

An ab Initio Molecular Orbital Study of Structures and Energies of Spiro Compounds: Spiropentane, Spiropentene, Spiropentadiene, Spiro[2.4]hepta-4,6-diene, Spiro[2.4]heptatriene, and Spiro[4.4]nonatetraene

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Abstract: Theoretical (STO-3G) structures for spiropentane, spiropentene, spiropentadiene, spiro[2.4]hepta-4,6-diene, spiro[2.4]heptatriene, and spiro[4.4]nonatetraene are reported. Single 4-31G calculations on STO-3G optimized structures are also presented. Comparison with experimental data is made in all cases where such data exist, and predictions are made for other cases. Structural variations due to spiro interaction are revealed by comparing the present calculated structures with results obtained from previous model studies of distorted cyclopropane, cyclopropene, and cyclopentadiene. Ring separation energy is defined and used to derive enthalpies of formation and strain energies for these spiro compounds. Strain energies are used to analyze stabilization or destabilization due to spiro interaction. Other molecular properties such as dipole moments and ionization potentials are also discussed.

Introduction

Spiro compounds consist of two perpendicular or near-perpendicular rings joined by a common tetracoordinate atom. The special structural characteristics of spiro compounds are of chemical interest¹ and have provoked detailed theoretical and experimental studies of their energies, strains, structures, and π -electron delocalization (spiro conjugation,² spiro aromaticity³). However, despite the activity in this area, direct experimental thermochemical and structural data are only available for a small number of the simplest members of this class of molecules. Such information is desirable in order to analyze the structural and energetic consequences of spiro interactions.

An alternative source of such data which has yet to be applied to spiro compounds is ab initio molecular orbital theory. This technique has previously been used in systematic studies of equilibrium geometries, relative energies, charge distributions, electric dipole moments, and conformational analysis of a variety of small hydrocarbons with considerable success.⁴⁻⁹ In this paper, we use ab initio molecular orbital theory to study the structures and stabilities of spiro hydrocarbons. We report theoretical structures and energies for spiropentane, spiropentene, spiropentadiene, spiro[2.4]hepta-4,6-diene, spiro[2.4]heptatriene, and spiro[4.4]nonatetraene. In order to assess the consequences of spiro interactions, we utilize in addition the previously reported results^{6,10} for cyclopropene, cyclopropane, and cyclopentadiene.

Method and Results

Structural parameters of spiropentane, spiropentene, and spiropentadiene were fully optimized using a direct search procedure¹¹ and the minimal STO-3G basis set¹² subject only to an overall symmetry constraint. The geometries of spiro[2.4]heptatriene, spiro[2.4]hepta-4,6-diene, and spiro[4.4]nonatetraene were also fully optimized with the exception that the C-H bond lengths were taken from the theoretical (STO-3G) structures of the appropriate separate rings. This assumption, which was introduced to reduce computation time for these large systems, is justified in the light of appropriate data for the smaller molecules (vide infra). The split-valence 4-31G basis set¹³ is generally found to be more reliable than STO-3G for energetic comparisons.^{13,14} For this reason, single 4-31G calculations were carried out on STO-3G optimized structures for all molecules except spiro[2.4]-

hepta-4,6-diene and spiro[4.4]nonatetraene. All computations were performed using a modified version of the Gaussian 70 system of computer programs.¹⁵

The complete set of STO-3G structures is listed in Table I, which also includes available experimental data. The geometries of cyclopropane, cyclopropene, and cyclopentadiene have been reported previously^{6,10} but are included in Table I for easy comparison. The corresponding STO-3G and 4-31G energies are given in Table II. Also shown in Table II are the previous results for methane⁵ which will be used as a reference in the calculation of reaction energies.

Discussion

Comparison with Experimental Structural Data. For the monocyclic compounds in Table I, agreement with experimental parameters is generally good. Largest errors occur for the carbon-carbon double bonds, which are consistently and characteristically^{5,6} (of STO-3G) underestimated by about 0.02 Å.

Only two of the spiro compounds, spiro[2.2]pentane¹⁶ and spiro[2.4]hepta-4,6-diene,¹⁷ have had their structures experimentally determined. For spiro[2.2]pentane, agreement with experimental parameters is good except for the HCH angles, for which the experimental value¹⁶ is a surprisingly high 118.4°. However, the accuracy of this experimental value may be doubtful since similar angles in spiro[2.4]hepta-4,6-diene¹⁷ are reasonably reproduced at the STO-3G level.

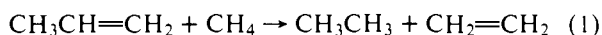
Eleven structural parameters, out of a total of 13, were considered by Chiang and Wilcox in their electron diffraction study¹⁷ of gaseous spiro[2.4]hepta-4,6-diene. Agreement between their results and our values is generally acceptable but there are certain notable large discrepancies for which no immediate answers can be afforded. The experimental C-H bond lengths (1.100 and 1.120 Å) are rather long compared with experimental values found in cyclopropane (1.089 Å),¹⁸ cyclopropene (1.070 Å),¹⁹ cyclopentadiene (1.077 Å),²⁰ and spiropentane (1.091 Å).¹⁶ Again the experimental H₆C₅C₄ bond angle is surprisingly low (119.2°) compared with the observed value in cyclopentadiene (126.3°)²⁰ while the H₅C₄C₁ angle (131.2°) is significantly larger than its counterpart in cyclopentadiene (127.2°).²⁰ The theoretical parameters, on the other hand, appear to be more in line with those expected on the basis of the data for the related molecules. We note that the reported C-H distances¹⁷ were de-

terminated directly from the radial distribution function without any further refinement and the structural parameter $H_{12}C_2C_1$ was not considered at all. We suggest that by taking our theoretical results into account, a further refinement may lead to an improved structure.

