magnetic fields are frequently applied in studies employing NMR spectroscopy, EPR techniques, or even magnetic stirrers, the evaluation of these effects seems of critical importance.

Experimental Section

Materials. Benzophenone (Aldrich) was recrystallized twice from ethanol; benzophenone-^{13}C (carbonyl ^{13}C), 90% isotopic purity from Merck Sharp and Dohme, was used as received. 1,4-Cyclohexadiene (PCR) was chromatographed on alumina and distilled twice. Gas chromatography showed that it was free from 1,3-cyclohexadiene and benzene; low yields of formation of the latter were observed in the experiments described in this paper. Sodium dodecyl sulfate, SDS (BDH, specially purified), was used as received. Cetyltrimethylammonium chloride, CTAC, was obtained as a 50% solution from K & K and precipitated with acetone. Repeating this procedure did not seem to affect the benzophenone triplet lifetimes. Cetyltrimethylammonium bromide (CTAB) from BDH was used as received.

Steady-State Photolysis. All irradiations were carried out under oxygen-free conditions and by using the same sample cells as in the laser experiments (see below). A Hanovia 150-W Xe/Hg lamp installed in a Bausch & Lomb housing was used for these experiments. Two different magnets were employed: one was a Varian system capable of fields of up to 20 000 G. The other was a home-built magnet capable of fields of up to 2500 G. Both were calibrated by using a Varian E-500 NMR gaussmeter. In both systems the lamp was located 50–80 cm from the center of the magnet. In the high-field system we observed that there was enough leakage to substantially affect the arc in the lamp. A screen was placed past the cell holder and behind the magnet, so as to have a clear projection of the cell and cell holder. We found that frequently this image would reveal dramatic changes in the beam shape and alignment. When this was the case, reversing the field direction would modify substantially the LAT yields measured. We found that the simplest practical solution to this problem (in addition to supplementary magnetic shielding in the lamp housing) was to locate small permanent magnets near or attached to the housing, so that their effect would override any changes due to leakage. In addition, the screen mentioned before provided the means for a simple visual check. Experiments at high fields were always repeated reversing the field direction.

UV spectra were recorded on a Varian 219 spectrophotometer.

Laser Flash Photolysis. The samples, usually 1 or 2 mL, were contained in Suprasil cells made of rectangular (3 × 7 mm) tubing. Oxygen-free nitrogen was used to deaerate the solutions. A Molectron UV-24 nitrogen laser (337.1 nm, ~8 ns, up to 10 mJ) was used to excite the samples. Transient absorptions were monitored by using a detection system with nanosecond response. The signals, initially acquired by an R-7912 Tektronix transient digitizer, were processed by a PDP-11/03L computer, which also controlled the experiment and provided suitable storage and hard-copy facilities. Further details have been reported elsewhere.[70] Experiments in a magnetic field were carried out with the home-built magnet mentioned before.

Acknowledgment. Thanks are due to Dr. A. Braun and Professor N. J. Turro for the communication of unpublished results and for valuable discussions, to S. E. Sugamori for his technical assistance, and to Drs. D. F. Williams, J. Park, and A. H. Reddoch for their help with the use and calibration of the magnets.

Registry No. SDS, 151-21-3; CTAB, 57-09-0; CTAC, 112-02-7; $(C_6H_5)_2\dot{C}OH$, 4971-41-9; benzophenone, 119-61-9; bromide, 24959-67-9; 1,4-cyclohexadiene, 628-41-1.

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Enthalpies of Formation of Fused Cyclobutane Derivatives

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Abstract: The energies of 1,2- and 1,3-bridged cyclobutanes have been calculated with several basis sets. The differences in energy between isomeric compounds are essentially constant when extended basis sets (6-31G* and 6-31G**) are used. The geometries of the compounds are discussed, and it is concluded that the published structure for bicyclo[2.1.1]hexane must be incorrect. The only unusual geometries are found for *trans*-bicyclo[2.2.0]hexane and "windowpane". The enthalpies of formation are estimated on the basis of the calculated energies along with zero-point energies and the change in enthalpy from 0 to 298 K. The strain energies derived from these results are discussed in the context of the reactions of the compounds.

