DFT study and NBO analysis of the mutual interconversion of cumulene compounds

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ABSTRACT: The B3LYP/6-31G* method was used to investigate the configurational properties of allene (1,2-propadiene) (**1**), 1,2,3-butatriene (**2**), 1,2,3,4-pentateriene (**3**), 1,2,3,4,5-hexapentaene (**4**), 1,2,3,4,5,6-heptahexaene (**5**), 1,2,3,4,5,6,7-octaheptaene (**6**), 1,2,3,4,5,6,7,8-nonaoctaene (**7**), and 1,2,3,4,5,6,7,8,9-decanonaene (**9**). The calculations at the B3LYP/6-31G* level of theory showed that the mutual interconversion energy barrier in compounds **1**–**8** are: 209.73, 131.77, 120.34, 85.00, 80.91, 62.19, 55.56, and 46.83 kJ mol^{-1}, respectively. The results showed that the difference between the average C=C double bond lengths ($\overline{d}$) values in cumulene compounds **1** and **2**, is larger than those between **7** and **8**, which suggest that with large n (number of carbon atoms in cumulene chain), the $\overline{d}$ values approach a limiting value. Accordingly, based on the plotted data, the extrapolation to $n = \infty$, gives nearly the same limiting $\overline{d}$(i. e., $\overline{d}_{\mathrm{lim}}$). Also, NBO results revealed that the sum of π-bond occupancies, $\overline{\pi}_{\mathrm{occupancy}}$, decrease from **1** to **8**, and inversely, the sum of π-antibonding orbital occupancies, $\overline{\pi}^*_{\mathrm{occupancy}}$, increase from compound **1** to compound **8**. The decrease of $\Delta(\overline{\pi}_{\mathrm{occupancy}} - \overline{\pi}^*_{\mathrm{occupancy}})$ values for compounds **1**–**8**, is found to follow the same trend as the barrier heights of mutual interconversion in compounds **1**–**8**, while the decrease of the barrier height of mutual interconversion in compounds **1**–**8** is found to follow the opposite trend as the increase in the number of carbon atom. Accordingly, besides the previously reported allylic resonant stabilization effect in the transition state structures, the results reveal that the $\overline{d}$ values, $\Delta(\overline{\pi}_{\mathrm{occupancy}} - \overline{\pi}^*_{\mathrm{occupancy}})$, $\Delta(\mathrm{E_{HOMO}} - \mathrm{E_{LUMO}})$, and the C atom number could be considered as significant criteria for the mutual interconversion in cumulene compounds **1**–**8**. This work reports also useful predictive linear relationships between mutual interconversion energy barriers (ΔE_0^a) in cumulene compounds and the following four parameters: $\overline{d}$, $\Delta(\overline{\pi}_{\mathrm{occupancy}} - \overline{\pi}^*_{\mathrm{occupancy}})$, $\Delta(\mathrm{E_{HOMO}} - \mathrm{E_{LUMO}})$, and $\mathrm{C_{Number}}$. Copyright © 2007 John Wiley & Sons, Ltd.

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KEYWORDS: cumulene; molecular modeling; DFT calculations; NBO; configurational properties

INTRODUCTION

Cumulenes are the homologous series of hydrocarbons that contain multiple, sequential double bonds sharing common atoms.[1] Allene (1,2-propandiene) (**1**), 1,2,3-butatriene (**2**), and 1,2,3,4- pentatetraene (**3**) are the first three members of this series. All these compounds have linear equilibrium geometries, with the four attached ligands alternating along the series between planar (D_{2h}) and orthogonal (D_{2d}) arrangements. Many aspects of

cumulene stereochemistry, synthesis, and reactivity have been investigated, and some of these aspects, are reported in several reviews.[2–6] Generally, linear cumulenes are not inherently 'strained.' Usually, strain implies some deviation from an ideal bonding geometry; however, this is not true for allene (1,2-propadiene) (**1**) ([2]cumulene), 1,2,3-butatriene (**2**) ([3]cumulene), 1,2,3,4-pentateriene (**3**) ([4]cumulene), 1,2,3,4,5-hexapentaene (**4**) ([5]cumulene), 1,2,3,4,5,6-heptahexaene (**5**) ([6]cumulene), 1,2,3,4,5,6,7-octaheptaene (**6**) ([7]cumulene), 1,2,3,4,5,6,7,8-nonaoctaene (**7**) ([8]cumulene), and 1,2,3,4,5,6,7,8,9-decanonaene (**9**) ([9]cumulene), which contain ordinary sp- and sp^2-hybridized carbons. Nevertheless, the electronic structure of cumulenes and their ability to form stabilized intermediates do render them highly reactive.

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Many allenes dimerize easily, but unsubstituted higher cumulenes, such as **6** and **7**, readily polymerize when they are not in dilute solution.

Cis-trans isomerism exists not only in monoenes but also in polyenes of the cumulene type, with an odd number of double bonds [ab(C=)$_n$Ccd, where *n* is odd], as was previously recognized by van't Hoff.[7] It is also well known that when *n* is even in cumulene compounds (e.g., allenes, etc...), there is enantiomerism due to the fact that successive planes of π bonds are orthogonal to each other. The *cis-trans* isomerism in butatriene derivatives was first observed by Kuhn and Blum.[8] The $\Delta H^{\#}$ values between the diastereoisomers is relatively low: 129.64 kJ mol^{-1} for CH$_3$CH=C=C=CHCH$_3$ and only 112.91 kJ mol^{-1} for *t*-Bu(C$_6$H$_5$)C=C=C= C(C$_6$H$_5$)*t*-Bu.[9,10] The values of $\Delta G^{\#}$ for the two cases, 132.15 and 125.26 kJ mol^{-1},[11] are in agreement with the values for RR'C=C=C=CRR' (R=C$_6$H$_5$, R'=C(CH$_3$)$_2$ CH$_2$C$_6$H$_5$), for example, 125.04 kJ mol^{-1}.[10] The *t*-Bu/ C$_6$H$_5$ compound has a remarkably negative activation entropy for isomerization ($\Delta S^{\#} = -31.99$ J mol^{-1} K^{-1}). The low barriers are presumably due to zwitterionic or biradical resonance. It is therefore not surprising that the *cis-trans* isomers interconvert readily, either photochemically or thermally at 160 °C. In the case of the substituted hexapentaenes, 1,2,3,4,5-hexapentaene ([5]cumulene), the barrier is considerably lower. The energy barrier of the *cis-trans* isomerization of RR'C=C=C=C= C=CRR' (R=C$_6$H$_5$, R'=C(CH$_3$)$_2$CH$_2$C$_6$H$_5$) is 79.88 kJ mol^{-1}.[10] This barrier is too low for the separation of *cis* and *trans* isomers, but since the equilibrium constant in such isomers is near unity,[9] it is relatively easy to measure the barrier by coalescence in the NMR spectrum.

