

Carbon Rings Snapping

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Abstract: Gaseous carbon begins to aggregate in the form of linear chains and rings. While chains have consistently been observed in a variety of conditions that led to their spectroscopic characterization, rings remain elusive, a fact that seemingly conflicts with their well-known higher stability (from 10 atoms onwards). The increase in temperature favors thermodynamically the chain population. Calculations, for C₈, C₁₀, and C₁₂, of the temperature-dependent rate constants for chain–ring and ring–chain interconversion from ab initio B3LYP/6-311G* data shows that from ~1000 K, that is, at temperatures just below the lower end of those used in the clusters production, the conversion is rapid in the experimental time-scale both in the singlet and the triplet multiplicities.

Pure carbon molecules exist in a rich variety of structures whose atoms have hybridizations that range from sp¹ to sp^{2.2} and even, in some cases, to sp³.³ The sp hybridization appears in the low nuclearity regime, while sp² hybrids are formed when more than 20 atoms are present.⁴ For a low number of atoms, each sp carbon is connected to one or two others, and either chains or rings can be produced. Both types of structures may be present when the environment allows the existence of these very stable, but highly reactive, species. The interstellar media and the electric arcs used in the preparation of fullerenes are some such environments.

Fullerene production is achieved at ~1800 °C in flames.⁵ Somewhat higher temperatures are used in experiments in which carbon cylinders in a He atmosphere at 150 kPa are treated with high-frequency (500 kHz) inductive heat where carbon starts to sublime at 2500 °C.⁶ The standard electric arcs for fullerene production reach temperatures well above 4000 °C.⁷ In the case of smaller clusters, it is known that production of C₂ to C₇ requires temperatures of 2660–2850 K.⁸ Similar high-temper-

ature conditions are also likely to occur in the production of carbon clusters in acetylene electric discharge.⁹

A temperature increase enhances entropic—in the present context, mainly vibrational—effects that ultimately lead to a distribution of the isomeric abundance that does not bear resemblance to the relative stabilities of the two forms either at 0 K or at room temperature. The competition between chains and rings can be further complicated by the quasi-degeneracy of the triplet and singlet spin states in many of these systems. It is now ascertained that in the low-temperature regime rings are the more stable form for nuclearities of about 10 or more atoms.¹ Common wisdom has it that since large amplitude motions occur with more difficulty in the cyclic forms, the formation of linear structures remains entropically favored (alternatively, one can think that connecting two chain-ends is entropically less favored than breaking any one of the bonds). Furthermore, not all rings are similar, and simple molecular orbitals considerations show that the HOMOs of C₃, C₆, C₇, and C₁₀ have the terminal carbons with coefficients of the same sign, while they differ for C₄, C₅, C₈, and C₉. In the former set, soldering of the two ends should occur more easily and, in turn, should make these carbon chains more flexible.

In this scenario, the dynamics of carbon chains and rings can be rather complicated. It is the purpose of this contribution to provide insight, within a spin multiplicity, into the dynamics of small carbon clusters by (a) locating the minima and, more importantly, the transition states for the ring–chain and the chain–ring interconversions of C₈, C₁₀, and C₁₂ and (b) calculating the temperature-dependent rate constants for the isomerization, both in the singlet and triplet multiplicities. The possible intersystem crossing between them will not be considered here. The relative stabilities of rings and chains have been discussed to distraction and will not be presented here in detail (success and limitation of various forms of computational theory have been recently reviewed¹). The set of 10 points that emerges from the calculations can be of assistance in the investigation of these fascinating systems that appear in the interstellar medium, play a role in fullerene self-assembly, and are now becoming of interest to materials science.¹⁰