Cyclobutane derivatives have been of considerable interest with regard to the mechanisms of thermal cleavage of hydrocarbons,[2] the Cope rearrangement,[3] the factors that lead to accelerated solvolysis rates,[4] and the potential function for bond angle deformation.[5] Most of these studies require a knowledge of the enthalpies of formation of the compounds. These data are available for cyclobutane[6] and for some of its derivatives such as cyclobutene[7] and bicyclo[1.1.0]butane.[7] The enthalpies of hydrogenation of bicyclo[2.1.0]pentane and bicyclo[2.2.0]hexane have been determined,[8] and from these data the enthalpies of formation may be obtained. However, such data are not available for most of the compounds in which cyclobutane is fused onto another ring. Some molecular mechanics calculations have been carried out,[9–13] but one cannot be sure that the parameters used are appropriate for compounds that have relatively unusual bond angles. Similarly, some ab initio SCF calculations[14,15] have been

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Table I. Calculated Energies[a]

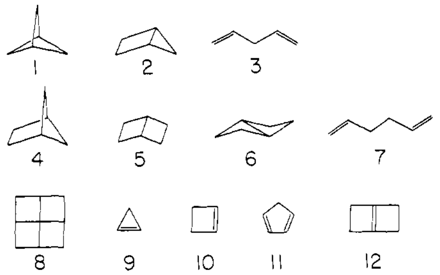
compound	STO-3G STO-3G	4-31G 4-31G	6-31G+BF 4-31G	6-31G* 4-31G	6-31G* 6-31G*	6-31G** 4-31G	6-31G** 6-31G**
hydrogen	−1.117506	−1.126827	−1.130511	−1.126828	−1.126828	−1.131329	−1.131333
methane	−39.726864	−40.139767	−40.194171	−40.195153	−40.195172	−40.201688	−40.201721
acetylene	−75.856248	−76.711413	−76.817621	−76.817734	−76.817826	−76.821758	−76.821807
ethylene	−77.073955	−77.922157	−78.028619	−78.031681	−78.031718	−78.038789	−78.038863
ethane	−78.306180	−79.115933	−79.223619	−79.228734	−79.228755	−79.238253	−79.238271
cyclopropene	−114.401157	−115.642589	−115.815366	−115.822544	−115.823048	−115.830037	−115.830557
cyclopropane	−115.666163	−116.883858	−117.051579	−117.058727	−117.058865	−117.068907	−117.069127
bicyclo[1.1.1]pentane	−191.615423	−193.610156	−193.888541	−193.904653	−193.905681	−193.917749	−193.918816
bicyclo[2.1.0]pentane	−191.630704	−193.632493		−193.926496	−193.926966	−193.939703	
1,4-pentadiene	−191.588754	−193.664593		−193.940844	−193.940925	−193.954702	−193.954801
bicyclo[2.1.1]hexane	−230.263755	−232.644758		−232.989294			
bicyclo[2.2.0]-1(4)-hexene	−228.947611	−231.365057		−231.718161	−231.718707		
cis-bicyclo[2.2.0]hexane	−230.242452	−232.620206		−232.965203			
trans-bicyclo[2.2.0]hexane	−230.142183	−232.538151		−232.889846			
1,5-pentadiene	−230.169057	−232.642724		−232.976148			
windowpane	−343.465943	−347.036029	−347.528561	−347.563374	−347.564282		
cyclopentadiene	−190.457107	−192.513166		−192.791633	−192.791718		
cyclobutene	−153.040285	−154.667920			−154.899621		−154.909836

[a] The energies are given in hartrees (1 hartree = 627.5 kcal/mol). In the basis set specifications, the upper is the one used in the calculation and the lower is the one used in the geometry optimization.

reported, but in most cases they did not include geometry optimization or polarization functions. The latter are now known to be important in considering the energies of strained molecules.[16] The semiempirical SCF calculations on fused cyclobutane rings[17,18] are faced with the difficulty that the energies of cyclobutane rings are generally not well calculated by these methods.[19]

The ideal solution for obtaining further information concerning the energies of these compounds would be to obtain either the enthalpy of combustion or the enthalpy of conversion to another compound having a known enthalpy of formation. Most of the compounds of interest can only be obtained in relatively small quantities and are quite volatile. Therefore, they are not suitable candidates for combustion calorimetry. We have yet to find a process by which most cyclobutanes may be quantitatively converted to less strained compounds quickly and at relatively low temperatures.[20] Thus, reaction calorimetry has not as yet proven generally useful.

It has been found that extended basis set ab initio calculations generally give satisfactory values for enthalpies of rearrangement, such as cyclopropene to 1-propyne.[16] This approach has the advantage that it may be applied to compounds that have not been prepared and thus has the potential of guiding experiments. The compounds of interest include those having 1,3 bridges such as bicyclo[1.1.1]pentane (**1**) and bicyclo[2.1.1]hexane (**4**); those having cis 1,2-bridges such as bicyclo[2.1.0]pentane (**2**) and *cis*-bicyclo[2.2.0]hexane (**5**); and those having a trans-1,2 bridge as in *trans*-bicyclo[2.2.0]hexane (**6**). In these cases, the simplest energy comparison is with the corresponding dienes (**3** and **7**, respectively) that would be formed on thermolysis.[21-25] In addition we were interested in the tetracyclic hydrocarbon **8**, variously known as "windowpane"[12] or "fenestrane".[26] Here, one could compare its energy with that of three cyclopropenes (**9**) or with cyclobutene (**10**) plus cyclopentadiene (**11**). In this group of compounds, **6** and **8** have not as yet been prepared. Finally, we have examined both cyclopropene (**9**) and bicyclo[2.2.0]-1(4)-hexene (**12**)[27] so that we might obtain an estimate of the relative strain energies of these very reactive alkenes.