The higher cumulenes with an odd number of double bonds, 1,2,3,4,5,6,7-octaheptaenes (**6**) ([7]cumulenes) and 1,2,3,4,5,6,7,8,9-decanonaenes (**8**) ([9]cumulenes), polymerize with extreme ease and are only fleetingly stable even in dilute solution.[12,13] Though their UV spectra have been recorded, there is no information about the mutual interconversion of these compounds.

Ultraviolet photoelectron spectra of linear chain cumulene compounds with phenyl terminal groups to stablize the chain have been measured and assigned with semi-empirical molecular orbital (MO) calculation.[14] Previously, B3LYP/D95* and B3LYP/aug-cc-Pvdz results have showed that the results of these methods are sufficiently accurate for the calculation of energies of neutral and anion carbon chains.[15] Also, these results have shown that the bond lengths of carbon–carbon bonds decrease rapidly toward an asymptotic limit, as the number of bonds in the cumulene chain increase.

Alkorta and Elguero[16] have estimated, for a series of polyyne/cumulene pairs at the B3LYP/6-311++G** level, the differences in stability obtained through the following isodesmic equation:

$$H\text{—}(C\equiv C)_n\text{—}H + H_2C\text{=}CH_2$$
$$\rightarrow H_2(C\text{=}C)_nH_2 + HC\equiv CH$$
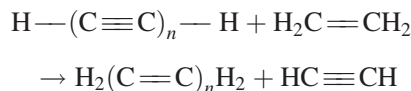
They have, particularly, concluded that as the length increases, the difference in stability also increases.

Zahradnik and Sroubkova[17] have also used a very simple procedure for estimating Hartree–Fock (HF) energy and accurate non-relativistic energy with simple hydrocarbons possessing C=C or CC bonds and for the acetylene dimer. They have discussed the experimental characteristics (heats of formation, ionization potentials, electron affinities), structural features, and reactivity in terms of quantum chemistry characteristics at the HF level, and also at level including a part of the electron correlation. Moreover, they have related the deviations from linearity with derivatives of long polyacetylenes and cumulenes to the lowest energy deformation vibrations. In fact, these lowest energy deformation vibrations decrease rapidly when passing from short to long acetylenic and culmulenic chains. Finally, they have mentioned the role of derivatives, with enhanced stability, which are potentially promising as construction materials for molecular devices and also resources for the preparation of defined clusters of C-atoms.

The results reported in this work suggest that $\overline{d}$ (average C=C double bond lengths), $\Delta(\overline{\pi}_{occupancy} - \overline{\pi}^*_{occupancy})$, $\Delta(E_{HOMO} - E_{LUMO})$, and carbon atom number (C_{Number}) could conveniently be considered as four predictive criteria for evaluating the mutual interconversion energy barriers in cumulene compounds (see Scheme 1). For this purpose the ground and transition state structures of compounds **1–8** have been optimized by density functional theory (DFT) based method, at B3LYP/6-31G* level of theory, using the GAUSSIAN 98 package of programs.[18–21] The B3LYP functional method combines Becke's three-parameter
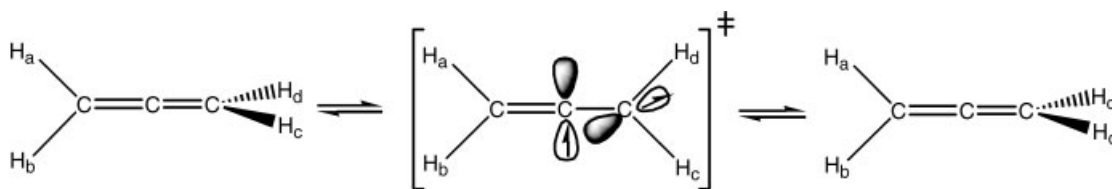
Scheme 1. Typical mutual interconversion process

exchange function with the correlation function of Lee *et al.* Also, NBO (natural bond orbital) analysis was used to investigate the nature of the bonds in compounds **1–8**.[22,23]

COMPUTATIONAL DETAILS

DFT calculations were carried out using B3LYP/6-31G* and unrestricted B3LYP/6-31G* (e.g., UB3LYP/6-31G*) levels of theory for ground and transition state structures, respectively, with the GAUSSIAN 98 package of programs[16] implemented on a Pentium–PC computer with 550 MHz processor.

Manually constructed appropriate Z-matrix files of initial geometries of the compounds **1–8** were used as input files for initial optimization by the PM3 method of the MOPAC 7.0 computer program.[24,25] The GAUSSIAN 98 program was finally used to perform DFT calculations at the B3LYP/6-31G* level. Energy minimum molecular geometries were located by minimizing the energy, with respect to all geometrical coordinates without imposing any symmetry constraints.