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Table 1. Selected Results for the Lowest Singlet and Triplet States of C₈, C₁₀, and C₁₂

system	theory	state	ΔE^a	energy ^a	$\tilde{\nu}^b$	zpe ^c	R_{CC}^d	$\hat{C}\hat{O}\hat{C}^e$
C ₈ (linear)	f	singlet	0.	-304.477878	61	21.68		
	g		0.	-303.543127				
C ₈ (ring)	f		0.227	-304.469526	120	23.16		
	g		-0.242	-303.552003				
C ₈ (tr. st.)	f		2.569	-304.383473	<i>i</i> 197	19.61	2.748	74.42
	g		2.128	-303.464931				
C ₈ (linear)	f	triplet	0.	-304.495010	63	21.25		
	g		0.	-303.542045				
C ₈ (ring)	f		0.981	-304.458965	136	21.82		
	g		0.353	-303.529087				
C ₈ (tr. st.)	f		2.940	-304.386980	<i>i</i> 330	19.69	2.343	64.22
	g		2.299	-303.457568				
C ₁₀ (linear)	f	Singlet	2.615	-380.660581	41	28.87		
C ₁₀ (ring)	f		0.	-380.756680	188	30.12		
C ₁₀ (tr. st.)	f		5.025	-380.572002	<i>i</i> 175	26.41	2.936	63.76
C ₁₀ (linear)	f	Triplet	0.192	-380.675056	42	28.07		
C ₁₀ (ring)	f		0.	-380.682121	103	28.31		
C ₁₀ (tr. st.)	f		2.831	-380.578096	<i>i</i> 272	26.00	2.532	56.88
C ₁₂ (linear)	f	Singlet	1.496	-456.841701	29	36.03		
C ₁₂ (ring)	f		0.	-456.896694	109	35.87		
C ₁₂ (Tr. st.)	f		3.609	-456.764074	<i>i</i> 126	32.31	3.009	52.96
C ₁₂ (linear)	f	Triplet	0.161	-456.854326	30	34.87		
C ₁₂ (ring)	f		0.	-456.862800	121	32.46		
C ₁₂ (tr. st.)	f		2.556	-456.766306	<i>i</i> 199	32.11	2.501	44.54

^a Energy difference in eV with the most stable structure of that spin multiplicity and absolute electronic energy; the total energy is in hartrees. ^b Lowest or imaginary wavenumber (cm⁻¹). ^c Zero point energy in kcal/mol. ^d Length of the incipient bond in Å. ^e Angle, in degrees, with the center of mass of the cluster, \hat{O} , with the two carbon atoms forming the incipient bond. ^f B3LYP/6-311G*//B3LYP/6-311G*. ^g B3LYP/6-311G*//CCSD(T)/cc-pVDZ.

Quantum chemical calculations were performed at the B3LYP/6-311G*¹¹ level with the Gaussian94¹² suite of programs. This level of calculations is deemed adequate (see, however, below for a test calculation) to obtain data of sufficient accuracy to calculate the rate constants of interconversion (structures, energies, and most importantly vibrational frequencies which are ultimately responsible for the high-temperature rates). Molecular partition functions were calculated in the rigid rotor-harmonic oscillator approximation in analogy with previous treatment limited to the stable structures.¹³ Temperature-dependent rate constants, $K(T)$, were obtained using transition state theory.¹⁴ All of the quantities of interest were obtained in the quantum chemical calculations and not modified. The present treatment does not include anharmonic effects and therefore leaves room for improvement.

Three all-carbon species, C₈, C₁₀, and C₁₂ were selected because they bracket the region of nuclearities where rings become more stable than chains and are therefore ideal candidates to ascertain the influence of the variation of the temperature on the rate constants of interconversion. For each species, the two minima and the transition state responsible for

the isomerization were located, both for the lowest singlet and the lowest triplet states. Overall, 18 stationary points were found. It is not the intent of this work to compare the relative stabilities of the two spin multiplicities that will therefore be considered separately.

