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AN *AB INITIO* MOLECULAR ORBITAL STUDY OF STRUCTURES AND ENERGIES OF SPIRO-COMPOUNDS: SPIRO[3.3]HEPTANE AND SPIRO[3.3]HEPTA-1,5-DIENE

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Abstract—*Ab initio* molecular orbital theory with the STO-3G and 4-31G basis sets is used to determine the equilibrium geometries, enthalpies of formation, strain energies and spiro-interactions for spiro[3.3]heptane and spiro[3.3]hepta - 1,5 - diene. For spiro[3.3]heptane, molecular mechanics calculations suggest that the component cyclobutane rings are puckered to a greater extent than in cyclobutane itself. For spiro[3.3]hepta - 1,5 - diene, STO-3G calculations predict that the component cyclobutene rings deviate slightly from an orthogonal arrangement. Spiro-interactions in spiro[3.3]hepta - 1,5 - diene are revealed by comparing the calculated structural parameters and strain energies with those of appropriate reference systems. The π-orbitals in spiro[3.3]hepta - 1,5 - diene are predicted to be split by about 0.4 eV.

INTRODUCTION

Spirocompounds consist of two perpendicular or near-perpendicular rings joined by a common tetracoordinate atom. The special structural arrangements of spirocompounds are of chemical interest and the energies, structures and π-electron interactions (spiroconjugation,[1] spiroaromaticity[2]) in these molecules have received considerable theoretical and experimental attention.[3] However, despite the activity in this area, direct experimental thermochemical and structural data are rather limited.

An alternative source of such data is from reliable theoretical calculations and, in particular, from *ab initio* molecular orbital theory. This technique has previously been used with considerable success in systematic studies of equilibrium geometries, molecular conformations, molecular energetics, charge distributions and dipole moments for a variety of hydrocarbons.[4–9] In an earlier paper,[10] we applied *ab initio* molecular orbital theory to spiro-hydrocarbons consisting of 3- and 5-membered rings. In this paper, we use a similar approach to study the structures and energies of spiro-hydrocarbons, namely spiro[3.3]heptane and spiro[3.3]hepta - 1,5 - diene, consisting of two 4-membered rings.

COMPUTATIONAL METHOD AND RESULTS

All *ab initio* calculations were performed with a modified version of the Gaussian 70 system of programs.[11,12] Structural parameters of spiro[3.3]heptane (D_{2d}) and spiro[3.3]hepta - 1,5 - diene (C_2) were fully optimized using the STO-3G basis set[13] and a gradient optimization procedure[12] with the exception that the C–H bond lengths and the HCH and remote HCC bond angles were taken from the theoretical STO-3G structures[5] of the appropriate component rings. This assumption, which was introduced to reduce computation time for these large systems, is justified in the light of the results of our previous studies of spiro-hydrocarbons[10] and distorted monocyclic hydrocarbons.[14] The cyclobutene rings in spiro[3.3]hepta - 1,5 - diene were taken to be planar.

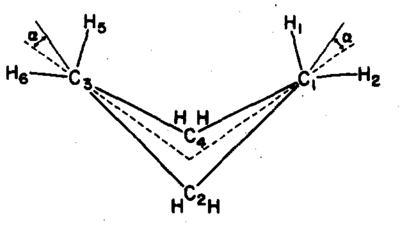
The STO-3G structural parameters obtained in this manner for the structures shown in Fig. 1 are listed in Table 1. The geometries of cyclobutane and cyclobutene have been reported previously [5,15] but are included in Table 1 for easy comparison. Also included in Table 1 are the available experimental data[16–18] for cyclobutane and cyclobutene. All energetic data obtained in this study as well as some previous results needed for later discussion are shown in Table 2. Included is the result of a single 4-31G calculation[19] on the STO-3G optimized structure of spiro[3.3]hepta - 1,5 - diene carried out to enable more reliable energy comparisons, particularly for ionization potentials.

Both theory[5,15] and experiment[16,17,20] indicate that the cyclobutane ring is non-planar. We would expect therefore that the component rings in spiro[3.3]heptane might likewise be non-planar. We have not attempted full STO-3G optimization of such a structure for two reasons. Firstly, the number of independent parameters in the C_2 structure is large and full optimization at the STO-3G level would be computationally expensive. Secondly, STO-3G is known to underestimate both the degree of ring puckering and the barrier to inversion in cyclobutane and it is likely that it would perform similarly in spiro[3.3]heptane. We have therefore used the computationally inexpensive molecular mechanics method[21] to study the ring puckering in spiro[3.3]heptane. Molecular mechanics calculations have been shown[21–26] to give structural and energetic results in good agreement with experiment for a large variety of molecules. We should note, however, that this method[26] underestimates the non-planarity of the cyclobutane ring by a considerable amount giving a puckering angle of 6° compared with experimental estimates of about 25°. We have carried out the molecular mechanics calculations with the limited aim of determining whether the ring puckering in spiro[3.3]heptane is greater than or less than in cyclobutane.

