843818875	0.694295313	1.100321583
C	-2.718918459	-0.217807144	1.350298579
H	-6.443105861	1.792629921	1.883730965
H	-6.339688041	0.494506815	3.117026294
H	-7.486805370	0.365156515	1.805224077
H	-1.825381026	0.267631574	0.931242481
H	-3.880746255	1.612879822	1.672858091
H	-2.523082271	-0.329949415	2.416988158
H	-5.276197649	1.500635320	-0.251565194
C	-4.552873430	-0.394832070	-1.136097821
H	-2.826689158	-1.185977855	0.871562639
H	-5.414074554	-1.088642600	1.385622520
H	-5.436684000	-0.474203955	-1.764876968
H	-4.287743205	-1.395063727	-0.800716297
H	-3.735313528	0.004231630	-1.732774505

Table 11 Isomer **11**⁺

C	-2.568279234	-4.287141808	1.053542300
C	-3.812342490	-5.471679868	0.337113522
C	-3.181242470	-4.285521497	-0.299503841
C	-2.987051146	-3.446429844	2.183453292
C	-5.156094641	-5.505854700	0.930043053
C	-4.042997572	-3.120852596	-0.735330112
H	-5.182631717	-6.132617978	1.821849427
H	-5.805108134	-6.003186872	0.195064545
H	-5.575064095	-4.525992468	1.132862098
H	-4.759026101	-2.810900402	0.020133718
H	-4.592777675	-3.396946790	-1.632670691
H	-3.405784183	-2.270600348	-0.969523130
H	-2.940539375	-3.994206731	3.125458772
H	-3.958549303	-2.981748085	2.054026130
H	-2.237923248	-2.646305809	2.267267980
H	-1.670309540	-4.877949262	1.185061854
H	-3.283483870	-6.412964498	0.256013527
H	-2.451331668	-4.606275055	-1.040811597

Table 12 Isomer **12⁺**

C	-7.912846947	1.220687724	0.408292595
C	-7.126506282	2.462262619	0.581968275
C	-6.705167187	0.941880418	-0.394689237
C	-5.535311344	0.202526858	0.100773497
C	-4.196346285	0.808420479	-0.335687756
C	-7.345273006	3.680460428	-0.209374789
H	-7.954098358	3.505681849	-1.093053029
H	-6.406952756	4.170476447	-0.471920892
H	-7.882728985	4.386341311	0.440014504
H	-6.427916361	2.498306599	1.408025069
H	-8.822470456	1.353037720	-0.167494721
H	-7.997286671	0.612798263	1.302788035
H	-6.716957578	1.238091975	-1.437433513
H	-5.632782932	-0.797860562	-0.350119331
H	-5.595645614	0.059325357	1.179564756
H	-4.149162228	0.910332986	-1.418422953
H	-3.381034212	0.164407314	-0.017961072
H	-4.049419445	1.789283182	0.113823814

Table 13 Isomer **13⁺**

C	-5.828333594	4.699526904	-0.369943802
C	-7.003466888	3.739818440	0.210563241
C	-6.630737936	2.347856535	-0.193832023
C	-5.354549084	1.846691898	0.397986687
C	-4.178227153	2.807842546	-0.181508646
C	-4.551664665	4.199313234	0.222476439
H	-6.114793168	5.700498079	-0.047673764
H	-5.838204257	4.639604323	-1.455928935
H	-7.918552541	4.113607877	-0.246960595
H	-7.048058885	3.863661871	1.290285536
H	-6.685041475	2.193960257	-1.270129227
H	-7.422660937	1.711100479	0.273323766
H	-5.067113638	0.846672927	0.073648910
H	-5.343902155	1.905355545	1.484024148
H	-4.132889681	2.683272960	-1.261096216
H	-3.264254213	2.433298736	0.277610480
H	-3.759844026	4.836552628	-0.244013741
H	-4.497952090	4.353349056	1.298783800

Table 14 Isomer 14⁺

C	-7.022239800	4.621603434	0.720009728
C	-6.944224100	3.242546637	0.156954936
C	-5.480602556	3.369285168	-0.392236382
C	-5.461842398	4.859677811	-0.448494177
C	-8.079848329	5.591530013	0.374736888
C	-4.441432213	5.694224291	0.215424949
H	-8.920671142	5.372510041	1.050380268
H	-8.441774201	5.472591688	-0.644307063
H	-7.782765360	6.620636952	0.567079042
H	-6.517134900	4.769318932	1.670914161
H	-5.979349672	5.303604019	-1.294810435
H	-3.597267630	5.753309464	-0.488382846
H	-4.067921225	5.248058649	1.134674590
H	-4.780748365	6.714223929	0.384976243
H	-5.373292248	2.890462141	-1.364622769
H	-4.755321026	2.979496905	0.315926940
H	-7.658323399	3.090259712	-0.647022332
H	-7.025830298	2.456018435	0.906046209