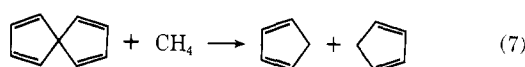
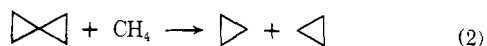
In concluding this section, we point out that not only is there a very limited amount of experimental structural data available for the spiro compounds but, in addition, the uncertainties associated with the experimental data are often of the same order of magnitude as the structural variations due to the spiro interactions which we wish to study. Our theoretical structures therefore provide a more complete and more reliable means of analyzing such structural variations.

Analysis of Energetic Data. Comparison with Experiment.

Some care must be taken in analyzing energetic data in ab initio molecular orbital calculations since heats of reaction are not always well described. Snyder and Basch²¹ were the first to point out that if the number of electron pairs is conserved, reasonable values of heats of reaction can be obtained from double ζ basis set calculations. Pople and co-workers^{14,22} subsequently found that if, in addition, the number of bonds of each type in a reaction is conserved, then good agreement with experiment is generally obtained, even with the minimal STO-3G basis set. Such reactions have been termed *isodesmic*.²² A particular example of an isodesmic reaction is the *bond separation reaction*²² where a molecule is formally broken up into component bonds between heavy atoms. The *bond separation energy* then measures the interaction between the bonds. For example, for propene, the bond separation reaction is

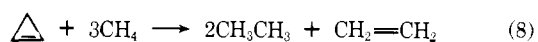


In the current work, we are interested in interactions between rings rather than between bonds. It is convenient then to define, by direct analogy with the bond separation reaction, a *ring separation reaction* in which a spiro compound is broken up into component rings. Newton and Schulman²³ have used a similar scheme for fused polycyclic compounds. For the spiro compounds treated in this paper, the ring separation reactions are given by eq 2-7. *Ring separation energies* (RSEs) for these



reactions then provide a measure of the interaction between the component rings.

We note at this point that unless the calculations are carried out with large basis sets and include electron correlation, poor values are often obtained for heats of reactions involving comparisons of cyclic and acyclic structures.^{6,22,24} An example is the bond separation reaction (8) for cyclopropane. However,

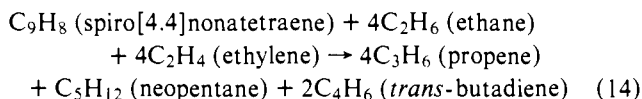
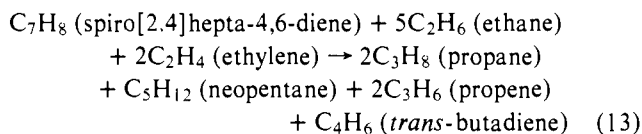
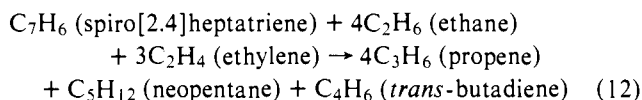
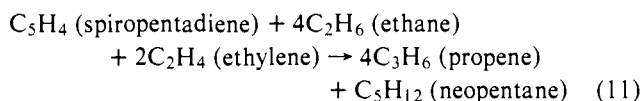
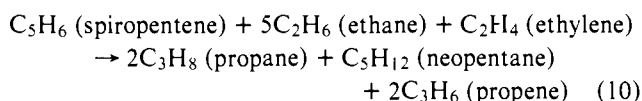
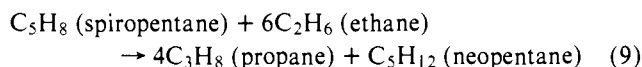


because our ring separation reactions conserve ring type, we might expect to get much better results, even with the modest-sized STO-3G and 4-31G basis sets. Indeed, there is good agreement (Table III) between theoretical and experimental

RSE values for spiro pentane, the only one of the spiro compounds for which an experimental value is available.

Theoretical RSEs may be used in conjunction with experimental enthalpies of formation²⁵ for methane, cyclopropane, cyclopropene, and cyclopentadiene to predict heats of formation for the spiro compounds. Values calculated in this way are also included in Table III. Again, the only molecule for which an experimental heat of formation is available is spiro pentane. The experimental value²⁵ is 44.3 kcal mol⁻¹ compared with calculated values of 43.8 (STO-3G) and 45.5 (4-31G) kcal mol⁻¹. Theoretical heats of formation obtained from MINDO/3 calculations have recently been reported for several spiro compounds by Bingham et al.²⁶ Their values for spiro pentane, spiro[2.4]hepta-4,6-diene, and spiro[2.4]heptatriene are respectively 28.7, 65.4, and 117.0 kcal mol⁻¹. These differ significantly from our calculated heats of formation (Table III) and from the experimental heat of formation for spiro pentane.

An additional energetic property of interest is the strain energy. This measures the energy cost in deforming a molecule from an idealized model structure in terms of bond stretching, bond-angle bending, torsion, and compression of nonbonded atoms.²⁷ It is well known that strain energies are large in small cycloalkanes and cycloalkenes. However, because of a lack of experimental data, it has previously only been possible among the spiro compounds to obtain a strain energy for spiro pentane. Here, we have used our calculated heats of formation (Table III) for spiro compounds as well as experimental data for reference molecules to evaluate conventional strain energies for all the spiro compounds in this study as the negative of the enthalpy changes in the following formal reactions.²⁸⁻³⁰



Results are also included in Table III. The experimental strain energy for spiro pentane (64.2 kcal mol⁻¹) is in good agreement with calculated values of 63.7 (STO-3G) and 65.4 (4-31G) kcal mol⁻¹. It is worth noting that strain energies derived in this manner are likely to be more reliable than those obtained from eq 9-14 using calculated total energies directly. Strain energies will be further discussed later in this paper.