DISCUSSION

(A) *Model studies of distorted methane and monocyclic systems*

In order to model the structural behavior of spirocompounds, calculations have previously been carried out for methane,[27,28] cyclopropane,[14] cyclopropene,[14] cyclobutane[14] and cyclopentadiene[14] with appropriate H–C–H angular deformations **6**.



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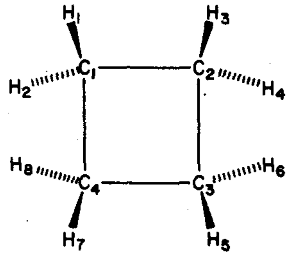

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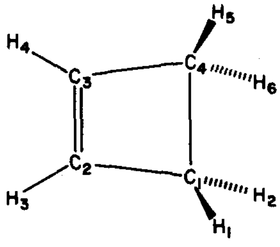

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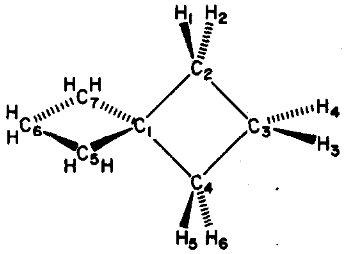

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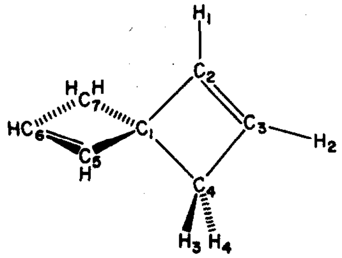

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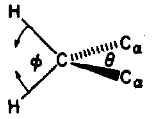
Fig. 1. Definition of structural parameters for cyclobutane (D_{2d}, 1), cyclobutane (D_{4h}, 2), cyclobutene (C_{2v} or C_s, 3), spiro[3.3]heptane (D_{2d}, 4) and spiro[3.3]hepta-1,5-diene (C_2, 5).



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A general conclusion of these studies was that without exception, a narrowing of the H–C–H angle (ϕ) results in an elongation of the C–H bonds due firstly to the increasing H···H nuclear repulsion, and secondly, to decreasing *s*-character of these bonds. Accordingly there is more carbon 2*s* contribution available for the C–C_α bonds and this leads to shorter C–C_α bonds and a larger C_α–C–C_α bond angle (θ).

The previous model studies, which were limited to monocyclic systems with C_{2v} symmetry, are supplemented here by model calculations on cyclobutene. One of the exocyclic H–C–H angles (ϕ) in cyclobutene was constrained at 85.3°, the approximate value of the spiro angle in spiro[3.3]hepta - 1,5 - diene and the remaining structural parameters were optimized with the STO-3G basis set. The structural parameters obtained in this manner are included in Table 1. We can see that the conclusions drawn on the basis of the monocyclic systems with C_{2v} symmetry still hold for the deformed cyclobutene (C_s). There are several additional points of interest. Firstly, the bond shortening is greater for C_1–C_4 (−0.011 Å) than for C_1–C_2 (−0.007 Å). Secondly, the bond changes for C_2–C_3 and C_3–C_4 caused by angular deformation are very small but the change is larger for C_3–C_4 (−0.004 Å) than for C_2–C_3 (+0.002 Å). These pairs of results are consistent with the relative bond strengths of the various bonds.

On the basis of these model calculations, we would therefore expect that because the C–C–C angles in the spiro-compounds studied here are smaller than the H–C–H angles in the monocyclic systems, the C–C bonds around the spiro-atoms will be shorter than those in the appropriate monocyclic parent ring. These predictions, of course, are likely to be realistic only if specific spiro interactions are unimportant. Conversely, if the calculated structure of a spiro-compound is at variance with that predicted on the basis of the model calculations, it is likely that specific spiro-interactions are significant.

(B) *Analysis of* STO-3G *energetic data*

Some care must be taken in analysing energetic data in *ab initio* molecular orbital calculations since heats of reaction are not always well described. For instance, although good agreement with experiment is generally obtained, even with the minimal STO-3G basis set, for heats of isodesmic reactions involving acyclic molecules alone, unsatisfactory values are obtained for reactions involving comparisons of cyclic and acyclic structures.[5,29–31]

In our earlier paper,[10] we defined a ring separation reaction in which a spiro-compound is broken up into its

