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Double Bond Deformation: Cumulenes, Cumulenones, and Group IV Ethylene Analogues

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Abstract: Double bond distortion is well-established in the analogues of ethylenes and in cumulenones, but the geometry of long cumulenes is not known. We show that cumulenes, e.g. pentatetraene and hexapentaene are *bent* rather than linear as has been assumed by experimentalists and predicted by theoretical models. Correlated ab initio electronic structural calculations were employed in our study. We also present an interpretation based on the second-order Jahn–Teller effect, which unifies the explanation and prediction of double bond distortion in all three types of compounds.

I. Introduction

Double bond deformation has been observed and studied in two classes of molecules: ethylene analogues of heavy group IV elements, and cumulenones. For the ethylene analogues, $H_2Si{=}SiH_2$, $H_2Ge{=}GeH_2$, and $H_2Sn{=}SnH_2$ and their substituted species, double bonds distort from a planar configuration.[1-8] Double bond deformation in cumculenones is reflected in their nonlinear geometry. Propadienone[9] is a well-known case but butatrienone remains controversial.[10,11] Similar deformation is also observed in the isoelectronic analogue of propadienone: carbon suboxide (which is known to be nonlinear both experimentally[12] and computationally[13]) and diazoethene (which ab initio calculations show to be nonlinear.[14]).

Several hypotheses have been proposed to explain the observed double bond deformation. Teramae[15] argued that disilene has diradical character since its restricted Hartree–Fock (RHF) solution undergoes triplet instability and that an unrestricted Hartree–Fock (UHF) wave function is necessary to obtain geometries insensitive to basis sets. He further proposed that digermene and distannene possess still more diradical character because of their smaller HOMO–LUMO separation (which is responsible for the diradical character). The trans-bent geometry of disilene, digermene, and distannene is thus attributed to their diradical nature. Goldberg et al.[6] employed an argument based on π–σ^* separation, but they emphasized orbital mixing only and did not envoke the diradical character argument. Thus, as X descends the group, the π–σ^* separation decreases, thereby allowing more orbital mixing and energy lowering when the molecule

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Table I. Comparison of HF/4-31G Calculated and Experimental[a] C=C Bond Lengths in Cumulenes (Å)

allene	1.294 (1.305)		
butatriene	1.302 (1.328)	1.262 (1.256)	
pentatetraene	1.299 (1.315)	1.267 (1.276)	
hexapentaene	1.302 (1.329)	1.264 (1.259)	1.274 (1.299)

[a] In parenthesis, data come from: Irngartinger, H.; Gotzmann, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 340.

distorts from planar D_{2h} to trans-bent C_{2h}. The bending of propadienone and its isoelectronic analogues, diazoethene and carbon suboxide, is more complicated (propadienone and carbon suboxide were thought to be linear in earlier experimental and theoretical studies[9]). These molecules represent rare cases where the Hartree–Fock method fails to reproduce experimental geometries.[16] State-of-the-art CASSCF calculations[17] showed that the doubly excited configuration from HOMO to LUMO+2 is responsible for the bending of the heavy-atom chain in propadienone. A similar argument was employed to rationalize the bending of diazoethene (here the doubly excited configuration responsible for bending comes from the HOMO to LUMO+1 excitation).[14]

The only attempt to give a unified explanation to the doubly bond deformation of both ethylene analogues and cumulenones was made by Trinquier and Malrieu.[18] They assumed that the fragments forming the double bond tend to preserve their "individualities" when possible. For example, when two XH_2 fragments form $H_2X{=}XH_2$, two dative bonds will be created from the singlet states of the fragments if those singlet states are much more stable than their triplet states, and the resulting molecule will be trans-bent. On the basis of this simple idea they proposed a set of criteria to predict possible deformations and applied them to a wide range of unsaturated systems including alkynes, olefins, ketenes, cumulenes, allenes, ylides, and diazo compounds.[18]

In this paper, a new kind of double bond deformation is reported in long cumulenes. Correlated electronic structural calculations have been employed to show that quite to the contrary of Trinquier and Malrieu's expectation, long cumulenes are *not* linear. Moreover, the favored bending ode of cumulenes is not the same as that of their isoelectronic analogues, the cumulenones. A model based on the second-order Jahn–Teller effect is presented to explain this new type of distortion as well as the cumulenones and the ethylene analogues.