Extended basis set calculations are relatively costly, and so geometry optimization was carried out first with the STO-3G basis, then with the 4-31G basis, and when practical, also with the 6-31G* basis.[28] This minimizes the number of calculations needed with the larger basis sets and has the additional advantage that it allows a comparison of the energy differences for each of these levels of approximation. In addition, the energies derived from these optimized geometries with the inclusion of polarization functions also were obtained. The energies are summarized in Table I, and the structural data are given in Table II. Besides the compounds **1**–**12**, the energies and structures of several simpler compounds also were determined. Some of these results are available in the literature[29] but are included here for convenience in comparison. All of the data given in the tables were obtained in the present study.

Let us first examine the calculated structures (Table II). The bond lengths and angles for the compounds having one to three carbons are in good accord with the observed values.[29] The calculated bond lengths are generally slightly smaller than those observed, and at least part of the difference results from the

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anharmonicity of the bond stretching potential which makes the average length at the zero-point level somewhat longer than that at the bottom of the potential well.[30,31] Except for possible problems introduced by angle strain,[16] one would expect correspondingly good structural agreement with the larger hydrocarbons.

Among the bicyclic compounds, the most precisely known structure is that of bicyclo[2.1.0]pentane (**2**).[32] The calculated structure is in good agreement with an average deviation in the bond lengths of 0.01 Å, and in bond angles of 0.6°. The carbon–carbon distances in bicyclo[1.1.1]pentane (**1**)[33] are well determined, and the calculated values agree within the experimental error. The experimental errors in the electron diffraction structure of *cis*-bibyclo[2.2.0]hexane (**5**)[34] are relatively large, but within these errors, there is agreement with the calculated structure. The latter is less puckered than the observed structure (which accounts for the difference in the C_2C_5 and C_3C_6 distances). The calculation found a rather flat potential surface for ring puckering, and the experimental distance could be accommodated with only a very slight increase in energy.[35]

In the case of bicyclo[2.1.1]hexane (**4**), there is serious disagreement between the calculated and observed structures. In the latter the C_2–C_3 bond is unusually short (1.513 Å)[36] whereas in the calculated structure this bond is slightly longer than normal. In the absence of any special electronic effects, one would expect this bond to be somewhat long in order to minimize the strain in the cyclobutane ring. Molecular mechanics also leads to a longer bond in accord with these expectations.[37] The short bond in the observed structure leads to severe distortions at the bridgehead.

A fundamental difficulty in determining structures of compounds with several C–C single bond distances via electron diffraction is that the components of the radial distribution curve for the different distances overlap strongly, and one has to resort to some method for separating them. It is then easily possible to find a false minimum for the solution, leading to an incorrect structure. We believe that bicyclo[2.1.1]pentane is such a case and that the electron diffraction data have been interpreted incorrectly.[38]

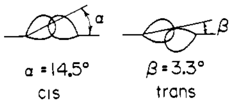
Since the geometries of cyclopropene and *cis*-bicyclo[2.2.0]hexane were satisfactorally calculated, the estimated structure of bicyclo[2.2.0]-1(4)-hexene (**12**) is probably also satisfactory. It can be seen that the C_2–C_3 bond is unusually long, which results in a smaller $C_2C_1C_3$ bond angle. This angle is one of the largest found for an organic compound and is probably in large part responsible for the large energetic destabilization (see below). The compound was found to prefer a planar geometry.[39]

The calculations lead to predictions concerning the geometries of the two unknown compounds, **6** and **8**. A structure for the tetracyclic hydrocarbon (**8**) has also been estimated via molecular mechanics calculations,[12] and there is essentially no difference in the bond angles obtained by the two methods. The structure and energy of **8** has been the subject of two semiempirical SCF calculations.[17,18] By use of MINDO/3, the C–C bond length to the central carbon was found to be 1.535 Å. The present calculation led to a much shorter bond length (1.47 Å) than the semiempirical calculation. The short length appears to result from the poor directionality of the bonds, leading to markedly bent bonds.

In all the cases discussed above, the bond angles could be satisfactorally predicted with molecular mechanics. This indicates that the molecules generally distribute the bond angle strain as well as possible among all available angles. The only case in which there is major disagreement between the two methods is found with *trans*-bicyclo[2.2.0]hexane (**6**).