Table 1. Molecular equilibrium geometries

Molecule	Symmetry constraint	Structural parameter[a,b]	STO-3G	Exptl
Cyclobutane 1	D_{2d}	C_1–C_2	1.554[c]	1.548[d]
		C_1–H_1	1.087	1.092
		C_1–H_2	1.087	1.092
		$H_1C_1H_2$	108.7	110.0
		$C_1C_{2,4}C_3$	173.1	145 ~ 153
		α	1.2	4.0
2	D_{4h}	C_1–C_2	1.554[c,e]	
		C_1–H_1	1.087	
		$H_1C_1H_2$	108.7	
Cyclobutene 3	C_{2v}	C_2–C_3	1.314[c]	1.342[f]
		C_1–C_2	1.526	1.517
		C_1–C_4	1.565	1.566
		C_2–H_3	1.082	1.083
		C_4–H_5	1.089	1.094
		$H_3C_2C_3$	134.2	133.5
		$H_5C_4H_6$	109.0	109.5
		$H_{5,6}C_4C_1$	136.3	135.8
	C_s[g]	C_2–C_3	1.316	
		C_3–C_4	1.522	
		C_1–C_4	1.554	
		C_1–C_2	1.519	
		(C_2–H_3)	1.082	
		(C_3–H_4)	1.082	
		(C_4–H_5)	1.089	
		C_1–H_1	1.098	
		$H_3C_2C_3$	134.5	
		$H_4C_3C_2$	134.0	
		$H_{5,6}C_4C_1$	136.7	
		$H_{1,2}C_1C_4$	136.0	
		($H_1C_1H_2$)	85.3	
		$H_5C_4H_6$	109.1	
		$C_1C_2C_3$	93.4	
Spiro[3.3]-heptane 4	D_{2d}	C_1–C_2	1.549	
		C_2–C_3	1.550	
		(C_2–H_1)	1.087	
		(C_3–H_3)	1.087	
		$C_2C_1C_4$	90.0	
		($H_3C_3H_4$)	108.7	
		($H_1C_2H_2$)	108.7	
		$H_{1,2}C_2C_1$	135.0	
Spiro[3.3]hepta-1,5-diene 5	C_2	C_1–C_2	1.526	
		C_2–C_3	1.318	
		C_1–C_4	1.567	
		C_3–C_4	1.524	
		(C_2–H_1)	1.082	
		(C_3–H_2)	1.082	
		(C_4–H_3)	1.089	
		$H_1C_2C_3$	134.4	
		($H_2C_3C_2$)	134.2	
		$C_2C_1C_4$	85.4	
		$C_5C_1C_2$	127.6	
		$C_5C_1C_2C_3$	127.7	
		$H_{3,4}C_4C_1$	136.3	
		($H_3C_4H_4$)	109.0	

[a] The symbol $X_{i,j}$ denotes the midpoint of $X_i \cdots X_j$. [b] Bond lengths in Angstroms, bond angles in degrees. Assumed values in parenthesis, see text. [c] From Ref. 5. [d] From Ref. 16. [e] From Ref. 15. [f] From Ref. 18. [g] Deformed structure, see text.

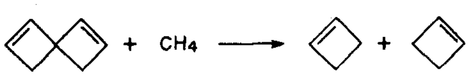
Table 2. Calculated total energies, ring separation energies, heats of formation and strain energies

	STO-3G	4-31G[a]
Total energies (hartrees)		
Methane	−39.72686[b]	−40.13976[b]
Cyclobutane (D_{2d})	−154.27390[c]	−155.86606[c]
Cyclobutane (D_{4h})	−154.27387[d]	−155.86594[c]
Cyclobutene (C_{2v})	−153.04028[c]	−154.66731[c]
Cyclobutene (C_s)	−153.01793	−154.65102
Spiro[3.3]heptane	−268.82810	
Spiro[3.3]hepta-1,5-diene	−266.36182	−269.20545
Ring separation energies (kcal mol^{-1})		
Spiro[3.3]heptane	4.5	
Spiro[3.3]hepta-1,5-diene	5.1	6.7
Heats of formation (kcal mol^{-1})[e]		
Spiro[3.3]heptane	26.9	
Spiro[3.3]hepta-1,5-diene	87.7	86.2
Strain energies (kcal mol^{-1})		
Spiro[3.3]heptane	56.8	
Spiro[3.3]hepta-1,5-diene	63.0	61.4

[a] Energy calculated using STO-3G optimized geometry. [b] From Ref. 7. [c] From Ref. 5. [d] From Ref. 15. [e] Obtained using calculated ring separation energies (see text).

component rings. The corresponding ring separation energy (RSE) then is a measure of the interaction between the component rings. Since the ring separation reaction is not only isodesmic but also conserves ring type, we might expect to get good ring separation energies even with STO-3G calculations. Indeed, there is good agreement (within 1 kcal mol^{-1}) between theoretical (STO-3G) and experimental RSE values for spiropentane, the only one of the spiro-compounds for which a gaseous enthalpy of formation is experimentally available. For the spiro-compounds treated in this paper, the ring separation reactions are given by eqns (1) and (2). Calculated RSE's are included in Table 2.

(1)



(2)

Theoretical RSE's may be used in conjunction with experimental enthalpies of formation[32] for methane, cyclobutane and cyclobutene to predict heats of formation for spiro-compounds through (1) and (2). Values calculated in this way are also shown in Table 2.