II. Computational Methods

ab initio calculations were performed with GA<<USSIAN 82[19] implemented on the Cyber 205 at the John von Neumann Supercomputer Center. Since electron correlation is shown to be necessary to obtain correct results for propadienone[16] and butatrienone,[10] we expect that the same should be true for cumulenes. To reduce the computation time required for geometry optimization with correlated wave functions, the method of Farnell and Radom[10] is employed. Thus, geometry optimization for a series of structures in which the central CCC bond angle is fixed at different values is done by using SCF wave functions with the split-valence 4-31G[20] basis set. Single-point, correlated calculations are then performed at the SCF optimized geometries with use of a larger basis set (6-31G[20]) and the Møoller-Plesset perturbation expansion truncated a third or fourth order.[21,22] It should be noted that this approach cannot locate the global minima of these molecules (and the carbon chain is always constrained to a plane in our calculations), but it should determine whether long cumulenes are linear or not since it has been successful for cumulenones.[11] The reliability of HF/4-31G calculated geometries is illustrated in Table I where the calculated bond lengths are compared to typical experimental ones (for this comparison we assumed a linear geometry). Calculated values agree with experiment to 0.03 Å. For the two critical molecules in this study, butatriene and pentatetraene, geometry optimization was carried out with the second-order Møller-Plesset perturbation theory and the 6-31G basis.

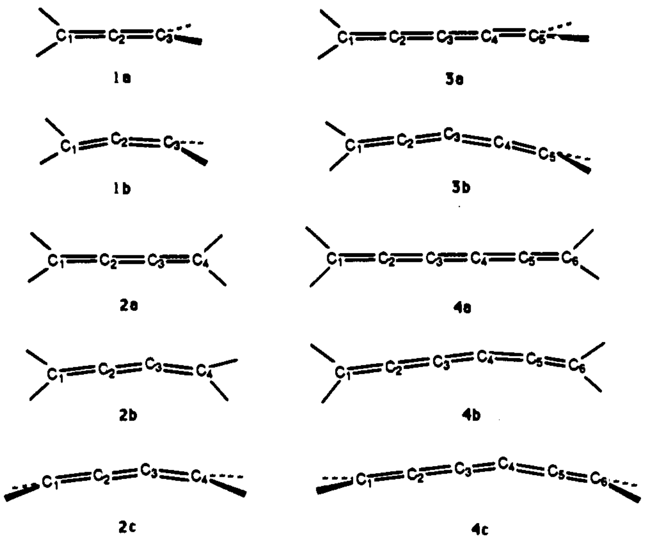

Figure 1. Cumulenes studied in this work.

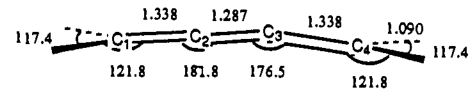

Figure 2. MP2/6-31G optimized geometry of butatriene.

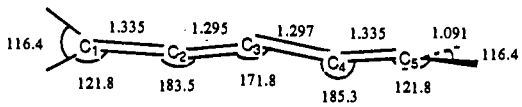

Figure 3. MP2/6-31G optimized geometry of pentatetraene.

III. Results

A. Molecules Studied. The molecules studied in this paper are shown in Figure 1. For butatriene and hexapentaene there are two bent structures, planar bent (**2b** and **4b**) and orthogonal bent (**2c** and **4c**). For allene and butatriene only the bent structure with a bending angle of 10° was calculated, and the results are reported in Table II together with the results of their linear structures (for butatriene the planar bent structure is reported). for pentatetraene and hexapentaene additional bent structures with bending angles of 5° and 15° were studied since their 10° bent structures are more stable than their linear ones when correlation is included. Table III collects the calculated geometries and total and relative energies of pentatetraene, and Table IV collects those f hexapentaene (linear and planar bent).

For butatriene and hexapentaene, the orthogonal bending mode is also studied. Single-point calculations with the MP3/6-31G method are performed at geometries assuming the same geometric parameters as the respective bent structures and the HCH planes being kept orthogonal to the plane of carbon atoms (in the planar bent geometry the HCH plane is the same as that of carbon atoms). The results are given in Table V.