Due to the limitation concerning the structure of cumulene compounds, a perpendicular geometry (with an even number of carbon atoms) and a planar geometry (with an odd number of carbon atoms), respectively, were considered as TS structures for **1–8** cumulene compounds. It has to be noted that based on MCSCF/3-21G*, MCSCF/6-31G*, and SOCI/6-31G* calculations, Schmidt *et al.*[26] have reported that Hund's rule is violated in the rotation of C=C bond (e.g., a singlet structure lies below the rotational maximum on the triplet surface). Usually, the triplet structures lie 1–13 kJ mol^{-1} below rotational maxima on the singlet surface.[26]

Effectively, in this work, the rotational energy barrier of mutual interconversion of compounds **1–8** (ΔE_0^a) is defined as the energy difference between the unrestricted B3LYP/6-31G* minimized triplet transition state structures and B3LYP/6-31G* minimized ground state structures. The choice of the unrestricted B3LYP/6-31G* method for the investigation of TS structures was based on the fact that this method could describe the biradical character of TS structures arising from the breaking of the C=C bonds in the mutual interconversion processes. Using the unrestricted B3LYP/6-31G* method with triplet spin multiplicity, the resulting ΔE_0^a values were found to be lower than those obtained using the same method but with singlet spin multiplicity for the transition state structures. It is interesting to note that the corresponding ΔE_0^a with triplet spin multiplicity (using the unrestricted B3LYP/6-31G* method for the transition state structures) were also closer to the reported experimental data.[9–10] Therefore, this fact is in accordance with Hund's rule which would predict that the triplet transition state structure energy is below the corresponding rotated singlet state, as shown below:

rotation around C=C double bond
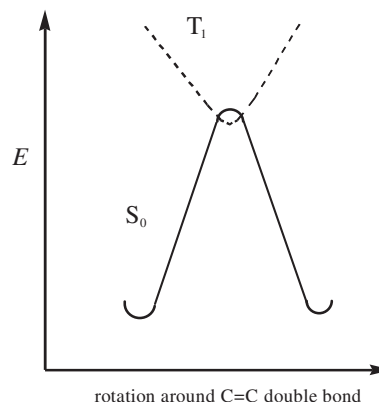
The vibrational frequencies and zero point energies (ZPE) were calculated by the FREQ subroutine. NBO analysis was then performed at the B3LYP/6-31G* level by the NBO 3.1 program[22,23] included in the GAUSSIAN 98 package of programs.

RESULTS AND DISCUSSION

Zero point (*ZPE*) and total electronic (E_{el}) energies ($E_o = E_{el} + ZPE$) for ground and transition state structures of compounds **1–8**, were calculated, respectively, using restricted and unrestricted B3LYP/6-31G* levels of theory (see Table 1). Table 2 shows the value of the thermodynamic functions *H*, *S*, *G* and the ΔG, ΔS, and ΔH parameters. As can be seen, ΔS values are relatively small, so that the calculated ΔH and ΔG parameters are close to the ΔE_0 values. The investigation of the energetic and structural parameters of the family of cumulene compounds present interesting relationships, as discussed below.

B3LYP/6-31G* results show that the mutual interconversion energy barriers for compounds **1–8** are: 209.73, 131.77, 120.34, 85.00, 80.91, 62.19, 55.56, and 46.83 kJ mol^{-1}, respectively. The mutual interconversion energy barriers by calculating the B3LYP/6-31G* level of theory for compounds **2** and **4** are in good agreement with the previously reported experimental data (for some derivatives of these compounds).[9,10] These results reveal that the mutual interconversion energy barriers for compounds **1–8** decrease on increasing the number of C atoms (chain length) in these compounds (see Table 1).

The representative restricted and unrestricted B3LYP/6-31G* calculated structural parameters of the ground and transition state geometries of compounds **1–8,** respectively, are given, in Figs 1 and 2. It can be noted that for the ground state of compounds **1** and **2**, the calculated structural parameters results using the B3LYP/6-31G* method are closer to the experimental data[15] than those obtained with the B3LYP/6-311G** method. Although, due to the nature of the various approximations involved

Table 1. B3LYP/6-31G* calculated total energies E, zero-point energies ZPE, and relative energies ΔE (E_h), (in Hartree), for the energy-minimum and energy-maximum geometries of compounds **1–8**

	Method							
	GS				TS			
Compound	E_{el}	ZPE^c	E_0	ΔE_0^a	E_{el}	ZPE^c	E_0	ΔE_0^a
1	−116.657674	0.054397	−116.603229	0.000000 (0.000000)^b	−116.573345	0.050578	−116.523368	0.079861 (209.726044)^b
2	−154.730753	0.059430	−154.671322	0.000000 (0.000000)	−154.677199	0.056053	−154.621146	0.050176 (131.768666)
3	−192.806625	0.064149	−192.742475	0.000000 (0.000000)	−192.757596	0.060946	−192.696650	0.045825 (120.342374)
4	−230.883113	0.069278	−230.813843	0.000000 (0.000000)	−230.847816	0.066341	−230.781476	0.032367 (84.999928)
5	−268.960897	0.074203	−268.886693	0.000000 (0.000000)	−268.926992	0.071109	−268.855883	0.030810 (80.911045)
6	−307.038539	0.078328	−306.960211	0.000000 (0.000000)	−307.013097	0.076567	−306.936530	0.023681 (62.189367)
7	−345.117186	0.084279	−345.032907	0.000000 (0.000000)	−345.091715	0.079965	−345.011750	0.021156 (55.558390)
8	−383.195503	0.088207	−383.107295	0.000000 (0.000000)	−383.176165	0.086703	−383.089462	0.017833 (46.831765)

^{a}Relative to the minimum.
^{b}Numbers in parenthesis are the corresponding $\triangle E$ values in kJ mol^{-1}.
^{c}Corrected by multiplying by a scaling factor (0.9804).

in theoretical calculations, it is not expected, in principal, to obtain exactly the experimental values.[27] However, it is possible to carry out theoretical calculations, from which many properties and structures can be obtained with an accuracy that is competitive with experiments.[28–29]

It can be seen that the chain length in transition state geometries is longer than those of the corresponding ground state structures (see Figs 1 and 2).