An additional energetic property of interest is the strain energy. The strain energy measures the energy increase in deforming a molecule from an idealized model structure in terms of bond stretching, bond–angle bending, torsion and compression of non-bonded atoms.[21,33] Here, we employ our predicted heats of formation for spiro-compounds as well as experimental data for reference molecules to evaluate strain energies as the negative of the enthalpy changes in the formal reactions (3) and (4).[†]

$$C_7H_{12}(\text{spiro[3.3]heptane}) + 8C_2H_6(\text{ethane}) \rightarrow C_5H_{12}(\text{neopentane}) + 6C_3H_8(\text{propane}) \quad (3)$$

$$C_7H_8(\text{spiro[3.3]hepta-1,5-diene}) + 2C_2H_4(\text{ethylene}) + 6C_2H_6(\text{ethane}) \rightarrow C_5H_{12}(\text{neopentane}) + 4C_3H_6(\text{propene}) + 2C_3H_8(\text{propane}). \quad (4)$$

Results are also included in Table 2. Strain energies will be further discussed later in this paper.

(C) *Spiro*[3.3]*heptane*

Spiro[3.3]heptane is an experimentally known compound.[35] However, neither its structure not its thermochemical properties have been experimentally characterized although these properties have been of theoretical interest.[27]

Initial calculations were carried out on the D_{2d} conformation in which the component rings are each taken to be planar. As expected, the C_1–C_2 length is shorter than the C_1–C_2 bond in cyclobutane. At the STO-3G level, the appropriate values are 1.550 and 1.554 Å, respectively, while molecular mechanics calculations yield 1.542 and 1.548 Å.

Molecular mechanics calculations were also performed on a structure of C_2 symmetry in which the cyclobutane rings are allowed to become non-planar. The C_2 form is found to be more stable than D_{2d} by about 0.29 kcal mol^{-1} compared with a similarly calculated inversion barrier in cyclobutane of 0.03 kcal mol^{-1}. The puckering angle in spiro[3.3]heptane (11°) is considerably larger than that predicted by the same method for cyclobutane (6°). Since the calculated cyclobutane values are considerably smaller than experimental values, it is likely that the ring puckering in spiro[3.3]heptane is also underestimated. In any case, we conclude that the four-membered rings in spiro[3.3]heptane are puckered and the degree of puckering appears larger than in cyclobutane.

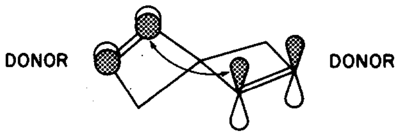
The calculated RSE is 4.5 kcal mol^{-1} which is much greater than that found in spiro[2.2]pentane (0.1 kcal mol^{-1} for STO-3G). This reflects the smaller distortion at the spiro-carbon in spiro[3.3]heptane. The calculated strain energy is 56.8 kcal mol^{-1} which is 3.4 kcal mol^{-1} greater than twice the strain energy in cyclobutane. Our results therefore support the notion of Wiberg *et al.*[27] based on their model study of methane that the distortion energy for the unsymmetric bending mode is less than half that for the symmetric bending mode. The excess strain in spiro[2.2]pentane compared with its component rings (8.3 kcal mol^{-1})[10] is somewhat larger than the corresponding value (3.4 kcal mol^{-1}) in spiro[3.3]heptane. Again, this reflects the decreased strain at the spiro-carbon in spiro[3.3]heptane compared with spiro[2.2]pentane. A rough estimate of the strain at the spiro-carbon can be obtained by assuming that all methylene groups have the same strain as in cyclobutane. This yields about 17 kcal mol^{-1} while a similar analysis for spiro[2.2]pentane results in a much larger value, 27 kcal mol^{-1}.

(D) *Spiro*[3.3]*hepta*-1,5-*diene*

Spiro[3.3]hepta - 1,5 - diene has attracted experimental and theoretical interest because it represents a dissymmetric, homoconjugated, rigid and spiro-linked 1,4-diene system. Spectroscopic studies[36] have suggested the existence of spiroconjugative interactions in this molecule.

The structure of spiro[3.3]hepta - 1,5 - diene is of interest. The C_2–C_1–C_4 bond angle (85.3°) is less than the H_1–C_1–H_2 angle in cyclobutene (109.0°) and, according to our model study of cyclobutene, we would expect bond contraction in the C_1–C_2 and C_1–C_4 bonds. However, the calculated C_1–C_2 bond length is almost identical to the corresponding length in cyclobutene. Moreover, the C_1–C_4 bond (1.567 Å) is about 0.002 Å longer than the corresponding bond in cyclobutene. It seems then that specific spiro-interactions are influencing the structure of spiro[3.3]hepta - 1,5 - diene.

In order to rationalize the structural effects, it is useful to examine the orbital interactions in the system. The HOMO–HOMO interaction **7** between the two ethylenic fragments involves four electrons and is net destabilizing.[6,37] This would cause a lengthening of C_1–C_2 so as to partially relieve such unfavorable interaction. Contributions to the lengthening of C_1–C_2 as well as C_1–C_4 may also be attributed to repulsive interactions (**8** and **9**) between filled Walsh orbitals[38,39] of one cyclobutene and the HOMO of the other.