Since cumulenes change their geometries (from linear to bent) at butatriene and pentatetraene according the results obtained by the method above, geometry optimization with use of the second-order Møller–Plesset perturbation theory and the 6-31G basis is carried out on these two molecules. Again, the carbon chains are constrained to a plane. The optimized geometries are shown in Figures 2 and 3.

B. Geometries and Energies. Although there is a great deal of experimental interest in cumulenes and many substituted ones have been synthesized and structurally characterized,[23] the ge-

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Table II. Calculated Geometries, Total Energies, and Relative Energies of Allene and Butatriene[a]

	allene		butatriene	
		Geometric Parameters[b]		
C_1C_2	1.294	1.295	1.301	1.301
C_2C_3	1.294	1.295	1.262	1.264
C_3C_4			1.301	1.302
CH	1.073	1.073	1.073	1.073
$\angle C_1C_2C_3$	180.0	170.0[c]	180.0	176.8
$\angle C_2C_3C_4$			180.0	170.0[c]
∠HCC1[d]	121.5	120.6, 122.4	121.6	122.2, 121.0
∠HCC2[d]	121.5	121.5, 121.5	121.6	121.7, 121.5
		Energies		
HF/4-31G	−115.698 77 (0)	−115.696 95 (400)	−153.475 23 (0)	−153.473 82 (309)
HF/6-31G	−115.821 43 (0)	−115.819 62 (397)	−153.638 22 (0)	−153.636 88 (294)
MP2/6-31G	−116.080 56 (0)	−116.079 30 (277)	−153.981 70 (0)	−153.981 17 (116)
MP3/6-31G	−116.101 37 (0)	−116.100 13 (272)	−154.003 58 (0)	−154.003 03 (120)

[a] Throughout this paper, bond lengths are in Å, angles are in deg, total energies are in hartree, relative energies (in parenthesis) are in cm^{-1}. [b] HF/4-31G. [c] Fixed bending angles, for butatriene the bent one is planar. [d] HCC1 and HCC2 represent the HCC angles of each CH_2 group, respectively.

Table III. Calculated Geometries, Total Energies, and Relative Energies of Pentatetraene at Linear and Bent Configurations[a]

		Geometric Parameters[b]		
$\angle C_2C_3C_4$[c]	180.0	175.0	170.0	165.0
C_1C_2	1.299	1.299	1.299	1.299
C_2C_3	1.267	1.268	1.268	1.270
C_3C_4	1.267	1.267	1.268	1.269
C_4C_5	1.299	1.299	1.299	1.298
CH	1.073	1.073	1.073	1.073
$\angle C_1C_2C_3$	180.0	181.1	182.3	183.7
$\angle C_3C_4C_5$	180.0	179.6	179.3	179.2
$\angle HC_1C_2$	121.5	121.6	121.7	121.7
$\angle HC_5C_4$	121.5	121.5	121.5	121.5
∠HCH	117.0	117.0	117.0	117.0
		Energies		
HF/4-31G	−191.255 78 (0)	−191.255 43 (77)	−191.254 41 (224)	−191.252 77 (661)
HF/6-31G	−191.458 40 (0)	−191.458 10 (66)	−191.457 16 (272)	−191.455 59 (617)
MP2/6-31G	−191.887 08 (0)	−191.887 43 (−77)	−191.887 62 (−119)	−191.886 99 (20)
MP3/6-31G	−191.908 26 (0)	−191.908 54 (−61)	−191.908 65 (−86)	−191.908 03 (50)
MP4(SDQ)/6-31G	−191.923 67 (0)		−191.923 98 (−68)	

[a] Units as in Table 11. [b] HF/4-31G. [c] Fixed bending angles.