The average bond length ($\overline{d}$) of C=C in cumulene chain, in the ground state structures, can be defined by:

$$\overline{d} = \frac{\sum_{i=1}^{n-1} d_i}{n-1}, \quad (n \geq 3)$$

Using the B3LYP/6-31G* calculated bond lengths (d_i), the average bond length ($\overline{d}$) of C=C double bonds in the ground state geometry of cumulene compounds was calculated by the above equation and the results are reported in Table 3. It is interesting to note the linear relationship between the corresponding mutual inter-conversion energy barriers and these average bond lengths ($\overline{d}$) in cumulene compounds **1–8** (see Table 4). As can also be seen from Table 3, the difference between the average bond lengths ($\overline{d}$) in cumulene compounds **1** and **2** is larger than those between **7** and **8**. Therefore, it could be expected that with large n (number of carbon atoms in cumulene chain) the differences between the corresponding $\overline{d}$ would disappear. However, as can be seen from the Table 4, when the analysis of these compounds are separated into odd and even number of C atoms the quality of linear correlation results improve significantly (e.g., giving higher determination coefficients) in all three cases. Effectively, the quality of the linear correlations, resulting from the separate fit of ΔE_0^a (kJ mol^{-1}) *versus* $\overline{d}$ (the average bond length in angström (Å)) for odd and even number of C atoms, improve (e.g., higher determination coefficient R^2), in all three cases (see Table 4 and Figs 3 and 4). These results do not confirm the previous statement[15] concerning cumulene compounds, for which 'the bond lengths have no remarkable alternation within the chain, although this alternation converge gradually to an asymptotic limit as the value of n is getting larger.'

NBO analysis was used to calculate the bonding and antibonding orbital occupancies in the ground state structures of compounds **1–8** (see Fig. 5). In the NBO analysis[22–23] the electronic wavefunctions are interpreted in terms of a set of occupied Lewis and a set of unoccupied non-Lewis localized orbitals. The delocalization effects (or donor–acceptor charge transfers) can be estimated from the presence of off-diagonal elements of the Fock matrix in the NBO basis. The NBO program searches for an optimal natural Lewis structure, which has the maximum occupancy of its occupied NBOs, and in general agrees with the pattern of bonds and lone pairs of the standard structural Lewis formula. Therefore, the new

Table 2. Calculated thermodynamic functions (enthalpies, Gibbs free energies (in kcal mol^{-1}), and entropies (in kcal mol^{-1} K^{-1}), for the energy-minimum and energy-maximum geometries of compounds **1–8**

Geometry	H (kJ mol^{-1})	S (kJ mol^{-1} K^{-1})	G (kJ mol^{-1})	ΔH^{a} (kJ mol^{-1})	ΔS^{a} (kJ mol^{-1} K^{-1})	ΔG^{a} (kJ mol^{-1})
1-GS, (D_{2d})	−306200.08	0.24	−306272.26	0.00	0.00	0.00
1-TS, (D_{2h})	−305991.06	0.25	−306065.09	209.03	0.01	207.17
2-GS, (D_{2h})	−406169.14	0.27	−406248.21	0.00	0.00	0.00
2-TS, (D_{2d})	−406036.45	0.28	−406120.20	132.69	0.02	128.00
3-GS, (D_{2d})	−506146.33	0.29	−506232.02	0.00	0.00	0.00
3-TS, (D_{2h})	−506024.92	0.31	−506116.20	121.41	0.02	115.86
4-GS, (D_{2h})	−606124.05	0.31	−606216.44	0.00	0.00	0.00
4-TS, (D_{2h})	−606038.42	0.32	−606134.85	85.63	0.01	81.59
5-GS, (D_{2d})	−706105.60	0.33	−706204.52	0.00	0.00	0.00
5-TS, (D_{2h})	−706024.07	0.35	−706127.35	81.53	0.01	77.17
6-GS, (D_{2h})	−806088.24	0.36	−806194.87	0.00	0.00	0.00
6-TS, (D_{2d})	−806026.28	0.38	−806139.07	61.96	0.02	55.80
7-GS, (D_{2d})	−906069.98	0.39	−906185.74	0.00	0.00	0.00
7-TS, (D_{2h})	−906013.28	0.39	−906130.65	56.70	0.01	55.10
8-GS, (D_{2h})	−1006054.85	0.40	−1006174.92	0.00	0.00	0.00
8-TS, (D_{2d})	−1006008.40	0.42	−1006134.36	46.45	0.02	40.56