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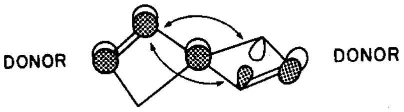

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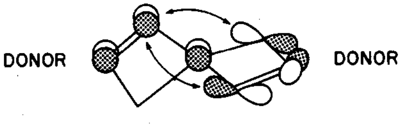

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Orbital interactions which are likely to be more important involve pseudoconjugative interaction of the filled Walsh orbitals of one cyclobutene with the LUMO of the other (**10, 11**). Such interactions should lead to decreased bonding and hence a lengthening of C_1–C_4. Pseudoconjugative interaction similar to **10** is found to be important in interpreting structural variations due to spiro-interactions for spiro[2.4]hepta - 4,6 - diene and spiro[2.4]heptatriene.[10]

Finally, we note that the bond lengthening of C_2–C_3 is greater for spiro[3.3]hepta - 1,5 - diene (0.004 Å) than for the distorted cyclobutene (0.002 Å). This may be due to interaction between the HOMO of one cyclobutene ring and the LUMO of the other (**12**). Interaction **12** should lead to a bond elongation for C_2–C_3.

In short, we believe that interactions **7**–**12** may all be

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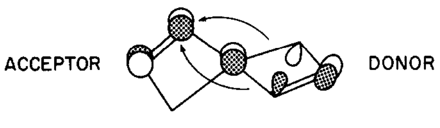
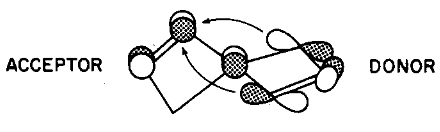
[†] These equations represent a particular class of isodesmic reactions which have been named "homodesmotic reactions" (Ref. 34a). Alternatively, the conventional strain may be obtained by considering branching effects in addition to an appropriate isodesmic reaction (Ref. 34b).



(10)



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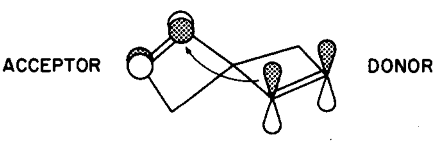

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operative and the equilibrium structure reflects the balance of the forces involved. Because there are several opposing effects, the net effect of geometric distortion and spiro-interaction turns out to be quite small.

Another point of interest concerns the angle between the two cyclobutene planes in spiro[3.3]hepta - 1,5 - diene. Symmetry considerations demand a distortion (of indeterminate magnitude) from a fully orthogonal structure. Indeed, our STO-3G calculations indicate that the two planes are twisted very slightly (0.5°) from orthogonality. The distortion occurs in a direction such that the two ethylene fragments are moving closer to coplanarity which would be favored by conjugative interaction. Of course, a large distortion of this type would be energetically expensive as evidenced in the extreme by the large energy difference (about 150 kcal mol^{-1})[40] between planar and tetrahedral methane.

The small structural variations do not tell us whether the ground state of spiro[3.3]hepta - 1,5 - diene is stabilized or destabilized by spiro-interactions. However, the calculated strain energies shed some light on this problem. Since the bond angles around the central carbon atom of spiro[3.3]hepta - 1,5 - diene are more distorted than those of spiro[3.3]heptane, we would expect that the excess strain energy of the former compared with its component rings would be larger than the corresponding value for the latter. In fact, we find the opposite behavior (2.8 vs 3.4 kcal mol^{-1}) suggesting some stabilizing effect in spiro[3.3]hepta - 1,5 - diene. Equally, the slight stabilizing effect in spiro[3.3]hepta - 1,5 - diene is revealed by comparing the calculated ring separation energy for spiro[3.3]hepta - 1,5 - diene (5.1 kcal mol^{-1}) with that for spiro[3.3]heptane (4.5 kcal mol^{-1}).

It is of interest to compare spiro[3.3]hepta - 1,5 - diene with its isomer spiro[2.4]hepta - 2,4 - diene which we have studied in detail elsewhere[10] at the same level (STO-3G) of theory. The calculated total energies and heats of formation indicate that spiro[2.4]hepta - 2,4 - diene is considerably more stable than spiro[3.3]hepta - 1,5 - diene with calculated energy differences of 28.2 and 31.6 kcal mol^{-1} respectively. On the other hand, the two molecules have nearly identical ring separation energies indicating that they are about equally stabilized by spiro-interactions. The marked difference in stabilities must therefore be attributed to differences in the component rings, cyclopropane and cyclopentadiene in the one case and two cyclobutene rings in the other. Indeed, the energy differences between these pairs are 26.8 (STO-3G) and 30.2 (experimental) kcal mol^{-1}. This result can in turn be attributed to the reinforcing effects of conjugative stabilization in the first pair and greater strain destabilization in the second.