Distorted Methane and Monocyclic Systems as Models for Spiro Compounds. In order to model the structural behavior of spiro compounds, calculations have previously been carried out for methane,³¹ cyclopropane,¹⁰ cyclopropene,¹⁰ cyclobutane,¹⁰ and cyclopentadiene¹⁰ with appropriate H-C-H angular deformation (1). It is useful to summarize here the results

Table I. Molecular Equilibrium Geometries^a

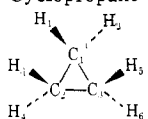
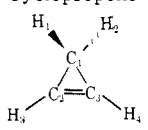
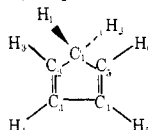
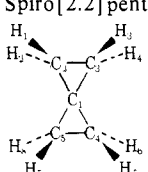
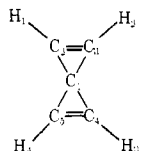
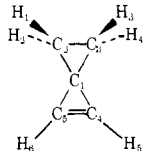
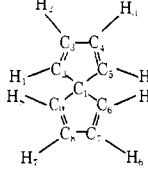
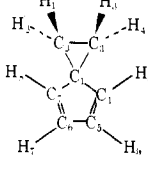
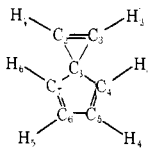
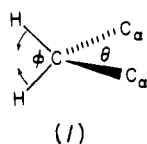
Molecule	Symmetry constraint	Structural parameter ^b	STO-3G ^c	Exptl
Cyclopropane 	D_{3h}	C_1-C_2 C_1-H_1 $H_1C_1H_2$	1.502 ^d 1.081 113.8	1.510 ^e 1.089 115.1
Cyclopropene 	C_{2v}	C_1-C_2 C_2-C_3 C_1-H_1 C_2-H_3 $H_1C_1H_2$ $H_3C_2C_3$	1.493 ^d 1.277 1.087 1.075 112.5 150.3	1.515, ^f 1.509 ^g 1.300, 1.296 1.087, 1.088 1.070, 1.072 114.7, 114.6 149.9 149.9
Cyclopentadiene 	C_{2v}	C_1-C_2 C_2-C_3 C_3-C_4 C_1-H_1 C_2-H_3 C_3-H_4 $H_1C_1H_2$ $H_3C_2C_1$ $H_4C_3C_2$ $C_2C_1C_5$	1.522 1.319 1.490 1.091 1.080 1.081 107.4 122.6 127.1 101.7	1.506, ^h 1.509 ⁱ 1.345, 1.342 1.468, 1.469 1.099 1.078 1.080 106.3 123.6 126.0 102.9, 102.8
Spiro[2.2]pentane 	D_{2d}	C_1-C_2 C_2-C_3 C_2-H_1 $H_1C_2H_2$ $H_{12}C_2C_1$	1.486 1.514 1.082 113.9 151.2	1.469 ^j 1.519 1.091 118.4 152.8
Spiro[2.2]pentadiene 	D_{2d}	C_1-C_2 C_2-C_3 C_2-H_1 $H_1C_2C_3$	1.473 1.296 1.077 147.0	
Spiro[2.2]pentene 	C_{2v}	C_1-C_2 C_1-C_4 C_2-C_3 C_4-C_5 C_2-H_1 C_4-H_5 $H_5C_4C_5$ $H_1C_2H_2$ $H_{12}C_2C_1$	1.485 1.475 1.527 1.287 1.082 1.076 146.5 113.5 153.1	
Spiro[4.4]nonatetraene 	D_{2d}	C_1-C_2 C_2-C_3 C_3-C_4 C_2-H_1 C_3-H_2 $C_2C_1C_5$ $H_1C_2C_1$ $H_2C_3C_2$	1.534 1.318 1.491 (1.081) (1.081) 100.8 122.0 127.0	
Spiro[2.4]hepta-4,6-diene 	C_{2v}	C_1-C_2 C_2-C_3 C_1-C_4 C_4-C_5 C_5-C_6 C_2-H_1 C_4-H_5 C_5-H_6 $C_4C_1C_7$ $H_1C_2H_2$ $H_{12}C_2C_1$ $H_5C_4C_1$ $H_6C_5C_4$	1.518 1.495 1.506 1.321 1.488 (1.081) (1.081) (1.081) 103.3 114.2 148.6 123.0 127.1	1.510 ^k 1.510 1.509 1.341 1.460 1.120 1.100 1.100 102.6 114.0 (150.0) 131.2 119.2

Table I (Continued)

Molecule	Symmetry constraint	Structural parameter ^b	STO-3G ^c	Exptl
Spiro[2.4]heptatriene	C_{2v}	C_1-C_2	1.505	
		C_1-C_4	1.512	
		C_2-C_3	1.275	
		C_4-C_5	1.321	
		C_5-C_6	1.488	
		C_2-H_1	(1.075)	
		C_4-H_3	(1.081)	
		C_5-H_4	(1.081)	
		$C_4C_1C_7$	103.0	
		$H_1C_2C_1$	144.1	
		$H_3C_4C_1$	123.2	
		$H_4C_5C_4$	127.2	

^a Throughout this paper, bond lengths are in Å, bond angles in degrees. ^b The symbol H_{ij} denotes a point on the bisector of the bonds C-H_i and C-H_j. ^c Assumed values in parentheses; see text. ^d From ref 6. ^e From ref 18. ^f From ref 19a. ^g From ref 19b. ^h From ref 20a. ⁱ From ref 20b. ^j From ref 16. ^k From ref 17.

of these studies. The general conclusion is that, without exception, pinching down 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 2s 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 shrinkage of C_α-C bonds also results in a small but significant opening of the C-C_α-H bond angles. An important point to note is that because of the inherent weaker nature of C-C compared with C-H bonds, the bond shortening in the monocyclic systems occurs to a greater extent than in methane.