The molecular mechanics calculation led to C–C–H angles at the bridgehead that were larger than tetrahedral and C–C–C angles at the bridgehead of 83° and 139°.[12] The corresponding values derived from the present calculations are less than tetrahedral for the C–C–H angles and 88° and 151° for the C–C–C angles. Thus, the present calculation concentrates all of the extra bond angle deformation, beyond that already present in cyclobutane, into the external C–C–C angle at the bridgehead, whereas the molecular mechanics calculation distributes the angle deformation over all of the angles.

In order to gain an understanding of the reason for the unusual (and probably correct) angle strain distribution found in the present calculations, we have converted the molecular orbitals for both **5** and **6** into localized orbitals[40] so that the hybridization and orientation of each of the bonds could be examined. The orbitals forming the central bond of **5** were bent, with an angle between the orbital and the line of centers for the bridgehead carbons of 14.5°. The orbitals in **6** were found to point in opposite directions from the line of centers with a 3.3° angle. The twist of the orbitals in **6** away from each other should result in reduced overlap, and the short calculated central bond length may result from an attempt to increase the overlap.



The apparent percentage of character in the C–C bonds is given in Table III. The values should be taken as relative values, and the results for ethane and cyclopropane are included for comparison. It can be seen that the central bond in **5** has slightly reduced s character, as is characteristic of bent bonds. In **6**, however, the s character in the central bond is markedly reduced to a value similar to that for cyclopropane, and there is a corresponding large increase in the s character of the bonds to the adjacent carbons. This suggests an unusually weak central bond.

We may now compare the experimental and calculated energies. For a more convenient comparison, the relative energies with reference to a key compound for each group of molecules is given in kcal/mol in Table IV. It is immediately obvious that the STO-3G energies are meaningless, since the energies of the alkenes are overestimated. This problem has previously been recognized.[29] The 4-31G and the extended basis set results are generally comparable, and there is little difference between the 6-31G* and 6-31G** results. In order to compare these values with experimental results, it is necessary to take both zero-point energy and partition function differences between molecules into account. Table V presents the thermochemical data for the compounds studied in this investigation. When the enthalpy of formation was available, along with the thermodynamic functions, these data were used. In some cases, the thermodynamic functions were recalculated from the experimental data. When they were not available, the ab initio geometry was used to obtain the moments of inertia, the vibrational frequencies were taken from a molecular mechanics calculation,[37] and the energy difference from a key compound derived from the calculation was used.

The "classical" energies of formation given in Table V correspond to the energies of forming the compounds in the vibrationless

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Table II. Calculated and Observed Geometries