Spiro[3.3]hepta - 1,5 - diene is predicted to have a small dipole moment (0.06 D for STO-3G, 0.11 D for 4-31G) pointing along the C_2 axis from the spiro-carbon into the quadrant containing the double bonds. The small moment is consistent with expectations based on calculations for the optimized and distorted structures of cyclobutene. The dipole moment of cyclobutene is small (0.13 D experimentally[41] and 0.05–0.07 D theoretically[5]) with the double bond at the positive end of the dipole. This moment is reinforced, but only slightly, in distorted cyclobutene (to 0.11–0.13 D theoretically). Because the angle between the two component dipoles in spiro-[3.3]hepta - 1,5 - diene is larger than 120°, the resultant moment in this molecule is reduced from these values.

An orbital interaction diagram for the π-type orbitals of spiro[3.3]hepta - 1,5 - diene constructed using our 4-31G results is displayed in Fig. 2. The first ionization potential for cyclobutene (9.57 eV), calculated according to Koopmans' theorem,[42] is in good agreement with the experimental value (9.59 eV) determined from the photoelectron spectrum.[43] A slightly different theoretical value (9.37 eV, 4-31G) was obtained by Wiberg *et al.*[43] using the experimental geometry as opposed to our STO-3G optimized geometry.

As the H_1–C_1–H_2 angle of cyclobutene decreases from 109.0° to 85.3°, the energy of the HOMO increases from −9.57 to −9.45 eV while the LUMO energy decreases from 5.28 to 5.17 eV. Quite similar trends occur in cyclopropene and cyclopentadiene.[14] The destabilization of HOMO levels and stabilization of LUMO levels is related to the C=C bond lengths: the HOMO levels are bonding across C=C and are destabilized when the bond

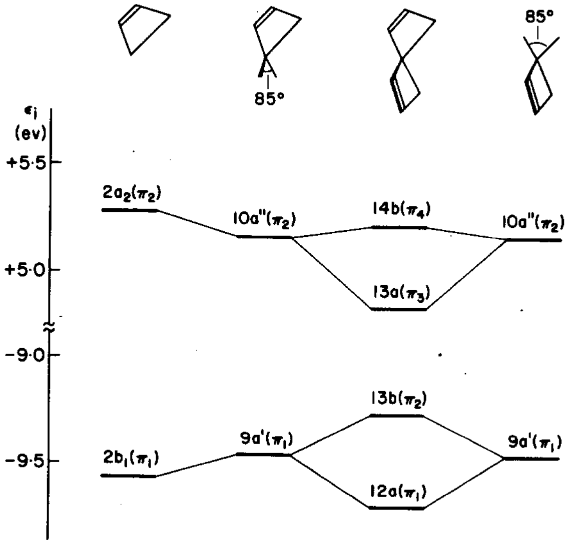

Fig. 2. Correlation of 4-31G π-orbital energies for cyclobutene, distorted cyclobutene and spiro[3.3]hepta-1,5-diene with orbitals classified under C_{2v}, C_s and C_2 symmetries respectively. Note that the component cyclobutene rings in the spiro compound have no elements of symmetry within the C_2 point group.

length is increased while the LUMO levels are antibonding across C=C and show the opposite behavior.

The two ethylene fragments of spiro[3.3]hepta - 1,5 - diene are able to interact and this of course leads to a splitting of the ground and excited state energy levels of the diene as shown in Fig. 2. Accordingly, a bathochromic (red) shift of the lowest $\pi \rightarrow \pi^*$ transition ($\pi_2 \rightarrow \pi_3$ in Fig. 2) relative to the transition band in cyclobutene is expected.† However, we emphasize here that the observed red shift should be attributed in part to the consequences of the H–C–H angular deformation.

The calculated energy splitting between the two highest occupied orbitals is only 0.34 eV for STO-3G and 0.43 eV for 4-31G, which is about one quarter of the corresponding orbital energy splitting in spiro-[4.4]nonatetraene (about 1.2 eV experimentally and 1.12 eV for STO-3G).[10,45] The reduced splitting is not unexpected since spiro[3.3]hepta - 1,5 - diene contains just one sideways interaction of p orbitals while spiro[4.4]nonatetraene has four such interactions However, the photoelectron spectroscopic data[46] for spiro[3.3]hepta - 1,5 - diene (Table 3) seem to suggest that the splitting is as high as 1.28 eV. In the light of Wiberg's demonstration[43] of the reliability of 4-31G calculations in interpreting photoelectron spectra of hydrocarbons, we suggest the possibility of an additional band in the spectrum, somewhere between 9.02 and 10.30 eV corresponding to ionization from the 12a (π_1) molecular orbital. Due to the low resolution of the spectroscopic measurements[46] and the low symmetry of spiro[3.3]hepta-1,5 - diene, it is possible that the missing band (12a) may have an intensity which is very low or it may overlap with the 13b (9.02 eV) band. A reinvestigation of the photoelectron spectrum with higher resolution may solve this problem.