On the basis of these model calculations, we would therefore expect that because the C-C-C angles in the spiro compounds are smaller than the H-C-H angles in the monocyclic systems, the C-C_α bonds in the spiro compounds 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.

Analysis for Individual Spiro Compounds. A. Spiropentane. The C₁-C₂ bond in spiropentane is found to be shorter than the C-C bond in cyclopropane, both theoretically (0.02 Å) and experimentally (0.04 Å). These results compare with a 0.03 Å shortening in the cyclopropane model study¹⁰ when the H-C-H angle is reduced to 60°. Other theoretical structural variations in spiropentane compared with cyclopropane include changes (spiropentane - cyclopropane values) in C₂-C₃ (-0.02 Å), C₂-C₁-C₃ (+1.2°), and H₁₂-C₂-C₁ (+1.2°). These values are again in qualitative agreement with the increments (-0.03 Å, +2.7°, +3.1°) predicted on the basis of the model study of cyclopropane.

The calculated strain energies for spiropentane are 63.7 (STO-3G) and 65.4 (4-31G) kcal mol⁻¹ which exceed the sum of the strain energies of two cyclopropane rings³² by about 9 kcal mol⁻¹. This increase can be attributed to greater strain at the central carbon. 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 cyclopropane. This yields about 27 kcal mol⁻¹ which is about three times the strain (9 kcal mol⁻¹) per carbon in cyclopropane.

The calculated ring separation energies are very slightly negative. We note that the RSE provides a measure of the total

Table II. Theoretical Total Energies (hartrees)

Molecule	STO-3G	4-31G ^a
Methane	-39.726 86 ^b	-40.139 76 ^b
Cyclopropene	-114.401 16 ^c	-115.641 68 ^c
Cyclopropane	-115.666 16 ^c	-116.883 50 ^c
Cyclopentadiene	-190.457 11 ^d	-192.512 13 ^d
Spiro[2.2]pentadiene	-189.075 66	-191.140 23
Spiro[2.2]pentene	-190.340 17	-192.380 74
Spiro[2.2]pentane	-191.604 87	-193.623 86
Spiro[2.4]heptatriene	-265.146 31	-268.028 46
Spiro[2.4]hepta-4,6-diene	-266.406 83	
Spiro[4.4]nonatetraene	-341.190 04	

^a Energy calculated using STO-3G optimized geometry. ^b From ref 5. ^c From ref 6. ^d From ref 10.

interactions in the spiro compound relative to the component rings. Thus the RSE includes contributions from angular distortion (destabilizing), branching (stabilizing), as well as specific spiro interactions (stabilizing or destabilizing) such as spiro conjugation. It is not possible from the RSE alone to obtain conclusive information about any one of these three effects. Nevertheless, the near-zero RSE together with the close agreement with structural predictions from distorted cyclopropane suggests the absence of strong specific spiro interactions in spiropentane.

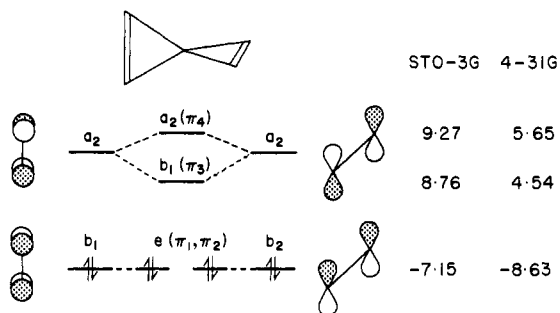
B. Spiropentadiene. For the experimentally unknown molecule spiropentadiene, the C₁-C₂ bond is calculated to be 0.02 Å shorter while the C₂-C₃ bond is 0.02 Å longer than corresponding bonds in cyclopropane. Both the C₂-C₁-C₃ and H₁-C₂-C₁ bond angles are found to be slightly larger than their counterparts in cyclopropane by 1.6 and 4.0°, respectively. Again, the predicted values based on pinching the exocyclic H-C-H angle of cyclopropane are in qualitative agreement with calculated differences of -0.02 Å, 0.02 Å, 1.5°, and 2.4°, respectively.

The strain energy of spiropentadiene is greater than the sum of the strains of the component rings by 8 (STO-3G) or 10 (4-31G) kcal mol⁻¹. Again, this may be attributed largely to the strain increase at the central carbon. An estimate of the strain at the spiro carbon using a similar argument to that for spiropentane would be of interest. However, this is not possible at present because the methylene and methyne strain energies in cyclopropane cannot be accurately evaluated from currently available data. The development of a molecular mechanics model for small rings would be desirable for this purpose.

Perturbation molecular orbital theory predicts^{2,3} a splitting of the LUMO levels of spiropentadiene (Figure 1). Calculated orbital energies³³ for both STO-3G and 4-31G basis sets are also shown in Figure 1. The predicted orbital splittings are 0.5 (STO-3G) and 1.1 (4-31G) eV, of which we believe that the

Table III. Calculated Ring Separation Energies (RSE), Heats of Formation ($\Delta H_f^\circ(g)$), and Strain Energies (kcal mol⁻¹)

Molecule	RSE		$\Delta H_f^\circ(g)$		Strain energy	
	STO-3G	4-31G	STO-3G	4-31G	STO-3G	4-31G
Spiropentadiene	0.1	-2.1	150.2	152.4	115.5	117.7
Spiropentene	-0.2	-2.9	97.0	99.7	89.6	92.3
Spiropentane	-0.4	-2.1	43.8	45.5	63.7	65.4
Spiro[2.4]heptatriene	9.4	9.0	106.6	107.0	58.3	58.7
Spiro[2.4]hepta-4,6-diene	6.5		56.1		35.1	
Spiro[4.4]nonatetraene	1.7		80.1		18.1	

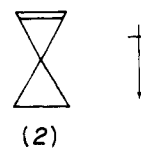
**Figure 1.** π -Orbital interaction diagram and calculated orbital energies (eV) for spiropentadiene. Component orbitals classified under C_{2v} symmetry and resultant orbitals under D_{2d} symmetry.

latter is the more reliable, considerably greater than MINDO/3 estimates³⁶ of 0.14 and 0.28 eV. Interestingly, both ab initio and MINDO/3 calculations predict that *each* of the split bands should be shifted bathochromically (i.e. to low energy) from the $\pi \rightarrow \pi^*$ transition of cyclopropene owing to the destabilization of the HOMO of spiropentadiene relative to that of cyclopropene. This destabilization is largely due to the angular distortion at the spiro carbon atom as evidenced¹⁰ by a similar effect on decreasing the exocyclic H-C-H angle in cyclopropene.