Table IV. Calculated Geometries, Total Energies, and Relative Energies of Hexapentaene at Linear and Planar Bent Configurations[a]

		Geometric Parameters[b]		
$\angle C_3C_4C_5$[c]	180.0	175.0	170.0	165.0
C_1C_2	1.302	1.302	1.302	1.302
C_2C_3	1.264	1.263	1.263	1.263
C_3C_4	1.274	1.275	1.275	1.276
C_4C_5	1.264	1.264	1.265	1.266
C_5C_6	1.302	1.302	1.302	1.302
CH[d]	1.08	1.08	1.08	1.08
$\angle C_1C_2C_3$	180.0	180.2	180.1	180.0
$\angle C_2C_3C_4$	180.0	178.7	178.3	178.1
$\angle C_4C_5C_6$	180.0	181.0	182.5	183.9
∠HCC[d]	121.0	121.0	121.0	121.0
		Energies		
HF/4-31G	−229.035 40 (0)	−229.035 04 (79)	−229.033 98 (312)	−229.032 24 (694)
HF/6-31G	−229.277 76 (0)	−229.277 66 (22)	−229.276 72 (228)	−229.275 08 (588)
MP2/6-31G	−229.793 76 (0)	−229.794 08 (−70)	−229.794 26 (−110)	−229.793 48 (61)
MP3/6-31G	−229.814 04 (0)	−229.814 30 (−57)	−229.814 41 (−81)	−229.813 69 (77)

[a] Units as in Table II. [b] HF/4-31G. [c] Fixed bending angles. [d] Not optimized.

ometries of the parent molecules have not been determined. For the cumulenones, little computational research has been carried out and the only ab initio calculation reported to-date is a STO-3G calculation of linear cumulenes.[25]

Our results in Table II shows that for both allene and butatriene a linear configuration is the more stable one at all levels of calculations. This agrees with MP2/6-31G geometry optimization

Table V. Energies of Orthogonal Bent Structures[a] for Butatriene and Hexapentaene (au)

	C_4H_4		C_6H_4	
bent angle	10	5	10	15
HF/6-31G	−153.636 39	−229.277 44	−229.276 05	−229.273 82
MP2/6-31G	−153.981 42	−229.794 43	−229.794 89	−229.793 94
MP3/6-31G	−154.003 28	−229.814 57	−229.814 89	−229.813 93

[a] Geometry is the same as the HF/4-31G optimized planar bent geometry with the HCH planes kept orthogonal to the plane of carbon atoms.

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(carbon atoms are constrined to a plane) for butatriene which gives an essentially linear structure (Figure 2). Also, it should be noted that butatriene is easier to bend than allene (Table II).

However, Tables III and IV show that the bent structures of pentatetraene and hexapentaene are more stable than linear ones when electron correlation is included. In particular, when pentatetraene is bent by 10° at the central carbon, its energy is lowered by 119 (MP2), 86 (MP3), and 68 (MP4) cm^{-1} (cm^{-1} = 2.8588 cal/mol), respectively, although its Hartree–Fock energy increases (Table III). When it is further bet (by 15°) its energy rises, becoming less stable than the linear structure. Curve fitting of the MP3/6-31G calculated energy and bending angle shows that the energy minimum occurs at 8.8° with an energy 90 cm^{-1} below that of the linear structure. This agrees with the MP2/6-31G calculated geometry, which shows that the central CCC angle is bent by 8.2° (Figure 3).[26]

For hexapentaene, planar bending lowers the energy too (Table IV). In this case, curve fitting gives an energy minimum at 8.7° and energ of 86 cm^{-1} below the linear reference point.

A comparison of Table V with Table II and IV shows that the orthogonal bent structures are more stale than planar bent ones for butatriene and hexapentaene when correlated wave functions are employed. This is surprising because their isoelectronic analogues, propadienone and pentatetraenone, prefer planar bending.[10,17] Hence, the mechanism of deformation in cumulene and cumulenone is different.

IV. Interpretation

The finding that short cumulenes (allene and butatriene) are linear and long cumulenes (pentatetraene and hexapentaene) are nonlinear is exactly opposite to Trinquier and Malreu's prediction.[18] Their theory predicts that while butatriene is on the borderline of being linear and bent, longer cumulenes should be linear since the single–triplet separation of the fragments is smaller. In our interpretation we will employ Pearson's rule for predicting molecular structures[27] to explain this new type of double bond deformation as well as the other types of deformations.