^{a} Relative to the ground state structures.
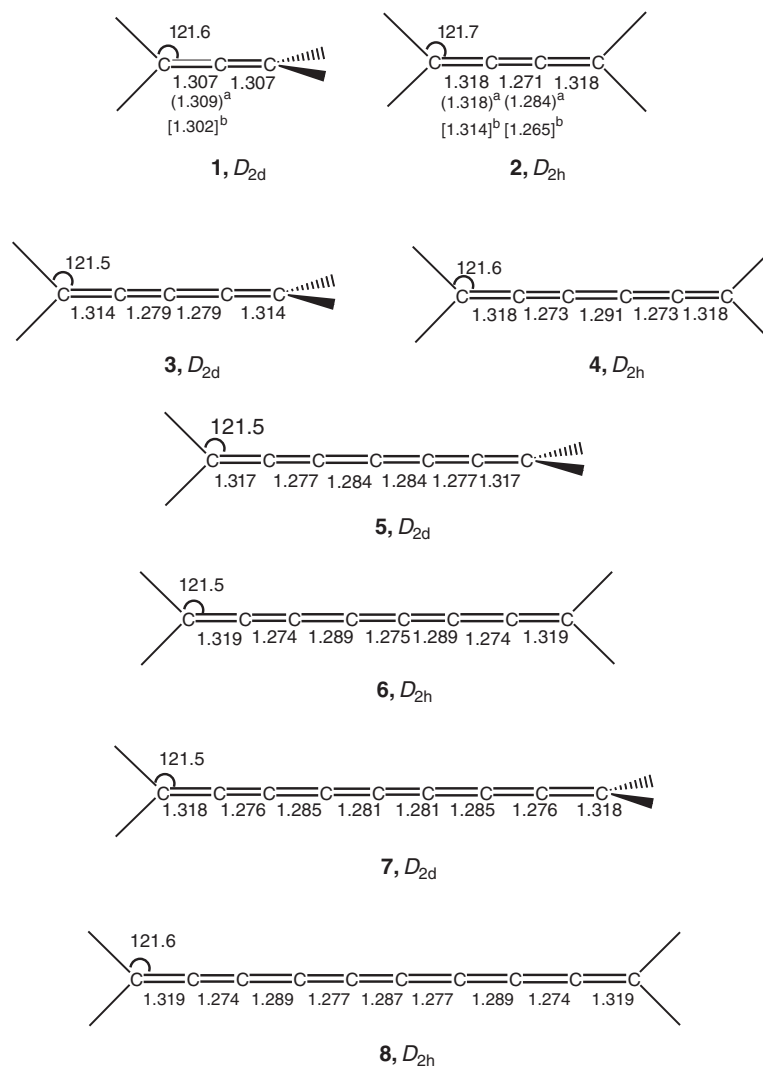
Figure 1. B3LYP/6-31G* calculated structural parameters of the ground state geometries of compounds **1–8**. ^{a}Experimental and ^{b}B3LYP/6-311G** data (see Ref.[15] and References therein). Bond lengths are in angström (Å) and angles are in degree (°)
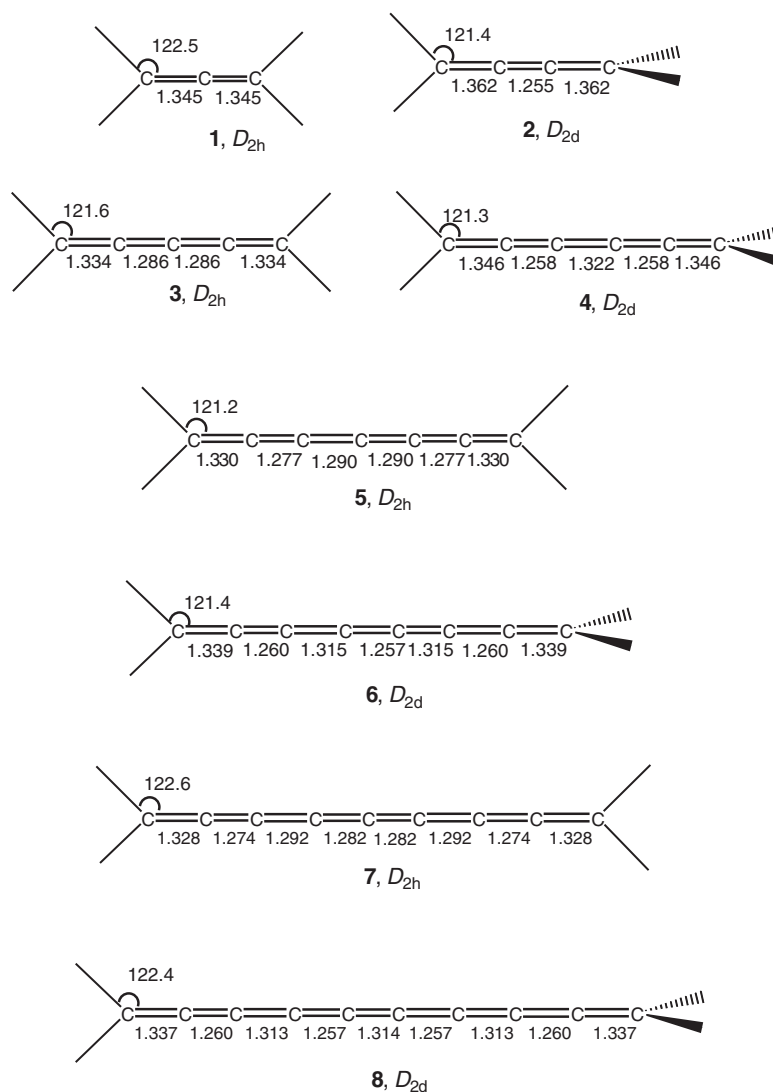
Figure 2. Unrestricted B3LYP/6-31G* calculated structural parameters for the transition state geometries of compounds **1**–**8**. Bond lengths are in angström (Å) and angles are in degree (°)

Table 3. NBO calculated mean π bonding and π^* anti bonding orbital occupancies, the difference between $\overline{\pi}$ and $\overline{\pi}*$ values (i.e., $\Delta = \overline{\pi}_{\text{occupancy}} - \overline{\pi}*$) and the average bond length ($\overline{d}$) for compounds **1**–**8**, based on the B3LYP/6-31G* optimized ground state geometries of compounds **1**–**8**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
$\overline{\pi}_{\text{occupancy}}$	1.97233	1.90752	1.88174	1.85488	1.83859	1.82335	1.81197	1.80191
$\overline{\pi}^*_{\text{occupancy}}$	0.05149	0.09964	0.12856	0.15011	0.16711	0.17985	0.19139	0.20000
$\Delta(\overline{\pi}_{\text{occupancy}} - \overline{\pi}^*_{\text{occupancy}})$	1.92084	1.80782	1.75318	1.70477	1.67148	1.64350	1.62058	1.60191
$\overline{d}$	1.307	1.302	1.297	1.294	1.292	1.291	1.290	1.289

Table 4. Calculated linear correlation results for ΔE_0^a (kJ mol^{-1}) *versus* $\overline{d}$ in compounds **1**–**8** with odd + even, odd and even number of C atoms, respectively

C atoms	ΔE_0^a *versus* $\overline{d}$	R^2
Odd + even	$\Delta E_0^a = 8379.1\,\overline{d} - 10755$	0.9621
Odd	$\Delta E_0^a = 9113.1\,\overline{d} - 11701$	0.9997
Even	$\Delta E_0^a = 6463.7\,\overline{d} - 8282.5$	0.9952

orbitals are more stable than pure Lewis orbitals, stabilizing the wave function, and giving a set of MOs equivalent to canonical MOs.