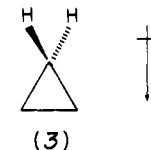
C. Spiropentene. Spiropentene is structurally a cyclopropene juxtaposed to a cyclopropane ring through a spiro carbon atom. It represents another experimentally unknown but chemically interesting molecule. Its high strain (about 90 kcal mol⁻¹) reveals probable difficulties involved in synthesis. The calculated structural features in each ring of spiropentene can be well accounted for in terms of the external spiro angles. For the cyclopropene ring, the external spiro angle $C_2-C_1-C_3$ is larger than that in spiropentadiene and, hence, the C_1-C_4 bond is expected to be longer than the C_1-C_2 bond in spiropentadiene. At the same time, the C_4-C_5 bond would be expected to be shorter than the C_2-C_3 bond in spiropentadiene. For the cyclopropane part of the molecule (in comparison with spiropentane), we would expect similar changes to these but in the opposite direction owing to the decreased external angle $C_5-C_1-C_4$. The direct calculations for spiropentene indeed support all the predicted trends.

The calculated strain is again greater than the sum of the strain energies of the component rings (by 8.1 kcal mol⁻¹ for STO-3G and 10.8 kcal mol⁻¹ for 4-31G). The most intriguing result is that the strain energy of spiropentene is essentially the same as the arithmetic mean of the strains of spiropentane and spiropentadiene (89.6 vs. 89.6 kcal mol⁻¹ for STO-3G and 92.3 vs. 91.6 kcal mol⁻¹ for 4-31G). This suggests that spiropentene may be considered energetically as a hybrid of spiropentane and spiropentadiene and, hence, a normal spiro compound in the sense that the ground state is not stabilized by specific orbital interactions. This interpretation is consistent with our discussion of the calculated structure and with the small calculated ring separation energy.

The calculated dipole moment is 0.89 D for both STO-3G and 4-31G with the cyclopropene ring at the positive end of the

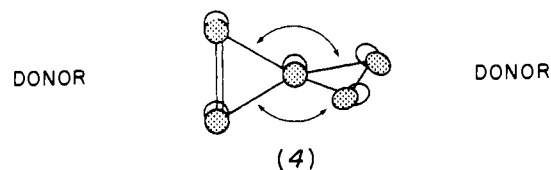


dipole (2). Although the calculated dipole direction for spiropentene is consistent with the theoretical dipole of cyclopropene,⁶ its magnitude is significantly larger (0.89 vs. 0.55 D). The increased dipole moment can be rationalized in terms of our previous model study on cyclopropane,¹⁰ in which we find that the dipole moment of cyclopropane increases rapidly in the direction shown in 3 as the H-C-H angle is decreased from its optimum value of 113.8°.



The calculated HOMO and LUMO energies for spiropentene are respectively -7.45 and 8.67 eV for STO-3G and -8.71 and 4.89 eV for 4-31G. The corresponding calculated values for cyclopropene are respectively -8.45 and 8.95 eV for STO-3G and -9.64 and 5.01 eV for 4-31G. Destabilization of the HOMO of spiropentene consequently should lead to a bathochromic shift for the $\pi \rightarrow \pi^*$ band of spiropentene relative to that of cyclopropene. As noted above, a similar destabilization of the HOMO is predicted when the exocyclic H-C-H angle in cyclopropene is decreased.

Our energetic and structural considerations suggest that pseudoconjugation³⁷ between the cyclopropane and cyclopropene rings (Walsh model)³⁸ is not very important. In the case of spiropentene, such an interaction (4) would involve two



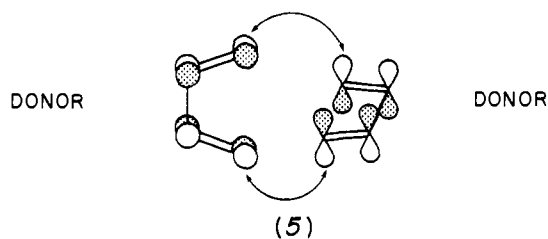
filled orbitals and hence would be destabilizing.³⁹

D. Spiro[4.4]nonatetraene. Spiro[4.4]nonatetraene is an experimentally known molecule whose spectra have received experimental^{40,41} and theoretical^{2,36,42} attention.

The structure of spiro[4.4]nonatetraene is of interest. The $C_2-C_1-C_5$ bond angle (100.8°) is less than the $H_1-C_1-H_2$ angle in cyclopentadiene (107.4°) and, according to our model study of cyclopentadiene,¹⁰ we would expect a slight bond contraction (from 1.522 Å) in the C_1-C_2 bond. In fact, our direct calculations predict (Table I) a C_1-C_2 bond length of 1.534 Å, i.e., an increase of 0.01 Å over the corresponding bond length in cyclopentadiene. It seems then that specific spiro interactions are influencing the structure of spiro[4.4]nonatetraene.

In order to rationalize the structural discrepancy, it is useful to examine the orbital interactions in the system (Figure 2).