A. Model. Pearson's rule for predicting molecular structures is based on the second-order Jahn–Teller effect.[28] First, a particular nuclear configuration (symmetry) for a molecule is assumed. Then, the nuclei are allowed to distort from the original positions by means of one of the normal displacements Q. Actual distortion occurs if it lowers the energy of the original, symmetric system. According to the second-order perturbation theory, the Hamiltonian after distortion may be written as

$$H = H_0 + \left(\frac{\partial U}{\partial Q}\right)Q + \frac{1}{2}\left(\frac{\partial^2 U}{\partial Q^2}\right)Q^2 + \ldots$$

where U is the potential function. Its corresponding energy is given by

$$E = E_0 + Q\left\langle\psi_0\left|\frac{\partial U}{\partial Q}\right|\psi_0\right\rangle + \frac{Q^2}{2}\left\langle\psi_0\left|\frac{\partial^2 U}{\partial Q^2}\right|\psi_0\right\rangle + \sum_k \frac{\left[Q\left\langle\psi_0\left|\frac{\partial U}{\partial Q}\right|\psi_k\right\rangle\right]^2}{E_0 - E_k} + \ldots$$

where E_0 and E are the total energies of the system before and after distortion, and ψ_0 and ψ_k are the wave functions of the ground and excited states of the original system. The first correction term is identically zero for the non-fully symmetric distortions that we are interested in. The second correction term can be identified as the intrinsic frequency of normal mode Q and is always positive. The last term corresponds to the adjustment of the wave function to the new nuclear configuration and is always negative. This adjustment is achieved by mixing excited states k of the original symmeric system into its ground state 0. Thus, the energy change (resulting from distortion Q) is given by

$$\Delta E = (f_{00} - \sum_k g_{0k})Q^2$$

This equation shows that two factors determine whether a system will distort. First is the frequency of its normal mode. The second is related to the mixing of excited states into the ground state when the molecule is distorted. The degree of mixing is largely determined by the density of states of the original system, that is, the $E_0 - E_k$ separation. Hence, a molecule will distort from a symmetric configuration when it possesses a low-frequency normal mode and a low-energy excited state with the same symmetry as that normal mode (note that only the excited states having the same symmetry as distorting normal mode contribute to the second-order perturbation energy).

For closed-shell molecules (which we are interested in here) mixing of excited states into the ground state is tantamount to the mixing of filled and unfilled molecular orbitals of different symmetry. Therefore, the criterion for molecular distortion in closed-shell molecules can be simplified as the following. If a molecule has filled and unfilled orbitals with small energy difference and their symmetry product corresponds to a normal mode of low frequency (usually angular deformation modes have low frequencies), that molecule is likely to distort following that normal mode.

It should be noted that there are limitations to this model. (1) It can only tell what is the favored distortion but not whether a molecule will actually distort nor the extent of such distortion. (2) Though it can show which excitation is important for a given distortion, it does not mean that the distorted molecule will possess a ground electronic configuration resulting from that excitation. For example, though both disilene and digermene distort the same way, distorted disilene might have some diradical character while the distorted digermen might not.[1,15]

B. Previous Applications. The model presented above has been used in a number of cases. Pearson[27a] employed it to predict the stable structures of XY_n (n = 2–7) with a different number of electrons. He also applied it to chemical reactions.[27b] However, he considered only the lowest lying one or two excited states. Recently, it has been generalized to determine molecular geometry changes following electronic excitation.[29,30] The same type of model (though termed vibronic coupling) has been employed to explain unusual phenomena in photoelectron spectra of radical cations.[31] Here we demonstrate that double bond deformations

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(26) After this paper was submitted, we carried out geometry optimization and frequency calculations for butatriene with D_{2h} symmetry and pentatetraene with C_{2v} symmetry (D_{2d} was not used because of program limitations) using the MP2/6-31G method. The program used in CADPAC (Amos, R. D.; Rice, J. E. CADPAC: *The Cambridge Analytic Derivative Package*, issue 4.0, Cambridge, 1987) implemented on the IBM 3090 at the University of Georgia. The D_{2h} symmetric butatriene was found to have an imaginary frequency (−285 cm^{-1}) corresponding to the orthogonal bending of the carbon chain. However, the energy of this linear structure (−153.99221 au) is only 0.02 kcal/mol higher than that of the optimized structure of Figure 2 (−153.99224 au). Thus, butatriene is probably linear or pseudolinear. The linear pentatetraene has two degenerate imaginary frequencies (−754 cm^{-1}) corresponding to the bendings of the central carbons in two directions. Its total energy (−191.90043 au) is 0.49 kcal/mol higher than that of the optimized structure of Figure 3 (−191.90121 au). Thus, pentatetraene is probably not linear. These new results support our previous calculations.