Our NBO analysis revealed that the mean occupancies of π bonding orbitals (e.g., $\overline{\pi}$) decrease from compound **1** to compound **8**, while the mean occupancies of π^* antibonding orbital occupancies ($\overline{\pi}*$) increase for these compounds (e.g., **1** to compound **8**) (see Table 3).
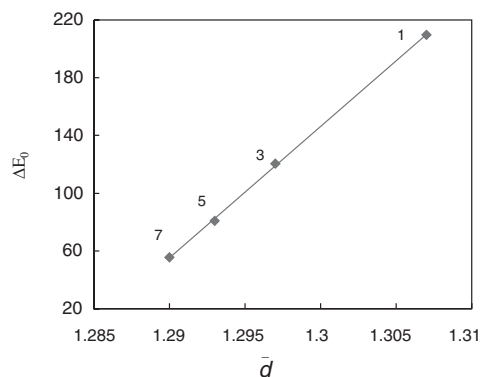
Figure 3. Fit of ΔE_0^a (kJ mol^{-1}) *versus* $\bar{d}$ (the average bond length in angström (Å)) for compounds **1,3,5,7,** with odd number of C atoms, which shows a linear correlation represented by: $\Delta E_0^a = 6463.7\,\bar{d} - 8282.5$ with $R^2 = 0.9997$
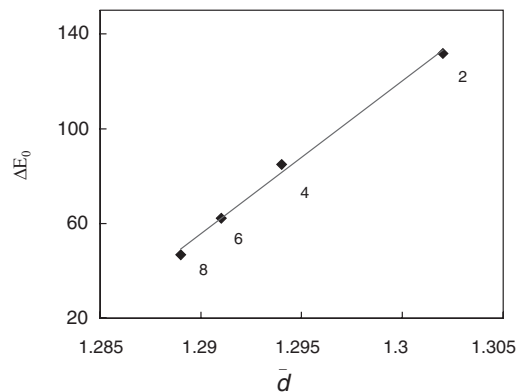

Figure 4. Fit of ΔE_0^a (kJ mol^{-1}) *versus* $\bar{d}$ (the average bond length in angström (Å)) for compounds **2,4,6,8,** with even number of C atoms, which shows a linear correlation represented by: $\Delta E_0^a = 6463.7\,\bar{d} - 8282.5$ with $R^2 = 0.9952$
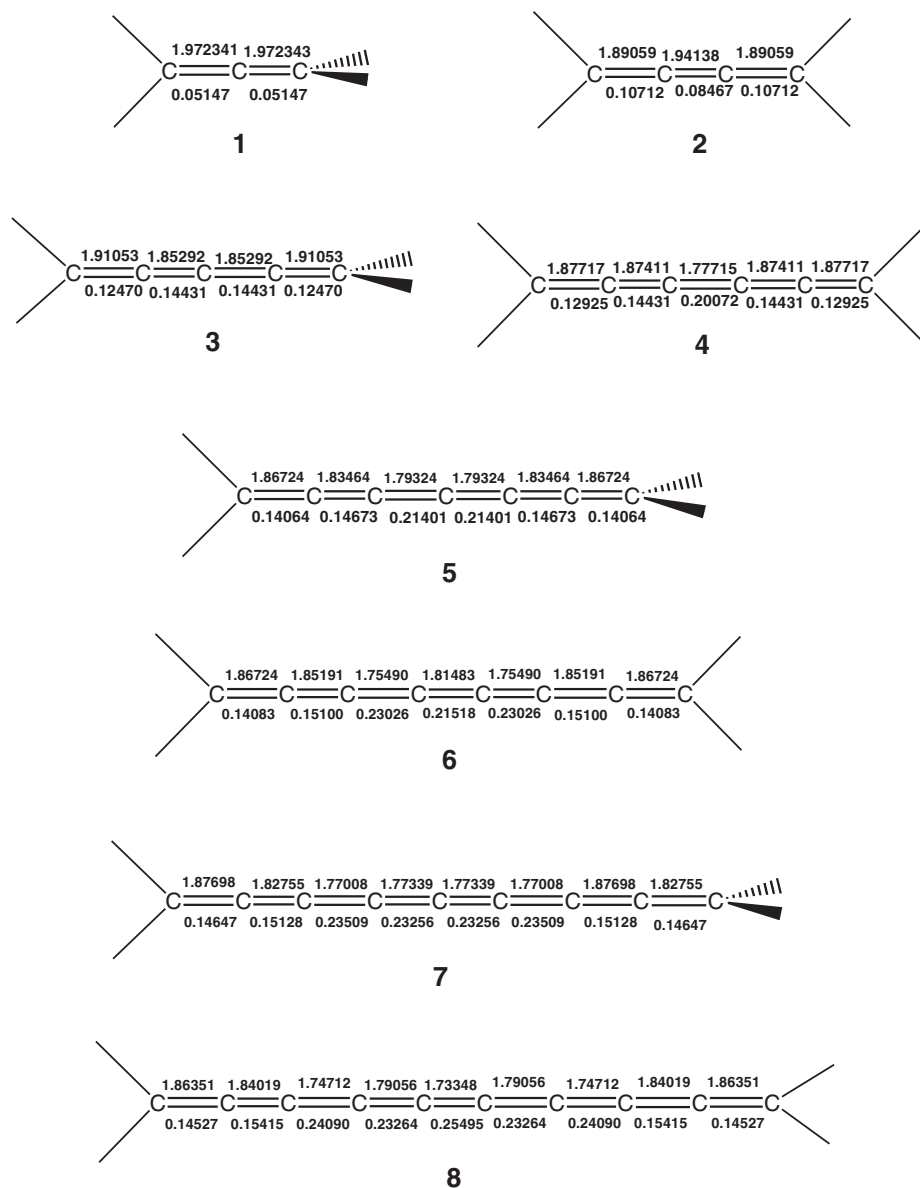

Figure 5. NBO calculated π bonding (numbers presented above the chain) and π^* antibonding (numbers presented below the chain) orbital occupancies, based on B3LYP/6-31G* optimized ground state geometries of compounds **1–8**

Table 5. Calculated linear correlation results for ΔE_0^a (kJ mol^{-1}) *versus* $\Delta(\overline{\pi}_{occupancy} - \pi^*_{occupancy})$ in compounds **1–8** with odd + even, odd and even number of C atoms, respectively

C atoms	ΔE_0^a *versus* $\Delta(\overline{\pi}_{occupancy} - \pi^*_{occupancy})$	R^2
Odd + even	$\Delta E_0^a = 494.89 \, \Delta - 749.94$	0.9814
Odd	$\Delta E_0^a = 513.77 \, \Delta - 778.11$	0.9995
Even	$\Delta E_0^a = 413.24 \, \Delta - 616.72$	0.9900

Using the obtained occupancy values, a 'Δ' parameter could be defined as $\Delta(\overline{\pi}_{occupancy} - \pi^*_{occupancy})$. There is a linear correlation between ΔE_o and $\Delta(\overline{\pi}_{occupancy} - \pi^*_{occupancy})$ (see Table 5). These results indicate that with the increase of Δ values, the corresponding ΔE_o (e.g., mutual interconversion energy barrier) increase. Consequently, the Δ parameter, that is, $\Delta(\overline{\pi}_{occupancy} - \pi^*_{occupancy})$, could be proposed as criterion for the evaluation of the easiness of mutual interconversion in cumulene compounds. As it can be seen from Table 6, when odd and even number of C atoms are separately fitted for these compounds, the quality of the linear trend between ΔE_0^a and $\Delta(\overline{\pi}_{occupancy} - \pi^*_{occupancy})$ improve perceptibly.