Table 15 Isomer 15⁺

C	-6.509831490	6.134170564	3.777336764
C	-7.934596462	6.433566440	3.498810553
C	-8.100870070	6.682236208	1.994633058
C	-7.476446123	5.463303405	1.294894525
C	-6.117338313	5.274466644	1.845923759
C	-6.083458234	5.115541210	4.747695280
H	-6.240185060	5.578577273	5.736614501
H	-5.025905048	4.872556686	4.681829992
H	-6.704465562	4.222010894	4.719070356
H	-5.808748320	6.939551535	3.574755229
H	-8.194291371	7.332372568	4.069547181
H	-8.572211642	5.617092927	3.835863407
H	-5.346235200	5.991006849	1.587208971
H	-5.767050884	4.300586407	2.163924127
H	-7.389018348	5.642262959	0.218361766
H	-8.086310339	4.575959130	1.449401000
H	-7.572754947	7.590836800	1.704449823
H	-9.146874476	6.797216340	1.724934342

Table 16 Isomer 16⁺

C	-1.397009026	-0.046086203	-0.316269757
C	-0.635846285	-1.321906679	-0.183442189
C	0.790326041	-1.126578966	0.485640216
C	-0.790326041	1.126578966	0.485640216
C	0.635846285	1.321906679	-0.183442189
C	1.397009026	0.046086203	-0.316269757
H	-2.387840888	-0.133374590	0.173804448
H	-1.567724021	0.241707603	-1.350601702
H	-0.518985142	-1.843183662	-1.128415594
H	-1.092645597	-2.004426206	0.551476429
H	-0.692677590	0.884987593	1.539436748
H	1.366851122	-2.040279799	0.381849351
H	2.387840888	0.133374590	0.173804448
H	1.567724021	-0.241707603	-1.350601702
H	1.092645597	2.004426206	0.551476429
H	0.518985142	1.843183662	-1.128415594
H	-1.366851122	2.040279799	0.381849351
H	0.692677590	-0.884987593	1.539436748

3 Thermochemical Analysis

Table 17 Energetic properties of the $C_6H_{12}^{+}$ radical cations studied herein at the DFT (M06-2X) and CCSD(T) levels. The E^{DFT} , H^{DFT} , $E^{CCSD(T)}$ and $H^{CCSD(T)}$ are given in hartree, while $\Delta H^{CCSD(T)}$ is given in kcal.mol⁻¹.

Species	E^{DFT}	H^{DFT}	$E^{CCSD(T)}$	$H^{CCSD(T)}$	$\Delta H^{CCSD(T)}$
1⁺	-235.5108	-235.3382	-235.1060	-234.9334	0.0
2⁺	-235.4958	-235.3230	-235.0918	-234.9189	9.1
3⁺	-235.4953	-235.3227	-235.0910	-234.9184	9.4
4⁺	-235.4916	-235.3187	-235.0873	-234.9145	11.9
5⁺	-235.4820	-235.3088	-235.0790	-234.9058	17.3
6⁺	-235.4804	-235.3076	-235.0777	-234.9050	17.9
7⁺	-235.4808	-235.3074	-235.0777	-234.9044	18.2
8⁺	-235.4809	-235.3071	-235.0777	-234.9039	18.5
9⁺	-235.4867	-235.3142	-235.0856	-234.9131	12.7
10⁺	-235.4779	-235.3056	-235.0773	-234.9050	17.8
11⁺	-235.4762	-235.3038	-235.0754	-234.9030	19.1
12⁺	-235.4739	-235.3009	-235.0731	-234.9001	20.9
13⁺	-235.4683	-235.2977	-235.0657	-234.8951	24.0
14⁺	-235.4642	-235.2914	-235.0649	-234.8920	26.0
15⁺	-235.4637	-235.2903	-235.0636	-234.8901	27.1
16⁺	-235.4582	-235.2874	-235.0556	-234.8848	30.5

4 Interference Energy Analysis

Table 18 Energy partitioning into quasi-classical and interference contributions of the elongated one-electron sigma bond of selected alkyl-substituted cycloalkane radical cations. For comparison, the C_3H_6 and $C_3H_6^{+}$ species are also shown. All values are in hartree.