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Table VI. Orbital Symmetry and Direct Products for C_4H_4, C_5H_4, and C_6H_4

molecule[a]	HOMO	LUMO	LUMO+1	LUMO+2	direct products
C_4H_4 (D_{2h})	b_{2g}	b_{3u}	b_{3g}	b_{1u}	B_{1u}, B_{1g}, B_{3u}
C_5H_4 (D_{2d})	e	e	a_1	b_2	(A_1, A_2, B_1, B_2), E, E
C_6H_4 (D_{2h})	b_{3u}	b_{2g}	b_{2u}	b_{3u}	B_{1u}, B_{1g}, A_g

[a] Symmetry assumed is given in parentheses.

can be understood using this model when higher excited states, as well as the lowest excited state, are considered.

C. Ethylene Analogues, $H_2X{=}XH_2$, where X = C, SI, Ge, Sn. As pointed out in the Introduction, these double bonded molecules undergo geometric change from planar to a trans-bent configuration.[1] The preference of ethylene for trans-bending over syn-bending has been lucidly discussed by Volland, Davidson, and Borden,[32] using the second-order Jahn–Teller effect. The result of that paper has been generalized by Goldberg et al.[16] to disilene, digermene, and distannene. Goldberg et al. concluded that the geometric change of $H_2X{=}XH_2$ is caused by the decreasing of $-\sigma^*$ separation and weakening of the X=X bond as X changes down the group, in agreement with the criterion discussed above. (We have previously noted that the electronegativity difference between X and H also contributes to the geometric change.[1])

D. Cumulenones. The computational results reported here have been focused on cumulenes, but in our intepretation we are interested in developing a model that will unify the three types of double bond distortion given in the title of our paper. Thus, our previous works and that of Goldberg et al. show how this is accomplished for the ethylene analogues. In this section we illustrate the model by application to propadienone.

A recent ab initio study[17] shwed that the main electronic influence leading to propadienone distortion is the lowest energy virtual σ-orbital changes of important configurations as a function of the CCC angle. However, a simple analysis based on orbital symmetry is able to reach the same conclusion. Thus, geometry optimization and frequency calculation were performed on propadienone with the 3-21G[33] basis assuming C_{2v} symmetry. The symmetry of the HOMO and the three lowest energy virtual orbitals is b_2, b_1, b_2, and a_1, respectively.[34] The direct product of b_2 with b_1 is A_2.[35] Since there is no normal mode with that symmetry, the mixing of the HOMO and LUMO does not contribute to any distortion. The direct product of b_2 with b_2 is A_1, and this normal mode does not distort the molecule from C_{2v} symmetry. But the excitation from the HOMO (b_2) to LUMO+2 (a_1) produces an electronic configuration with B_2 symmetry and that symmetry is the same as the lowest frequency normal mode, according to our 3-21G frequency calculation. Therefore, the molecule is most likely to distort as b_2, which corresponds to planar bending.

E. Cumulenes. The result that short cumulenes are linear and long ones are nonlinear is understandable from the second-order Jahn–Teller effect. As a cumulene becomes longer the density of state increases and the mixing of excited states with the ground state becomes larger. Therefore, longer cumulenes are more likely to bend than shorter ones.[36,37] A similar trend has been observed in related systems such as carbon clusters.[38]

The symmetry of HOMO and the three lowest virtual orbitals in butatriene, pentatetraene, and hexapentaene as calculated with the 4-31G basis at their most symmetric geometry and the direct product of HOMO with those virtual orbitals are listed in Table VI. For butatriene, the direct product of b_{2g} and b_{3u} is B_{1u} and that corresponds to a stretching mode with high frequency. The direct product of b_{2g} with b_{3g} is B_{1g}, but there is no such vibrational mode. Since $(b_{2g})(b_{1u})$ gives B_{3u} and it correspnods to the lowest frequency orthogonal bending mode, we predict that the most favored distortion for butatriene is orthogonal bending, in agreement with our a initio calculation. Therefore, the bending modes of propadienone and butatriene are governed by their molecular symmetry, and the fact that propadienone and butatriene prefer different bending modes (though they are isoelectronic) is understandable from their difference in molecular symmetry.