Also, B3LYP/6-31G* results showed that the HOMO – LUMO energy gap for compounds **1–8** are: 0.28362, 0.18933, 0.19247, 0.14435, 0.14800, 0.11780, 0.12135, and 0.10027 eV, respectively (see Table 6). That is, the HOMO – LUMO energy gap decreases in accordance with the increase of the chain length (i.e., number of π bond), and also with the decrease of the mutual interconversion energy barriers in compounds **1–8**. However, this trend is more sensitive with an odd number of π bands, resulting in a decreasing 'zigzag' aspect. This conclusion agrees with the previous PM3 Hamiltonian calculations[14] and would suggest instability for the longer cumulene type chain. There is again an improvement in the quality of linear correlation between ΔE_0^a (kJ mol^{-1}) *versus* $\Delta(E_{HOMO} - E_{LUMO})$, when odd and even number of C atoms are separately fitted for these compounds (see Table 7).

It is interesting to note another predictive linear correlation found between $\log \Delta E_0^a$ (kJ mol^{-1}) *versus* $\log C_{Number}$ in compounds **1–8** (see Table 8). The results in Table 8 show again that higher correlation coefficients are obtained, when odd and even number of C atoms are separately correlated for these compounds. Therefore, the

Table 7. Calculated linear correlation results for ΔE_0^a (kJ mol^{-1}) *versus* $\Delta(E_{HOMO} - E_{LUMO})$ in compounds **1–8** with odd + even, odd, and even number of C atoms, respectively

C atoms	ΔE_0^a *versus* $\Delta(E_{HOMO} - E_{LUMO})$	R^2
Odd + even	$\Delta E_0^a = 907.16 \, \Delta - 48.05$	0.9899
Odd	$\Delta E_0^a = 948.88 \, \Delta - 60.20$	0.9996
Even	$\Delta E_0^a = 954.3 \, \Delta - 50.19$	0.9976

Table 8. Calculated linear correlation results for $\log \Delta E_0^a$ (kJ mol^{-1}) *versus* $\log C_{Number}$ in compounds **1–8** with odd + even, odd, and even number of C atoms, respectively

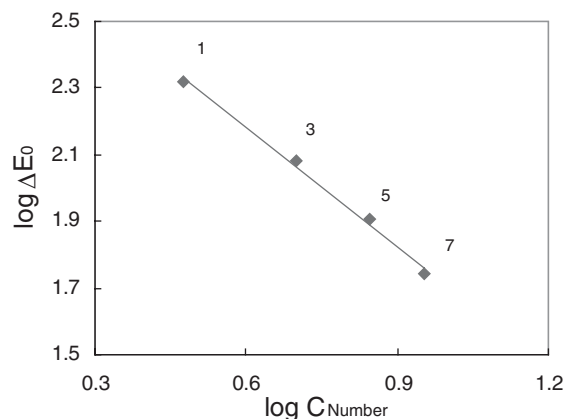| C atoms	$\log \Delta E_0^a$ *versus* $\log C_{Number}$	R^2
Odd + even	$\log \Delta E_0^a = -1.19 \log C_{Number} + 2.90$	0.9842
Odd	$\log \Delta E_0^a = -1.19 \log C_{Number} + 2.90$	0.9955
Even	$\log \Delta E_0^a = -1.12 \log C_{Number} + 2.80$	0.9988

Figure 6. Fit of $\log \Delta E_0^a$ (kJ mol^{-1}) *versus* $\log C_{Number}$ for compounds **1,3,5,7**, with odd number of C atoms, which shows a linear correlation represented by: $\log \Delta E_0^a = -1.19 \log C_{Number} + 2.90$ with $R^2 = 0.9955$

reported linear equations predict fairly the activation energy as a function of odd and even number of C atoms, in cumulene compounds (see Figs 6 and 7).

Similarly, a predictive linear correlation is also found in cumulene compounds **1–8** from the plot of $1/n$ *versus* $\overline{d}$ (see Table 9). Figures 8 and 9 show the corresponding linear plots found for $n =$ odd and $n =$ even number of C atom in these compounds, respectively.

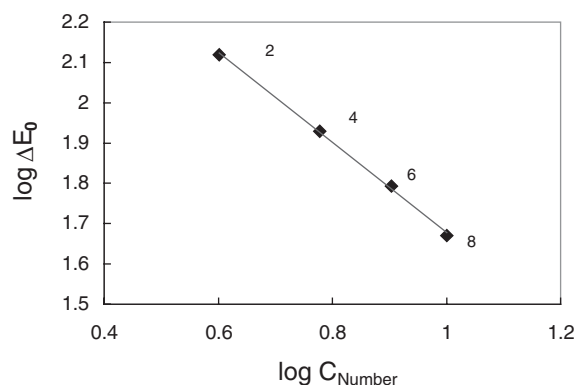**Table 6.** B3LYP/6-31G* calculated HOMO, LUMO energies (eV), and HOMO – LUMO gaps in the ground state geometries of compounds **1–8**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
HOMO	−0.26297	−0.23990	−0.23687	−0.22618	−0.22409	−0.21787	−0.21643	−0.21241
LUMO	0.02065	−0.05057	−0.04440	−0.08183	−0.07600	−0.10007	−0.09508	−0.11214
$\Delta(E_{HOMO} - E_{LUMO})$	0.28362	0.18933	0.19247	0.14435	0.14800	0.11780	0.12135	0.10027