C₈ exists in cyclic and linear forms.¹ Linear triplet was first detected in Ar matrix.¹⁵ Vibrational work was carried out, and the picture obtained was consistent with that provided by density functional theory calculations.¹⁶ More detailed information was obtained in photoelectron spectroscopy experiments.¹⁷ Very recently, two infrared absorption transitions observed in Ar matrix at 10 K were assigned to vibrational modes of cyclic C₆ and C₈.¹⁸ The assignment was made possible by a combination of isotopomer frequency shifts and density functional calculations. From a theoretical point of view, calculations on C₈ have consistently addressed the problem of stability of the two forms; different authors have expressed different opinions.¹⁹

The B3LYP/6-311G* results, Table 1, find the linear form more stable in both multiplicities, with the triplet the lowest energy structure. At low temperatures, in the absence of intersystem crossing, rings will comparatively be more abundant in the singlet than in the triplet manifold where the activation barrier for ring-to-chain interconversion is also lower than the chain-to-ring barrier. The longer C—C distance for the incipient bond in S₀ than in T₁, see Table 1, is attributed to the earlier electron coupling that occurs when two electrons of different

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Table 2. Transition State Rate Constants, $\log_{10} k$, $k(\text{s}^{-1})$, for the Interconversion from the Linear to the Cyclic Form and vice versa for the Lowest Singlet and Triplet States of C_8 , C_{10} , and C_{12}

Singlet						
$T(\text{K})$	C_8		C_{10}		C_{12}	
	$\log_{10} k_{\text{lr}}^{a,b}$	$\log_{10} k_{\text{rl}}^{a,b}$	$\log_{10} k_{\text{lr}}$	$\log_{10} k_{\text{rl}}$	$\log_{10} k_{\text{lr}}$	$\log_{10} k_{\text{rl}}$
300	-17.775(-12.623)	-14.193(-14.513)	-16.283	-45.373	-11.546	-28.362
600	-3.505(-0.929)	-1.118(-1.278)	-3.023	-16.589	-0.116	-7.817
1000	2.088(3.633)	4.103(4.007)	2.190	-5.077	4.413	0.389
1500	4.806(5.837)	6.678(6.614)	4.724	0.642	6.616	4.452
2000	6.118(6.891)	7.936(7.888)	5.945	3.472	7.673	6.454
3000	7.359(7.874)	9.150(9.118)	7.096	6.257	8.661	8.411
4000	7.927(8.313)	9.722(9.698)	7.619	7.615	9.103	9.354
Triplet						
$T(\text{K})$	C_8		C_{10}		C_{12}	
	$\log_{10} k_{\text{lr}}$	$\log_{10} k_{\text{rl}}$	$\log_{10} k_{\text{lr}}$	$\log_{10} k_{\text{rl}}$	$\log_{10} k_{\text{lr}}$	$\log_{10} k_{\text{rl}}$
300	-22.978(-15.498)	-11.346(-11.197)	-19.257	-20.961	-15.479	-18.984
600	-6.554(-2.814)	-0.388(-0.314)	-4.643	-4.872	-2.327	-3.714
1000	-0.111(2.134)	3.969(4.013)	1.093	1.525	2.849	2.303
1500	3.032(4.528)	6.100(6.130)	3.886	4.674	5.367	5.238
2000	4.555(5.677)	7.133(7.156)	5.236	6.217	6.580	6.665
3000	6.008(6.756)	8.118(8.133)	6.516	7.711	7.724	8.037
4000	6.681(7.242)	8.575(8.586)	7.103	8.422	8.244	8.684

^a k_{lr} , cyclization rate constant, k_{rl} , snapping rate constant. ^b In brackets, the rate calculated using the B3LYP/6-311G*/CCSD(T)/cc-pVDZ energies.

spins approach each other from infinite distance. Table 2 shows that the temperature-dependent rate constants are nearly 2 orders of magnitude larger for the chain-to-ring isomerization than viceversa. From ~ 1000 K, the rate constants for interconversion between the two species become fast on the time-scale of the cluster production.