For pentatetraene, the direct product of e with e gives a_1, a_2, b_1, and b_2. But that of e with a_1 or b_2 gives which corresponds to two lowest frequency bendings at the central carbon. Therefore, the favored distortion for pentatetraene is bending at the central carbon, again in agreement with ab initio calculations.

The case of hexapentaene is complicated and shows limitations of this simple model. None of the direct products in Table VI correspond to any one of the ten lowest frequency vibrational modes. The difficulty arises from the implicit assumption made in the above analysis that the excited, *total* electronic states are directly correlated with the order of their *one*-electron energies. While this assumption is generally correct for most small molecules (for example, the molecules discussed above), it may not hold for large molecules where orbital energies are closely spaced. In other words, it is possible that the large number of closely spaced excited electronic states in highly symmetric hexapentaene makes it impossible to determine their relative energy from the one-electron orbital energies.

However, the prefered bending mode of hexapentaene is understandable if it is taken as an analogue of butatriene (or even ethylene) simply with a higher density of states. Thus, hexapentaene and butatriene (and ethylene) should have the same kind of distortion and this is the case (see Table V and the discussion in section III). Moreover, a STO-3G frequency calculation of hexapentaene shows that the two lowest frequency modes (with nearly the same frequency) corresponds to planar and orthogonal bending modes of the carbon chain.

V. Summary

(1) It is shown that the bent structures of long cumulenes, pentatetraene and hexapentaene, are more stale than their linear ones. The bending angles were calculated to be about 9° for both molecules. For butatriene and hexapentaene, orthogonal bending is more favorable than planar bending, and this is not expected from the favored bending mode of their isoelectronic analogues. Although these conclusions are based on small energy differences

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(32) Volland, W. V.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 533.

(33) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(34) In Table 2 of Brown and Dittman's paper (ref 16), the 14a′ orbital in C_s symmetry is correlated to the b_2 orbital in C_{2v} symmetry. This may be in error because b_2 is a π^* orbital but 14a′ is identified as a σ orbital. Thus, 14a′ in C_s should correlate to a_1 in C_{2v} as our 3-21G calculation shows.

(35) In this paper the symmetry of an orbital is denoted by lower cases and that of electronic configuration is denoted by upper cases.

(36) Fisher, H. In *The Chemistry of Alkenes*; Patai, S., Ed.; Wiley: London, 1964; p 1025.

(37) Ripoll, L. J. *Helv. Chim. Acta* **1977**, *60*, 629.

(38) A recent ab initio study (Raghavachari, K.; Binkley, J. S. *J. Chem. Phys.* **1987**, *87*, 2191) shows that the HF/6-31G* calculated lowest vibrational frequencies for linear C_3, C_5, C_7, and C_9 (they presumably correspond to bending of carbon chain) decrease monotonically from 154 to 49 cm^{-1}. These authors suggested that C_{11} could be cyclic instead of linear. For even numbered carbon clusters (C_4–C_{10}), the cyclic forms are more stable than linear ones. When electron correlation is included in frequency calculations, Kurtz and Adamowicz (private communication, we thank Mr. Kurtz of University of Arizona for providing their results before publication) found that linear C_7 has actually an imaginary frequency at the MP2/6-31G* level. However, it should be noted that an experimental study (Moazzen-Ahmadi, N.; McKellar, A. R. W.; Amano, T. *Chem. Phys. Lett.* **1989**, *157*, 1) claims that C_5 is more rigid than C_3, in disagreement with above ab initio calculations.

obtained at moderate theoretical levels, they should be correct qualitatively. More accurate calculations are underway to check the validity of these results.