Figure 7. Fit of log ΔE_0^a(kJ mol^{-1}) *versus* logC$_{Number}$ for compounds **2**, **4**, **6**, and **8**, with even number of C atoms, which shows a linear correlation represented by: log $\Delta E_0^a = -1.12$ logC$_{Number}+2.80$ with $R^2 = 0.9988$
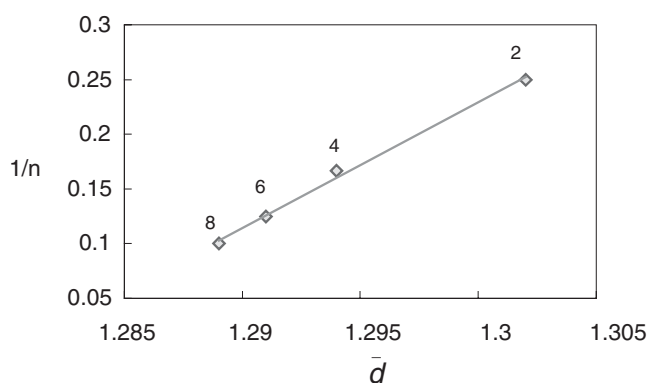

Figure 9. Fit of $1/n$ *versus* $\overline{d}$ for compounds **2**, **4**, **6** and **8**, with even number of C atoms, which shows a linear correlation represented by: $1/n = 11.48 \, \overline{d} - 14.694$ with $R^2 = 0.9958$

Table 9. Calculated linear correlation results for $1/n$ *versus* $\overline{d}$ for compounds **1–8** with odd and even number of C atoms, respectively. $\overline{d}_{lim}$ represents the extrapolation value to $n = \infty$

C atoms	$1/n$ versus $\overline{d}$	R^2	$\overline{d}_{lim}$
Odd	$1/n = 13.238 \, \overline{d} - 16.969$	0.9989	1.282
Even	$1/n = 11.48 \, \overline{d} - 14.694$	0.9958	1.280

From the corresponding linear correlation equations, $\overline{d}_{lim}$ (e.g., $\overline{d}$ value for $1/n \rightarrow 0$) can be estimated for cumulene compounds. Based on a few number of points in the linear correlation (e.g.. cumulene compounds **1–8**), approximately the same $\overline{d}_{lim}$ values are obtained. Effectively, the resulting values are found to be 1.282 and 1.280 Å, respectively, for cumulene compounds with odd and even number of C atoms.
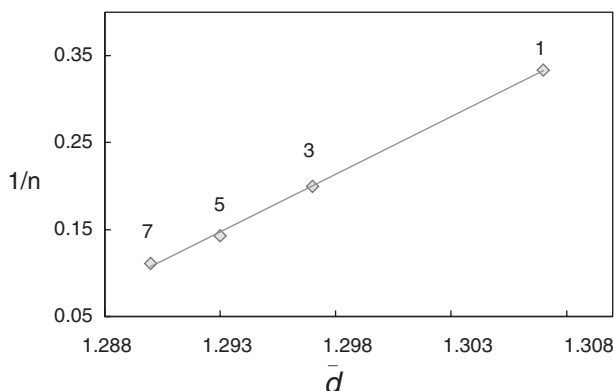
CONCLUSION

DFT calculations and NBO analysis provided a useful picture and also revealed interesting predictive linear relationships from structural, energetic, and bonding points of view, for cumulene compounds **1–8**. In summary, the application of B3LYP/6-31G* DFT showed, particularly, the following facts:

(a) A linear relationship between the corresponding mutual interconversion energy barriers and the average C=C double bond lengths ($\overline{d}$) in the ground state geometries of cumulene compounds. The results suggest that with the large number of carbon atoms in these cumulene compounds, the $\overline{d}$ values approach to a limiting value, which confirms the results obtained by Mölder *et al.*[15]

(b) NBO results revealed that the mean occupancies of π bonding orbital occupancies ($\overline{\pi}_{occupancy}$) decrease with the chain length in compounds **1–8**, while inversely, the mean occupancies of π^* antibonding orbital occupancies ($\overline{\pi}^*_{occupancy}$) increase in these compounds. The decrease of $\Delta(\overline{\pi}_{occupancy} - \overline{\pi}^*_{occupancy})$ values, from compound **1** to compound **8**, followed the same trend as the barrier heights of mutual interconversion in compounds **1–8**. This characteristic was found, fairly, to be expressed as a linear relationship between ΔE_o and $\Delta(\overline{\pi}_{occupancy} - \overline{\pi}^*_{occupancy})$.

(c) B3LYP/6-31G* results showed the HOMO − LUMO energy gap decreases in accordance with the increase of the chain length (i.e., number of π bond). Also, a linear relationship was found to express the decrease of the mutual interconversion energy barrier (ΔE_0^a) *versus* $\Delta(E_{HOMO} - E_{LUMO})$, in compounds **1–8**.

(d) The results revealed useful predictive linear relationships, for cumulene compounds **1–8**, between the

Figure 8. Fit of $1/n$ *versus* $\overline{d}$ for compounds **1**, **3**, **5**, and **7**, with odd number of C atoms, which shows a linear correlation represented by: $1/n = 13.238\overline{d} - 16.969$ with $R^2 = 0.9989$

corresponding mutual interconversion energy barriers ($\log \Delta E_0^a$ (kJ mol^{-1})) *versus* $\log C_{Number}$.

(e) From the corresponding linear plots of $1/n$ *versus* $\bar{d}$, approximately the same $\bar{d}_{lim}$ values (for $1/n \to 0$) were also obtained for cumulene compounds with n = odd and n = even number of C atoms.

Briefly, besides the reported allylic resonance stabilization effect in the transition state structure of the cumulene compounds, the results revealed, particularly, that the presented predictive linear relationships between mutual interconversion energy barriers and the following four parameters ($\bar{d}$, $\Delta(E_{HOMO} - E_{LUMO})$, $\Delta(\bar{\pi}_{occupancy} - \bar{\pi}^*_{occupancy})$, and C_{Number}) could be considered as significant criteria for evaluating the mutual interconversion in cumulene compounds.

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