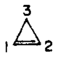
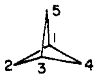
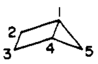
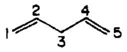
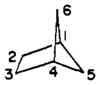
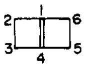
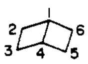
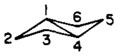
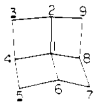
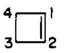
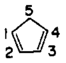
compound	bond or agl	STO-3G	4-31G	6-31G*	6-31G**	obsd[a]
methane	$r(CH)$	1.083	1.081	1.084	1.082	1.093 ± 0.002[b] [1.086][c]
ethane	$r(CC)$	1.538	1.529	1.527	1.526	1.531 ± 0.002[d] [1.531]
	$r(CH)$	1.086	1.083	1.086	1.086	1.095 ± 0.002 [1.096]
	∠(HCH)	108.2	107.7	107.7	107.7	107.8 ± 0.2
ethylene	$r(CC)$	1.306	1.316	1.317	1.316	1.335 ± 0.003[e] [1.330]
	$r(CH)$	1.082	1.073	1.076	1.076	1.090 ± 0.003 [1.076]
	∠(CCH)	122.2	122.0	121.8	121.7	121.7 ± 0.4
acetylene	$r(CC)$	1.168	1.190	1.185	1.186	1.207 ± 0.001[f] [1.203]
	$r(CH)$	1.065	1.051	1.057	1.056	1.057 ± 0.001 [1.061]
cyclopropane	$r(CC)$	1.502	1.503	1.497	1.497	1.514 ± 0.002[g]
	$r(CH)$	1.081	1.072	1.076	1.076	1.082 ± 0.003
	∠(HCH)	113.8	113.7	114.0	114.2	116.5[g]
cyclopropene	$r(C_1C_3)$	1.493	1.511	1.495	1.496	1.509 ± 0.002[h]
	$r(C_1C_2)$	1.277	1.282	1.276	1.275	1.296 ± 0.0004
	$r(C_1H)$	1.075	1.059	1.068	1.067	1.072 ± 0.001
	$r(C_3H)$	1.087	1.076	1.083	1.084	1.088 ± 0.002
	∠(HC_3H)	112.6	113.9	112.9	113.0	114.6 ± 0.2
	∠(HC_1C_2)	150.3	150.2	150.2	150.0	149.9 ± 0.1
bicyclo[1.1.1]pentane	$r(CC)$	1.551	1.563	1.546	1.545	1.545 ± 0.006[i]
	$r(C_1H)$	1.088	1.075	1.082	1.083	1.100 ± 0.010
	$r(C_2H)$	1.087	1.080	1.085	1.085	1.100 ± 0.010
	∠($C_1C_2C_3$)	74.9	74.7	74.4	74.4	73.3 ± 1.0
	∠(HC_2H)	111.1	111.4	111.0	111.0	103.9 ± 5.0
bicyclo[2.1.0]pentane	$r(C_1C_2)$	1.540	1.535	1.528		1.528 ± 0.002 (0.006)[j]
	$r(C_2C_3)$	1.562	1.569	1.558		1.565 ± 0.001 (0.003)
	$r(C_1C_4)$	1.509	1.527	1.513		1.536 ± 0.001 (0.003)
	$r(C_1C_5)$	1.503	1.503	1.494		1.507 ± 0.002 (0.004)
	$r(C_1H)$	1.081	1.069	1.075		1.082 ± 0.001 (0.003)
	$r(C_2H_e)$	1.087	1.080	1.083		1.085 ± 0.001 (0.007)
	$r(C_2H_n)$	1.088	1.082	1.086		1.097 ± 0.001 (0.009)
	$r(C_5H_e)$	1.081	1.073	1.077		1.088 ± 0.001 (0.002)
	$r(C_5H_n)$	1.082	1.074	1.079		1.090 ± 0.001 (0.003)
	∠(C_4C_1H)	129.5	129.4	129.0		128.6 ± 0.1 (0.3)
	∠(C_5C_1H)	122.6	122.2	121.7		121.2 ± 0.1 (0.3)
	∠($C_1C_2H_e$)	113.3	113.2	113.2		113.3 ± 0.1 (0.7)
	∠($C_1C_2H_n$)	115.6	115.7	115.9		115.2 ± 0.1 (0.4)
	∠($C_1C_5H_e$)	115.9	116.2	115.6		114.7 ± 0.1 (0.4)
	∠($C_1C_5H_n$)	120.4	119.9	120.5		119.0 ± 0.1 (0.2)
	∠($C_3C_2H_e$)	112.6	112.1	112.1		111.9 ± 0.1 (0.5)
	∠($C_3C_2H_n$)	116.2	116.7	117.0		116.6 ± 0.1 (0.7)
	C_2 tilt	−2.3	−2.9	−3.0		−2.6
	C_5 tilt	−2.7	−2.8	−2.8		−2.7
1,4-pentadiene	$r(C_1C_2)$	1.309	1.317	1.318	1.318	
	$r(C_2C_3)$	1.531	1.512	1.516	1.515	
	$r(C_1H)$	1.082	1.074	1.075	1.076	
	$r(C_1H)$	1.082	1.074	1.076	1.078	
	$r(C_2H)$	1.084	1.076	1.078	1.079	
	$r(C_3H)$	1.091	1.086	1.087	1.097	
	∠(HC_1H)	115.8	116.1	116.4	116.6	
	∠(C_1C_2H)	119.8	118.9	118.5	118.5	
	∠(HC_3H)	106.1	106.0	106.1	106.1	
bicyclo[2.1.1]hexane	$r(C_1C_2)$	1.548	1.542			1.565 ± 0.024[k]
	$r(C_2C_3)$	1.562	1.564			1.513 ± 0.015
	$r(C_1C_5)$	1.552	1.558			1.544 ± 0.015
	$r(C_1H)$	1.087	1.077			1.112 (av)
	$r(C_2H)$	1.087	1.082			1.112 (av)
	$r(C_5H_e)$	1.086	1.081			1.112 (av)
	$r(C_5H_n)$	1.097	1.082			1.112 (av)
	∠($C_1C_2C_3$)	99.1	99.2			
	∠($C_1C_5C_4$)	82.7	82.6			89.4
	∠($C_5C_1C_6$)	86.3	86.1			78.2
	∠(C_1C_2H)	112.2	112.2			
	∠($C_1C_5H_n$)	117.8	118.0			
	∠($C_1C_5H_e$)	112.9	112.9			
	∠(HC_2H)	108.4	108.1			109.2 ± 4.0
	∠(HC_5H)	110.3	110.3			100.8 ± 5.0
bicyclo[2.2.0]1(4)-hexene	$r(C_1C_2)$	1.532	1.535	1.527		
	$r(C_1C_4)$	1.295	1.303	1.298		
	$r(C_2C_3)$	1.596	1.614	1.596		
	$r(C_2H)$	1.090	1.081	1.086		
	∠($C_2C_1C_6$)	168.7	168.4	168.8		
	∠(C_1C_2H)	116.7	116.5	116.6		
	∠(C_2C_3H)	114.3	114.2	114.4		
	∠(HC_2H)	109.0	109.4	108.8		