C_{10} is the transition point between linear and ring structures.¹ Experimental evidence for high stability of cyclic C_{10} has recently been provided.²⁰ The cumulenic D_{5h} ring structure is believed to be the most stable of the possible cycles on can envisage.^{19,21} Linear C_{10} is the isomer consistently detected experimentally.^{15,22} Some vibrational lines²³ were tentatively assigned on the basis of calculations.²⁴ The present results, Table 1, find the cyclic form more stable in both multiplicities, with the singlet state the lowest energy structure. In agreement with the case of C_8 , the C–C distance for the incipient bond is longer in S_0 than in T_1 . In Table 2, the calculated rates of interconversion become fast on the time-scale of cluster production at 1000–1500 K.

C_{12} belongs to the region of higher ring stability,²⁴ although only linear systems have so far been observed in this region.^{23,25} The rings are the more stable form in both multiplicities, with the singlet state the lowest energy structure. The C–C distance of the incipient bond in both S_0 and T_1 , given in Table 1, appears to have reached a plateau. From ~ 1000 K, the rate constants for interconversion between the two species become similar and are very fast on the time-scale of the cluster production.

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To test the stability of the rate constants, the electronic energies of the smallest system, namely C_8 , were recalculated at the CCSD(T)²⁶ level with the cc-pVDZ basis set.²⁷ While the relative energies of the stable forms change by a few tenths of electronvolts and may, partly, contribute to the debate of their stability,^{1,15–19} the conclusion that their interconversion becomes rapid, at ~ 1000 K, on the time-scale of the experiment remains valid.

Although only few systems have been examined and more will have to be studied in the future, detailed inspection of Tables 1 and 2 shows some general trends (at the B3LYP/6-311G* level) that can be summarized in 10 points:

(i) the activation energy for cyclization shows a regular trend. A similar trend cannot be found for the snapping because of the more complicated electronic nature of the rings in which aromatic and anti-aromatic affects can occur, (ii) the decrease of the activation energies with the increase of the number of atoms in point (i) is not linear, for instance, in the singlet, $\Delta E(\text{C}_8) = 2.569$ eV, $\Delta E(\text{C}_{10}) = 2.410$ eV, $\Delta E(\text{C}_{12}) = 2.113$ eV, (iii) the variation of the zero point energies between a stable form and the transition state is linear only for cyclization, (iv) in the linear systems, the lowest wavenumber, $\tilde{\nu}$, decreases with the chain elongation in both spin states, (v) in the singlet, the lowest wavenumber of the ring form is inversely proportional to the imaginary wavenumber of the transition state, (vi) in the triplet transition states, the imaginary $\tilde{\nu}$ decreases with the chain elongation, (vii) the CC bond lengths for the incipient bond that is formed at the transition state are different in the two multiplicities, and their limiting values are ~ 2.5 Å for the triplet and ~ 3.0 Å for the singlet, (viii) fitting the activation energies versus the CÔC angle, α (see footnote e, Table 1), from the linear form gives for both singlet and triplet a straight line ($r = 0.99$) with $\Delta E_{\text{singlet}} = 1.093 + 0.021 \alpha$, and $\Delta E_{\text{triplet}} = 1.682 + 0.020 \alpha$, (ix) at 300 K, the interconversion is essentially frozen on the time-scale of the experiments that produce these clusters, but the (sub)second time-regime for isomerization is reached already at ~ 1000 K, (x) there is no general rule/trend that one

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can extrapolate from the temperature-dependent rate constants in terms of the number of carbon atoms or of the spin multiplicity.

In conclusion, the temperature-dependent rate constants for the ring-chain isomerization, and vice versa, of small carbon clusters have been calculated for the first time. The input parameters were obtained from density functional theory calculations of the minima and transition state structures and vibrational frequencies and were not modified. As a rule, at the temperatures of interest for the production of these species, cyclization is slower than ring snapping. The conversion is fast

on the time scale of cluster production which makes trapping of the rings a very unlikely process. However, in consideration of their well-known higher stability at low temperatures, the threshold for trapping can be set at ~ 1000 K. It is therefore envisaged that fast cooling to ~ 1000 K followed by slow annealing should generate enough ring species for spectroscopic characterization.

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