Table 3. Photoelectron spectra and MO energy levels ($-E_{mo}$, 4-31G) of spiro[3.3]hepta-1,5-diene (eV)

Symmetry	Calcd	Scaled[a]	Exptl[b]
13b	9.26	9.37	9.02
12a	9.69	9.70	
12b	11.38	11.01	10.30
11b	12.29	11.71	11.26
11a	12.51	11.88	
10a	13.73	12.82	12.41
10b	14.14	13.14	
9a	16.19	14.72	14.18
9b	16.24	14.76	
8a	16.56	15.00	(14.50)
8b	18.54	16.53	16.23
7a	18.77	16.71	
7b	19.94	17.61	
6a	23.05	20.01	(19.26)
6b	24.29	20.97	
5b	24.52	21.15	
4b	30.21	25.54	
5a	32.19	27.07	

[a]The scaled values are obtained by employing the correlation (Ref. 43) $-\mathrm{IP} = 0.772\ E_{MO} - 2.22$. [b]From Ref. 46.

We have listed in Table 3 for future reference the 4-31G energies for the several highest occupied molecular orbitals. Also shown are values scaled according to a formula proposed by Wiberg *et al.*[43] and the photoelectron spectroscopic values reported by Bodor *et al.*[46] These correspond to adiabatic ionization potentials while our calculated molecular orbital energies should be compared with vertical ionization potentials which are normally slightly higher. Because of the many missing bands in the experimental spectrum, it is impossible to comment on the quality of our attempted correlation between theoretical and experimental results. Again, a more highly resolved experimental spectrum would be desirable.

CONCLUSION

Our *ab initio* molecular orbital calculations for spiro[3.3]heptane and spiro[3.3]hepta - 1,5 - diene yield interesting information concerning the equilibrium geometries, enthalpies of formation, strain energies and spiro-interactions in these molecules. Structural variations in spiro[3.3]heptane may be explained in terms of the results of model calculations on cyclobutane. For spiro[3.3]hepta - 1,5 - diene, in addition to the results of model calculations on cyclobutene, we need to take into account the effects of specific spiro-interactions. Molecular mechanics calculations show that the component rings in spiro[3.3]heptane are each puckered to a greater extent than in cyclobutane itself. STO-3G calculations predict that in spiro[3.3]hepta - 1,5 - diene, the planes of the component rings deviate by about 0.5° from an orthogonal structure. The splitting of the π-orbitals in spiro[3.3]hepta - 1,5 - diene is predicted to be about 0.4 eV.

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REFERENCES

[1] H. E. Simmons and T. Fukunaga, *J. Am. Chem. Soc.* **89**, 5208 (1967); R. Boschi, A. S. Dreiding and E. Heilbronner, *J. Am. Chem. Soc.* **92**, 123 (1970).

[2] R. Hoffmann, A. Imamura and G. D. Zeiss, *J. Am. Chem. Soc.* **89**, 5215 (1967); M. J. Goldstein and R. Hoffmann, *J. Am. Chem. Soc.* **93**, 6193 (1971); A. Tajiri and T. Nakajima, *Tetrahedron* **26**, 6089 (1971).

[3] J. F. Liebman and A. Greenberg, *Chem. Rev.* **76**, 311 (1976).

[4] Reviews: J. A. Pople, In *Modern theoretical chemistry* (Edited by H. F. Schaefer), Vol. 4. Plenum Press, New York (1977); M. D. Newton, In *Modern theoretical chemistry* (Edited by H. F. Schaefer), Vol. 4. Plenum Press, New York (1977); J. A. Pople, *Tetrahedron* **30**, 1605 (1974); L. Radom and J. A. Pople, In *M.T.P. International Review of Science* (*Theoretical Chemistry*) (Edited by W. Byers Brown), Series I, p. 71. Butterworths, London (1972).

[5] W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.* **97**, 6941 (1975).

[6] W. J. Hehre, J. A. Pople, W. A. Lathan, L. Radom, E. Wasserman and Z. R. Wasserman, *J. Am. Chem. Soc.* **98**, 4378 (1976).

[7] W. A. Lathan, W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.* **93**, 808 (1971).

[8] L. Radom, W. A. Lathan, W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.* **93**, 5339 (1971).

[9] L. Radom and J. A. Pople, *J. Am. Chem. Soc.* **92**, 4786 (1970).

[10] J. Kao and L. Radom, *J. Am. Chem. Soc.* **100**, 760 (1978).

[11] W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton and J.

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†The use of calculated orbital energies in predicting excitation energies is a hazardous procedure and subject to the limitations of Koopmans' theorem[42] and a single determinant treatment (see, e.g. Refs. 44, 45). Ideally, we should calculate these quantities as energy differences between the appropriate states. This is a considerably more difficult computational task, for which a configuration interaction treatment is desirable. We would hope nevertheless that the approximate orbital treatment we employ here may provide useful qualitative results.

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[12] D. Poppinger, *Chem. Phys. Letters* **34**, 332 (1975).

[13] W. J. Hehre, R. F. Stewart and J. A. Pople, *J. Chem. Phys.* **51**, 2657 (1969).

[14] J. Kao and L. Radom, *J. Am. Chem. Soc.* **100**, 379 (1978).