Table II (*Continued*)

compound	bond or agl	STO-3G	4-31G	6-31G*	6-31G**	obsd[a]
cis-bicyclo[2.2.0]hexane	$r(\mathrm{C_1C_2})$	1.553	1.549			1.557 ± 0.011[l]
	$r(\mathrm{C_1C_6})$	1.554	1.552			
	$r(\mathrm{C_2C_3})$	1.557	1.560			1.542 ± 0.020
	$r(\mathrm{C_1C_4})$	1.556	1.573			1.577 ± 0.017
	$r(\mathrm{C_1C_3})$	2.198	2.202			
	$r(\mathrm{C_1C_5})$	2.200	2.206			2.198 ± 0.004
	$r(\mathrm{C_2C_6})$	2.617	2.608			2.608 ± 0.008
	$r(\mathrm{C_2C_5})$	3.054	3.064			
	$r(\mathrm{C_3C_6})$	3.036	3.011			2.910 ± 0.016
	$r(\mathrm{C_1H})$	1.087	1.078			
	$r(\mathrm{C_2H})$	1.087	1.082			
	$\angle(\mathrm{C_2C_1H})$	117.0	117.3			114.0 ± 2.0
	$\angle(\mathrm{C_1C_2H_e})$	113.4	113.4			
	$\angle(\mathrm{C_1C_2H_n})$	115.2	115.2			
	$\angle(\mathrm{C_4C_1H})$	122.9	123.5			133.8 ± 5.3
trans-bicyclo[2.2.0]hexane	$r(\mathrm{C_1C_2})$	1.561	1.570	1.567[o]		
	$r(\mathrm{C_1C_4})$	1.494	1.490	1.521		
	$r(\mathrm{C_2C_3})$	1.593	1.604	1.603		
	$r(\mathrm{C_1H})$	1.087	1.086	1.086		
	$r(\mathrm{C_2H_e})$	1.088	1.080	1.080		
	$r(\mathrm{C_2H_n})$	1.087	1.081	1.081		
	$\angle(\mathrm{C_1C_2C_3})$	84.7	84.4	84.8		
	$\angle(\mathrm{C_1C_4C_3})$	88.1	88.3	87.7		
	$\angle(\mathrm{C_2C_1C_6})$	150.9	150.7	150.3		
	$\angle(\mathrm{C_2C_1H})$	104.3	104.4	104.7		
	$\angle(\mathrm{C_4C_1H})$	107.2	108.0	107.5		
	$\angle(\mathrm{C_1C_2H_e})$	117.5	118.0	117.7		
	$\angle(\mathrm{C_1C_2H_n})$	114.6	114.0	114.1		
	$\angle(\mathrm{HC_2H})$	109.8	110.3	110.0		
windowpane	$r(\mathrm{C_1C_2})$	1.485	1.481	1.480		
	$r(\mathrm{C_2C_3})$	1.602	1.614	1.600		
	$r(\mathrm{C_2H})$	1.086	1.079	1.083		
	$r(\mathrm{C_3H_e})$	1.090	1.081	1.084		
	$r(\mathrm{C_3H_n})$	1.087	1.081	1.081		
	$\angle(\mathrm{C_1C_2C_3})$	84.9	85.2	84.8		
	$\angle(\mathrm{C_2C_1C_4})$	99.9	100.2	100.1		
	$\angle(\mathrm{C_2C_3C_4})$	90.4	89.5	90.3		
	$\angle(\mathrm{C_4C_1C_8})$	131.0	130.2	130.4		
	$\angle(\mathrm{C_3C_2C_9})$	133.9	133.4	133.4		
	$\angle(\mathrm{C_1C_2H})$	119.9	120.4	120.3		
	$\angle(\mathrm{C_3C_2H})$	112.1	112.1	112.2		
	$\angle(\mathrm{C_2C_3H_e})$	117.4	117.6	117.8		
	$\angle(\mathrm{C_2C_3H_n})$	111.1	111.2	111.1		
	$\angle(\mathrm{HC_3H})$	108.8	109.0	108.3		
cyclobutene	$r(\mathrm{C_1C_2})$	1.314	1.327	1.322	1.319	1.342 ± 0.004[m]
	$r(\mathrm{C_2C_3})$	1.526	1.525	1.514	1.513	1.517 ± 0.003
	$r(\mathrm{C_3C_4})$	1.565	1.574	1.562	1.560	1.566 ± 0.003
	$r(\mathrm{C_1H})$	1.082	1.070	1.075	1.075	
	$r(\mathrm{C_3H})$	1.089	1.082	1.086	1.085	
	$\angle(\mathrm{C_1C_2C_3})$	94.7	94.7	94.5	94.6	94.2 ± 0.5
	$\angle(\mathrm{C_2C_3C_4})$	85.3	85.3	85.5	85.4	85.8 ± 0.5
	$\angle(\mathrm{C_1C_2H})$	134.1	133.8	133.6	133.6	
	$\angle(\mathrm{C_2C_3H})$	115.7	115.9	115.9	115.9	
	$\angle(\mathrm{HC_3H})$	109.1	109.2	108.7	108.5	
1,3-cyclopentadiene	$r(\mathrm{C_1C_2})$	1.319	1.330	1.329		1.345 ± 0.001[n]
	$r(\mathrm{C_2C_3})$	1.490	1.474	1.476		1.468 ± 0.001
	$r(\mathrm{C_4C_5})$	1.522	1.509	1.507		1.506 ± 0.001
	$r(\mathrm{C_1H})$	1.081	1.069	1.073		1.078 ± 0.001
	$r(\mathrm{C_2H})$	1.081	1.069	1.074		1.080 ± 0.001
	$r(\mathrm{C_5H})$	1.091	1.087	1.089		1.099 ± 0.001
	$\angle(\mathrm{C_1C_2C_3})$	109.9	109.6	109.6		109.3 ± 0.1
	$\angle(\mathrm{C_2C_3C_4})$	109.3	109.2	109.2		109.2 ± 0.1
	$\angle(\mathrm{C_4C_5C_1})$	101.7	102.4	102.4		102.9 ± 0.1
	$\angle(\mathrm{C_5C_1H})$	122.7	123.5	123.6		127.1 ± 0.1
	$\angle(\mathrm{C_1C_2H})$	127.1	126.5	126.6		126.0 ± 0.1
	$\angle(\mathrm{HC_5H})$	107.4	107.0	106.7		106.3 ± 0.1