By symmetry, the only orbitals to interact are the a_2 orbitals. The HOMO-HOMO interaction (5) between the two buta-



diene fragments involves four electrons and is net destabilizing.^{8,39} Hence the C_1-C_2 bond tends to lengthen so as to partially relieve such unfavorable interaction. The decreased $C_2-C_1-C_5$ bond angle (100.8 vs. 101.7° in cyclopentadiene) may also be attributed to the same cause.

The calculated strain energy for spiro[4.4]nonatetraene is 18.1 kcal mol⁻¹ (STO-3G), which is considerably larger (by 6.3 kcal mol⁻¹) than the sum of the strain energies of two separate cyclopentadiene rings. At first glance, this result is surprising in that the spiro angle $C_2-C_1-C_5$ is not very different from the $H_1-C_1-H_2$ and $C_2-C_1-C_5$ angles in cyclopentadiene. It seems, therefore, that the calculated strain energy reflects the unfavorable π -orbital interactions. Our calculations do not support the proposition³⁶ (based on the results of semiempirical calculations) that spiro conjugation should impart a net stabilization for this molecule.

Calculated π -orbital energies are also included in Figure 2. Both the predicted bathochromic shift of the lowest $\pi \rightarrow \pi^*$ transition ($\pi_4 \rightarrow \pi_5, \pi_6$ in Figure 2) and the hypsochromic shift of the second lowest $\pi \rightarrow \pi^*$ transition ($\pi_3 \rightarrow \pi_5, \pi_6$) relative to the transition band in cyclopentadiene are experimentally observed.⁴⁰ Although the calculated first three orbital energies (-6.64, -7.76, and -9.84 eV) are systematically higher than the corresponding experimental values (-7.99, -9.22, and -10.55 eV) determined from the photoelectron spectra, the calculated orbital energy splitting between the first two orbitals (1.1 eV) is in good agreement with the experimental findings (1.2 eV)⁴¹ obtained both from electronic absorption and photoelectron spectra. It has been shown⁴¹ that both CNDO/2 and MINDO/2 yield as an artifact a high-lying σ orbital between the orbitals π_2 and π_3 , a result hardly compatible with the photoelectron spectroscopic result. Even MINDO/3 and its modified version with application of "through-space" interaction have the same drawback presumably owing to the exaggerated σ/π mixing inherent in MINDO parametrizations.³⁶ On the other hand, the ab initio calculations even at the simplest level, STO-3G, do not suffer from this fault and therefore appear to represent a better model for the interpretation of photoelectron spectra for these systems.

E. Spiro[2.4]hepta-4,6-diene. For spiro[2.4]hepta-4,6-diene, the $C_2-C_1-C_3$ and $C_4-C_1-C_7$ angles are calculated respectively as 59.0 and 103.3°. In the absence of spiro interactions, the C_1-C_4 and C_1-C_2 bond lengths would accordingly be expected to be shorter than 1.522 and 1.502 Å, respectively. The calculated C_1-C_4 bond length (1.506 Å) is indeed shorter than the corresponding bond in cyclopentadiene. On the other hand, the C_1-C_2 bond (1.518 Å) is about 0.016 Å longer than the cyclopropane C-C bond. These results may be rationalized in terms of pseudoconjugation (6) between the Walsh orbitals of cyclopropane and the LUMO of cyclopentadiene. Such an

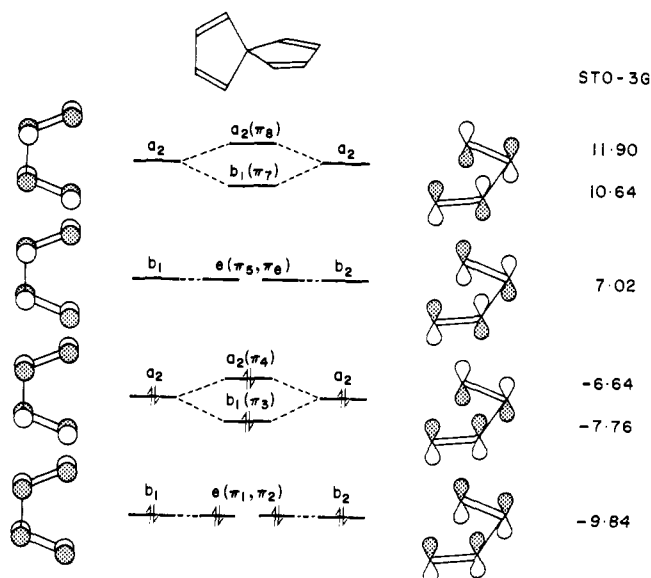
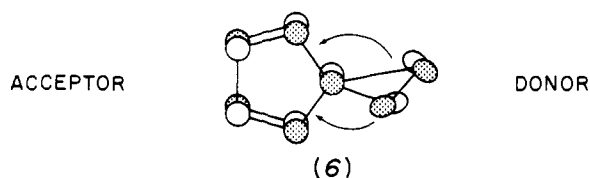


Figure 2. π -Orbital interaction diagram and calculated orbital energies (eV) for spiro[4.4]nonatetraene. Component orbitals classified under C_{2v} symmetry and resultant orbitals under D_{2d} symmetry.

interaction should lead to decreased bonding and hence a lengthening of C_1-C_2 and increased bonding and a shortening of C_1-C_4 as observed. The decrease in the C_2-C_3 length (from 1.502 Å in cyclopropane to 1.495 Å here) is also consistent with 6. The C_4-C_5 and C_5-C_6 bonds, on the other hand, are rather similar to their counterparts in cyclopentadiene. The calculated dipole moment is 0.58 D with the positive end of the dipole at the end of the molecule containing the cyclopropane ring. This again agrees with the electronic reorganization implied in 6.