[15] D. Cremer, *J. Am. Chem. Soc.* **99**, 1307 (1977).

[16] A. Almenningen, O. Bastiansen and P. N. Skancke, *Acta Chem. Scand.* **15**, 711 (1961); J. M. R. Stone and I. M. Mills, *Mol. Phys.* **18**, 631 (1970); S. Meiboom and L. C. Snyder, *J. Chem. Phys.* **52**, 3587 (1970).

[17] For a recent review, see F. A. Cotton and B. A. Frenz, *Tetrahedron* **30**, 1587 (1974).

[18] B. Bak, J. J. Led, L. Nygaard, J. Rastrup-Anderson and J. O. Sorensen, *J. Mol. Struct.* **3**, 369 (1969).

[19] R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.* **54**, 724 (1971).

[20] T. Ueda and T. Shimanouchi, *J. Chem. Phys.* **49**, 470 (1968).

[21] For reviews: N. L. Allinger, *Adv. Phys. Org. Chem.* **13**, 1 (1976); C. Altona and D. H. Faber, *Top. Curr. Chem.* **45**, 1 (1974); J. E. Williams, P. J. Stang and P. v. R. Schleyer, *Annu. Rev. Phys. Chem.* **19**, 531 (1968).

[22] N. L. Allinger and D. Y. Chung, *J. Am. Chem. Soc.* **98**, 6798 (1976).

[23] N. L. Allinger and J. Kao, *Tetrahedron* **32**, 529 (1976).

[24] N. L. Allinger, M. J. Hickey and J. Kao, *J. Am. Chem. Soc.* **98**, 2741 (1976); J. Kao and N. L. Allinger,, *Inorg. Chem.* **16**, 35 (1977).

[25] J. Kao and N. L. Allinger, *J. Am. Chem. Soc.* **99**, 975 (1977).

[26] D. H. Wertz and N. L. Allinger, *Tetrahedron* **30**, 1579 (1974).

[27] K B. Wiberg, G. B. Ellison and J. J. Wendoloski, *J. Am. Chem. Soc.* **98**, 1212 (1976); K. B. Wiberg and G. B. Ellison, *Tetrahedron* **30**, 1573 (1974).

[28] J. Kao and L. Radom, to be submitted for publication.

[29] R. Ditchfield, W. J. Hehre, J. A. Pople and L. Radom, *Chem. Phys. Lett.* **5**, 13 (1970); W. J. Hehre, R. Ditchfield, L. Radom and J. A. Pople, *J. Am. Chem. Soc.* **92**, 4796 (1970).

[30] L. Radom, W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.* **93**, 289 (1971); L. Radom, W. J. Hehre and J. A. Pople, *J. Chem. Soc.* A 2299 (1971).

[31] P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.* **16**, 217 (1972).

[32] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds.* Academic Press, New York (1970).

[33] E. M. Engler, J. D. Andose and P. v. R. Schleyer, *J. Am. Chem. Soc.* **95**, 8005 (1973).

[34a] P. George, M. Trachtman, C. W. Bock and A. M. Brett, *Tetrahedron* **32**, 317 (1976); [b] J. Kao and N. L. Allinger, to be submitted for publication.

[35] B. Weinstein, A. H. Fenselau and J. G. Thoene, *J. Chem. Soc.* 2281 (1965).

[36] L. A. Hulshof and H. Wynberg, *J. Am. Chem. Soc.* **96**, 2191 (1974); L. Flapper, L. A. Hulshof and H. Wynberg, *Tetrahedron* **30**, 3583 (1974).

[37] L. Salem, *J. Am. Chem. Soc.* **90**, 543 (1968); K. Muller, *Helv. Chim. Acta* **53**, 1112 (1970).

[38] A. D. Walsh, *Nature* 159, 167, 712 (1947); *Trans. Faraday Soc.* **45**, 179 (1949).

[39] R. Hoffmann and R. B. Davidson, *J. Am. Chem. Soc.* **93**, 5699 (1971).

[40] J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger and J. A. Pople, *J. Am. Chem. Soc.* **98**, 5419 (1976).

[41] R. D. Nelson, Jr., D. R. Lide, Jr. and A. A. Maryott, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* No. 10 (1967).

[42] T. Koopmans, *Physica* **1**, 104 (1933).

[43] K. B. Wiberg, G. B. Ellison, J. L. Wendoloski, C. R. Brundle and N. A. Kuebler, *J. Am. Chem. Soc.* **98**, 7179 (1976).

[44] E. Heilbronner, In *The World of Quantum Chemistry* (Edited by R. Daudel and B. Pullman). Reidel Publishing, Dordrecht (1974).

[45] C. Batich, E. Heilbronner, E. Rommel, M. F. Semmelhack and J. S. Foos, *J. Am. Chem. Soc.* **96**, 7662 (1974).

[46] N. Bodor, M. J. S. Dewar and S. D. Worley, *J. Am. Chem. Soc.* **92**, 19 (1970).