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[a] The experimentally observed average bond lengths and angles are given first, and this is followed by the estimated equilibrium bond lengths in brackets when they are available. The uncertainties are the reported statistically derived values. In one case (bicyclo[2.1.0]pentane), the effect of systematic errors was estimated, and these larger uncertainties are given in parentheses. [b] Herranz, J.; Stoicheff, B. P. *J. Mol. Spectrosc.* 1963, *10*, 448. A C–H bond length of 1.080 Å and a bond angle of 114.0° would fit the experimental data equally well. [c] Reference 30. [d] Shaw, D. E.; Lepard, D. W.; Welsh, H. L. *J. Chem. Phys.* 1965, *42*, 3736. [e] Kuchitsu, K. *J. Chem. Phys.* 1966, *44*, 906. [f] Lafferty, W. J.; Thibault, R. J. *J. Mol. Spectrosc.* 1964, *14*, 79. [g] Jones, W. J.; Stoicheff, B. P. *Can. J. Phys.* 1964, *42*, 2259. [h] Stigliani, W. M.; Laurie, V. W.; Li, J. C. *J. Chem. Phys.* 1975, *62*, 1890. Kasai, P. H.; Meyers, R. J.; Eggers, D. F., Jr.; Wiberg, K. B. *Ibid.* 1959, *30*, 512. [i] Cox, K. W.; Harmony, M. D. *J. Mol. Spectrosc.* 1970, *36*, 34. Chiang, J. F.; Bauer, S. H. *J. Am. Chem. Soc.* 1970, *92*, 1614. [j] Mather, S. N.; Harmony, M. D.; Suenram, R. D. *J. Chem. Phys.* 1972, *56*, 3837. [k] Chiang, J. F. *J. Am. Chem. Soc.* 1971, *93*, 5044. [l] Andersen, B.; Srinivasan, R. *Acta Chem. Scand.* 1972, *26*, 3468. [m] Bak, B.; Led, J. J.; Nygaard, L.; Rastrup-Andersen, J.; Soerensen, G. O. *J. Mol. Struct.* 1969, *3*, 369. [n] Damiani, D.; Ferretti, L.; Gallinella, E. *Chem. Phys. Lett.* 1976, *37*, 265. [o] 4-31G optimized geometry with the GVB procedure for the C$_1$–C$_4$ bond.

Table III. Percent s Character from Localized Molecular Orbitals for Bicyclo[2.2.0]hexanes

atom	bond	% s	
		cis	trans
C_1	C_1C_2	31.8	36.4
C_1	C_1C_4	28.3	21.4
C_2	C_1C_2	30.9	31.7
C_2	C_2C_3	30.8	31.7
C_1	C_1H	32.7	29.1
C_2	C_2H_{exo}	30.8	31.4
C_2	C_2H_{endo}	29.6	29.9
ethane	C_1C_2	32.2	
ethane	C_1H	28.3	
cyclopropane	C_1C_2	22.9	
cyclopropane	C_1H	34.8	

state at 0 K from normal graphite and from hydrogen gas in its vibrationless state:

$$\Delta E_f(\text{class}) = \Delta H_f(0\text{ K}) - \text{ZPE} + (m/2)(\text{ZPE},\text{H}_2)$$

where *m* is the number of hydrogens. This should include a term for the zero-point energy of graphite. However, it does not appear to be well established and therefore was deleted. It will not affect comparisons in which the number of carbons remains constant.