Molecule	E[tot]	E[ref]	E[x]	E[I]	E[II]	E[QC]	E[INT]
9⁺	-234.1472	-229.6511	-2.0758	-2.4404	0.0201	-231.7269	-2.4203
14⁺	-234.1195	-229.6613	-2.0327	-2.4456	0.0202	-231.6940	-2.4254
15⁺	-234.1307	-229.6980	-1.9896	-2.4638	0.0207	-231.6876	-2.4431
$C_3H_6^{+}$	-116.8605	-114.6939	-0.9953	-1.1804	0.0090	-115.6892	-1.1713
C_3H_6	-117.1986	-114.9840	-1.0063	-1.2553	0.0111	-115.9543	-1.2442

Table 19 Bond length (r_{12} , Å), overlap of the fractional lobe orbitals ($S_{\phi_1\phi_2}$), Interference Energy ($E[II]_{\phi_1\phi_2}$, kcal.mol⁻¹) and its partitioning into kinetic ($T[II]_{\phi_1\phi_2}$) and potential ($V[II]_{\phi_1\phi_2}$) contributions of the elongated one-electron sigma bond of selected alkyl-substituted cycloalkane radical cations. For comparison, the C_2H_6 , $C_2H_6^{+}$, C_3H_6 , $C_3H_6^{+}$ species are also shown. The C_2H_6 and $C_2H_6^{+}$ values were taken from de Sousa and Nascimento with the aug-cc-pVTZ basis set.¹²

Molecule	Bond	r_{12}	$S_{\phi_1\phi_2}$	$E[II]_{\phi_1\phi_2}$	$T[II]_{\phi_1\phi_2}$	$V[II]_{\phi_1\phi_2}$
9⁺	$(C^1 \cdot C^2)_\sigma$	1.906	0.651	-34.3	-104.1	69.8
9⁺	$(C^1 : C^3)_\sigma$	1.484	0.858	-89.8	-188.4	98.5
14⁺	$(C^1 \cdot C^2)_\sigma$	1.964	0.664	-37.4	-108.2	70.7
15⁺	$(C^1 \cdot C^2)_\sigma$	2.150	0.602	-40.1	-111.8	71.7
$C_2H_6^{+}$	$(C^1 \cdot C^2)_\sigma$	2.002	0.671	-38.8	-99.8	61.0
$C_3H_6^{+}$	$(C^1 \cdot C^2)_\sigma$	1.854	0.665	-31.4	-90.8	59.4
$C_3H_6^{+}$	$(C^1 : C^3)_\sigma$	1.474	0.863	-88.1	-183.3	95.2
C_2H_6	$(C^1 : C^2)_\sigma$	1.547	0.838	-86.8	-195.3	103.2
C_3H_6	$(C^1 : C^2)_\sigma$	1.501	0.837	-88.1	-188.9	100.8

5 One-Electron Ring Stabilization Energy (1e-RSE)

Table 20 One-electron ring stabilization energy (1e-RSE) as a function of the ring size and number of methyl groups in the vicinity of the one-electron bond. The calculations were done at the M06-2X/cc-pVTZ level of theory.

Ring size	Number of methyl groups	Molecular Formula	1e-RSE (kcal.mol ⁻¹)
3	0	C ₃ H ₆ ⁺	9.3
3	1	C ₄ H ₈ ⁺	22.8
3	2	C ₅ H ₁₀ ⁺	33.4
3	3	C ₆ H ₁₂ ⁺ (9 ⁺)	41.5
3	4	C ₇ H ₁₄ ⁺	49.5
4	0	C ₄ H ₈ ⁺	14.1
4	1	C ₅ H ₁₀ ⁺	20.2
4	2	C ₆ H ₁₂ ⁺ (14 ⁺)	28.3
4	3	C ₇ H ₁₄ ⁺	35.3
4	4	C ₈ H ₁₆ ⁺	42.1
5	0	C ₅ H ₁₀ ⁺	1.9
5	1	C ₆ H ₁₂ ⁺ (15 ⁺)	12.2
5	2	C ₇ H ₁₄ ⁺	20.2
5	3	C ₈ H ₁₆ ⁺	27.7
5	4	C ₉ H ₁₈ ⁺	34.2
6	0	C ₆ H ₁₂ ⁺ (13 ⁺)	12.5
6	1	C ₇ H ₁₄ ⁺	16.3
6	2	C ₈ H ₁₆ ⁺	21.5
6	3	C ₉ H ₁₈ ⁺	27.1
6	4	C ₁₀ H ₂₀ ⁺	33.2

Table 21 One-electron ring stabilization energy (1e-RSE) of distinct $C_6H_{12}^{+}$ isomers at the CCSD(T)/cc-pVTZ//M06-2X/cc-pVTZ(-f) level of theory.

Species	1e-RSE (kcal.mol ⁻¹)
9⁺	42.5
10⁺	38.8
11⁺	39.6
12⁺	36.1
13⁺	10.0
14⁺	27.7
15⁺	10.7
16⁺	9.9

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