(2) A simple model based on the second-order Jahn–Teller effect is shown to be able to explain double bond deformation observed in these long cumulenes as well as in group IV double bonds and cumulenones. Thus, a double bond will distort from its symmetric conformation when it possesses low-lying excited states (or high density of states) and vibrational modes with low intrinsic frequencies. The favored distortional mode for small molecules may be predicted from analysis based on orbital symmetry. This odel, which is based on the second-order perturbation theory, should be universal, while Trinquier and Malrieu's model, though successful for a number of cases, failed to predict the geometries of long cumulenes. The reason is that in Trinquier and Malrieu's model, only the four electrons forming the double bond are considered. Therefore, the collective behavior of delocalized electrons, which leads to bending in long cumulenes as studied here and distortions of other large systems with extensive electron delocalization,[38,39] is not adequately accounted for.

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Registry No. 1a, 463-49-0; **2a**, 2873-50-9; **3a**, 21986-03-8; **4a**, 13703-38-3.

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(39) It is known that large cyclic polyenes prefer bond alternation (see, for example: Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc.* **1959**, *A251*, 172. Paldus, J.; Chin, E. *Int. J. Quantum Chem.* **1983**, *24*, 373). This can be taken as a kind of distortion from more symmetric polyenes with equal or nearly equal ring bonds because the density of states would be too large if large polyenes assume extensively delocalized, bond equalized structures.

σ-Bridged-π Bonding in Small-Ring Compounds

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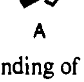
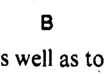
Abstract: σ-Bridged-π orbitals characterize the three-center bonds that often occur in electron-sufficient, small-ring compounds made of atoms such as C, N, O, Si, P, and S. This bonding pattern proves efficient in explaining bond length changes and strain energies in three-membered rings and the unusual geometries of some four-membered rings. It is also shown that explanations based on this type of orbital are compatible with a number of other theoretical models in the literature and that use of the σ-bridged-π-bonding concept helps extend and unify them.

I. Introduction

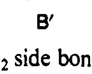
The term σ-bridged-π (hitherto abbreviated as σ-b-π) and its use to characterize key features of the bonding in [1.1.1]propellane was proposed several years ago,[1] but its basic construct of three-center bonding orbitals (Chart I) in electron-sufficient and electron-excess species goes back as far as Dewar[2] and Chatt and Duncanson's σ-donation, π-back-donation model[3] and more specifically to Hoffmann et al.[4] and Rohmer and Roos[5] for the bonding in three-membered rings. It is also implicit in the more recent work of Cremer and Kraka,[6] West et al.,[7] and Grev and Schaefer.[8] The σ-b-π bond can be taken as a manifestation of σ-electron delocalization.[9,6b,c] In the C_1–C_3 bond between bridgehead carbons in [1.1.1]propellane (A) this bond contributes to the bonding of C_1 to C_3 as well as to the C_1–C_2 side bonds. This pattern of interaction is appealing in the sense that it offers an "economical" way of forming bonds out of limited valence electrons. This becomes more apparent when one compares [1.1.1]propellane to 1,3-diborabicyclo[1.1.1]pentane (B). Although the latter has two fewer valence electrons than the former, their bonding patterns are essentially the same.[1] In addition to six normal B–C bonds, B has a strong B–B bond[1] since the B_1–B_3 separation is only 1.61 Å as compared to 1.60–1.90 Å, a range for typical B–B bonding distances in carboranes and boron hydrides.[10] That is, structure B′ is not unreasonable because of the σ-bridged-π bonding in B.



A

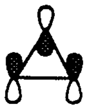


B



B′

Chart I



In this paper, we explore this type of bonding by systematic ab initio calculations for 16 three-membered-ring (3MR) compounds. The results are employed to explain the strain energy of some 3MR compounds and also the unusual geometries of several four-membered-ring (4MR) molecules. In particular, recent developments in silicon chemistry have raised many interesting questions concerning the bonding in silicon ring compounds, and we offer an interpretation to these questions using σ-b-π bonding.

The bonding in 3MR compounds has been extensively studied in the literature.[2-9,11-15] In the 1940s, Coulson and Moffitt[11]

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