The structural variations due to spiro interaction are quite small and can be easily masked by experimental uncertainties. Indeed, Chiang and Wilcox¹⁷ on the basis of their gaseous electron diffraction study concluded that spiro interactions are not important for the ground state of spiro[2.4]hepta-4,6-diene. On the other hand, UV,⁴⁴ NMR,⁴⁵ and photoelectron⁴⁶ spectroscopic studies suggest considerable conjugation of the cyclopropane and diene electrons. Our own results also support the existence of spiro interactions in spiro[2.4]hepta-4,6-diene.

The calculated first ionization potential is 6.98 eV (STO-3G), which is smaller than the corresponding value (7.07 eV) for cyclopentadiene. This result is in agreement with the experimental observation⁴⁴ of a bathochromic shift (7 nm or 0.14 eV) relative to 1,1-dimethylcyclopentadiene. In the light of the favorable spiro interactions in spiro[2.4]hepta-4,6-diene, we might have expected a hypsochromic shift. The explanation may lie in the decreased ionization potential (6.83 eV) calculated for cyclopentadiene when the exocyclic methylene angle is reduced to 60°. Thus, whereas spiro interactions lead to a stabilization of the HOMO level in spiro[2.4]hepta-4,6-diene, bond angle distortion has the opposite, and slightly greater, effect.

The stabilization of the ground state of spiro[2.4]hepta-4,6-diene is further revealed by its strain. The calculated strain (35.1 kcal mol⁻¹) is only 1.5 kcal mol⁻¹ larger than the sum of strains of cyclopropane and cyclopentadiene. Since the bond angles around the central carbon atom are highly distorted, a much larger strain increase than 1.5 kcal mol⁻¹ could be expected in the absence of spiro interaction. This is strong evidence for the existence of a stabilizing effect in the spiro[2.4]hepta-4,6-diene system. The stabilization in spiro[2.4]hepta-4,6-diene relative to spiro[2.4]hepta-4,6-diene and spiro[4.4]nonatetraene may be obtained by comparing the

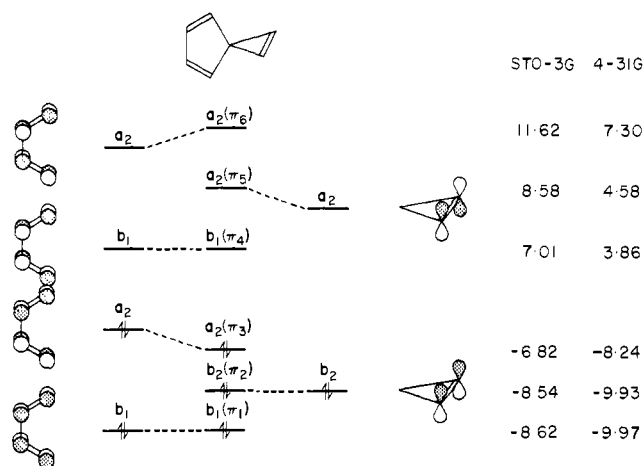
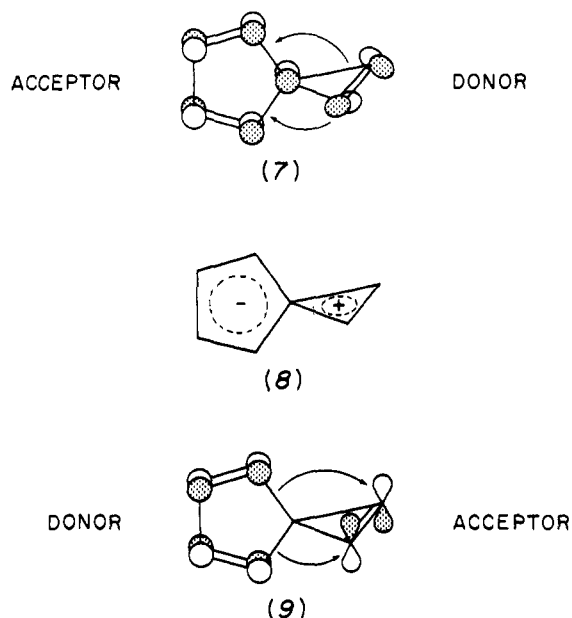


Figure 3. π -Orbital interaction diagram and calculated orbital energies (eV) for spiro[2.4]heptatriene. Component and resultant orbitals classified under C_{2v} symmetry.

strain of the former with the mean of strains of the last two molecules. The calculated mean is $40.9 \text{ kcal mol}^{-1}$, which is about $5.8 \text{ kcal mol}^{-1}$ larger than the strain energy of spiro[2.4]hepta-4,6-diene. Equally, the stabilizing interactions in spiro[2.4]hepta-4,6-diene are reflected in the positive value ($6.5 \text{ kcal mol}^{-1}$) for the ring separation energy.

F. Spiro[2.4]heptatriene. Spiro[2.4]heptatriene represents another interesting spiro molecule. Several dialkyl derivatives of spiro[2.4]heptatriene have been experimentally isolated and spectroscopically studied with particular emphasis on the possibility of spiro conjugation.^{2,37a,43}

Our calculated $C_2-C_1-C_3$ and $C_4-C_1-C_7$ bond angles for spiro[2.4]heptatriene are respectively 50.1 and 103.0° . Our model studies¹⁰ of cyclopropene and cyclopentadiene predict that in the absence of specific spiro interactions, the C_1-C_2 and C_1-C_4 bond lengths should be respectively shorter than the 1.493 \AA of the cyclopropene C_1-C_2 bond and the 1.522 \AA of the cyclopentadiene C_1-C_2 bond. Although the calculated results do show the C_1-C_4 bond being shortened by 0.01 \AA , the C_1-C_2 bond, on the other hand, increases its length by about 0.01 \AA . This result may be rationalized in terms of interaction (7) between one of the filled Walsh orbitals of the cyclopropene



ring with the LUMO of the cyclopentadiene ring in a manner directly analogous to that discussed above for spiro[2.4]hep-

tadiene. Such an interaction effectively leads to a contribution from the resonance structure (8) involving the "aromatic" cyclopropenyl cation and cyclopentadienyl anion rings.

A point of interest is that the lengthening of C_1-C_2 is slightly less for spiro[2.4]heptatriene than for spiro[2.4]heptadiene. This may be due to interaction 7 being less effective than 6 because of the lower energy and hence decreased availability for electron donation of the appropriate Walsh orbital of cyclopropene compared with cyclopropane. An alternative explanation involves the additional interaction (9) of the filled HOMO of the cyclopentadiene fragment with the π^* system of the cyclopropene ring. This should lead to a slight reduction in the C_1-C_2 length.

The calculated dipole moments are 1.22 (STO-3G) and 1.29 D (4-31G) with the positive end at the cyclopropene ring. The dipole moments expected on the basis of distortion of the exocyclic HCH angle in cyclopentadiene to 50° are even greater (2.0 D with STO-3G) and this supports the opposing electron reorganization of the type 9.

Inspection of the coefficients of the appropriate 2p atomic orbitals in the HOMO of spiro[2.4]heptatriene shows that these are only slightly different from those for the HOMO of cyclopentadiene itself. The calculated (STO-3G) coefficients are -0.023 , $+0.023$, $+0.532$, $+0.403$, -0.403 , and -0.532 , respectively, for C_2 , C_3 , C_4 , C_5 , C_6 , and C_7 , which represents only a minor spiro mixing. Similar results are obtained with 4-31G and have also been reported from recent MINDO/3 calculations.³⁶

In summary, we believe that both interactions 7 and 9 are operative and the equilibrium structure reflects the balance of the forces involved. The net result is that C_1-C_4 shortens and C_1-C_2 lengthens.

An important point to note is that although 7 and 9 lead to opposite structural variations, both interactions are energetically favorable. The stabilization of spiro[2.4]heptatriene is reflected in the calculated strain. This comes out at $58.5 \text{ kcal mol}^{-1}$, which is less than the sum of the strains of the cyclopropene and cyclopentadiene rings despite the deformed bond angles about the spiro carbon. This result is consistent with the favorable orbital interactions. The energetic consequences of orbital interactions lead to the following observation: whereas the strain energy of spiropentene is approximately equal to the arithmetic mean of the strain energies of spiropentadiene and spiropentane, the strain of spiro[2.4]heptatriene is much less than the mean ($66.8 \text{ kcal mol}^{-1}$) of the strains of spiro[4.4]-nonatetraene and spiropentadiene. Equally, we note that whereas the ring separation energy for spiropentene is slightly negative, the RSE values (9.4 and $9.0 \text{ kcal mol}^{-1}$ with STO-3G and 4-31G) for spiro[2.4]heptatriene are quite large and positive indicating a stabilizing interaction.

Because of the availability of relevant spectroscopic data, it is of interest to examine the orbital interaction diagram for spiro[2.4]heptatriene in somewhat more detail. This is shown in Figure 3 together with our calculated (STO-3G and 4-31G) orbital energies. Simple perturbation molecular orbital theory suggests^{2,3} that the HOMO level should be stabilized as a consequence of orbital interaction leading to a widening of the $\pi_4(b_1)-\pi_3(a_2)$ energy gap and hence a hypsochromic shift. This prediction is consistent with results of a recent UV spectroscopic study^{37a} in which the lowest energy absorption of dialkyl spiro[2.4]heptatrienes appears at shorter wavelength than that for comparable non-spiro-conjugated reference molecules. On the other hand, it seems to be in conflict with recent data⁴³ from the photoelectron spectra of 1,2-diethylspiro[2.4]heptatriene and 1,2-diethylspiro[2.4]hepta-4,6-diene. The first ionization potential of the former (7.87 eV) is found to be smaller than that of the latter (8.20 eV). Our calculated (STO-3G) first ionization potentials for spiro[2.4]heptatriene and spiro[2.4]hepta-4,6-diene are respectively 6.82 and 6.98

eV and thus show a similar trend to the photoelectron data. The photoelectron spectroscopic results may be rationalized in terms of the relationship¹⁰ between the HOMO energy and the exocyclic H-C-H angle of cyclopentadiene. As noted above, we find that decreasing the exocyclic angle leads to an increase in the HOMO energy. The difference between the appropriate angles in spiro[2.4]heptatriene and spiro[2.4]hepta-4,6-diene would then account for a difference of about 0.20 eV (STO-3G) in the calculated ionization potentials. Since the directly calculated difference (0.17 eV) is fairly close to this value, it seems that the extent of spiro interaction in spiro[2.4]heptatriene (spiroconjugation plus pseudoconjugation⁴⁷) and spiro[2.4]hepta-4,6-diene (pseudoconjugation only) is quite similar. It remains difficult to explain the UV spectroscopic results.^{37a} We can only suggest that the large hypsochromic shift (over 10 nm or 0.21 eV) observed in dialkyl spiro[2.4]-heptatrienes may be due to solvent and/or substituent effects.

Conclusions

We have employed single determinant ab initio molecular orbital theory to study equilibrium geometries, enthalpies, strain energies, and spiro interactions for spiropentane, spiro-pentene, spiro-pentadiene, spiro[2.4]hepta-4,6-diene, spiro[2.4]heptatriene, and spiro[4.4]nonatetraene. Our results are generally in good agreement with the available experimental data. Several predictions are made in cases where experimental results are still unavailable. Structural variations in spiro molecules may usually be explained in terms of our previous model studies of cyclopropane, cyclopropene, and cyclopentadiene. In other cases, the results can be rationalized in terms of specific spiro interactions. Spiro interaction is also revealed in other calculated molecular properties.

Acknowledgments. We are indebted to Dr. Dieter Poppinger for the gradient optimization program and to Dr. Peter J. Stiles and Dr. J. F. Liebman for helpful comments.

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