In the cases for which the enthalpies of formation are not known, we wish to make use of the theoretical energies to provide an estimate of ΔE_f(class). It is known that the energies calculated with single-determinant wave functions are in error because they do not take into account the correlation between the movement of electrons and thereby overestimate electron repulsion.[41] Pople has shown that the correlation energy is largely a function of the atoms contained in the molecule and will approximately cancel when enthalpies of reactions are calculated.[41] The most satisfactory results are obtained when compounds having the same numbers and types of groups are compared.[42] The enthalpies of formation of bicyclo[2.1.0]pentane and *cis*-bicyclo[2.2.0]hexane have recently become available as a result of enthalpy of hydrogenation measurements.[8] The ΔE_f(class) of bicyclo[2.1.0]pentane could be obtained from its ΔH_f and the other quantities in Table V. The difference in calculated energy between it and bicyclo[1.1.1]pentane provides an estimate of the classical energy of the latter. Similarly, the data for bicyclo[2.2.0]hexane, *trans*-bicyclo[2.2.0]hexane, and bicyclo[2.1.1]hexane allow an estimate of the energies of the latter two compounds.

Windowpane (**8**) and bicyclo[2.2.0]-1(4)-hexene (**12**) do not have such convenient reference compounds. The calculated energy of **8** might be compared with three cyclopropenes or with cyclopentadiene and cyclobutene. Although it is not desirable to compare saturated and unsaturated compounds,[42] it can be seen from Table IV that the errors should not be large. The first comparison gives ΔE_f(class) = 79.5 kcal/mol whereas the latter gives ΔE_f(class) = 82.8 kcal/mol. The energy of cyclopropene as compared to a saturated compound, cyclopropane, is overestimated (Table IV), suggesting that the latter comparison is the more satisfactory. The enthalpy of formation is based on this value. The calculated difference in ΔE_f(class) between **12** and *cis*-bicyclo[2.2.0]hexane (**5**) is 82.3 kcal/mol. Calculated enthalpies of hydrogenation are usually about 3 kcal/mol too large (Table IV). Therefore, the value 79.3 kcal/mol was used, leading to ΔE_f(class) = 57.6 kcal/mol for **12**.

The enthalpies of formation of several of these compounds have recently been estimated by molecular mechanics.[13] The calculated ΔH_f for **4** (18.3 kcal/mol) and **5** (27.4 kcal/mol) are in reasonable agreement with the present values. The ΔH_f obtained for **1** (68.5 kcal/mol) appears to be much too high, presumably because the bond angle bending function is not well parameterized for such large angular deformations. The value found for **12** (82.4 kcal/mol) is much smaller than the present value, again suggesting a deficiency in the bond angle bending function. The enthalpy of formation of **8** has been estimated by semiempirical SCF calculations. MINDO/3 gave ΔH_f = 108.5 kcal/mol.[17,18] A MNDO calculation gave ΔH_f = 146.5 kcal/mol,[18] in good agreement with the present value. The calculated bond lengths were, however, quite different from those found in our study.

It is of interest to examine the enthalpies of some of the reactions involving the compounds in Table V. The calculated values are compared with the experimental results in Table IV. The calculated enthalpies of reaction are generally in good agreement with the available experimental data. The largest difference is found in the hydrogenation of cyclopropene. This might be expected to be one of the cases in which the cancellation of correlation energies between reactants and products would not be complete.[16]

The enthalpies of the rearrangement to dienes is generally exothermic, and the calculated values appear to have reasonable magnitudes. The rearrangement of bicyclo[2.1.1]hexane (**4**) to 1,5-hexadiene (**7**) is interesting in that the reaction is calculated to be endothermic. Thus, there is a suggestion that the observed rearrangement of **4** to **7** may be entropy driven and may not proceed to completion. At 298 K, the calculated free energy of formation of **4** is slightly less than that of **7**. The reaction has been studied at temperatures of about 600 K.[17] At this temperature, the free energies for **4** and **7** are calculated to be 72.4 and 67.1 kcal/mol, respectively, leading to a calculated equilibrium constant of 85 favoring the diene.[43] If this were correct, there should be about 1% of **4** present at equilibrium. The kinetic studies carried the reaction only to 70% completion, and thus the equilibrium constant is not known. We are attempting to measure this quantity, but this is complicated by the products due to the further reactions of **7**.

The difference in energy changes resulting from 1,2 vs. 1,3 bridging of a cyclobutane ring has been of particular interest to us.[44] A one-carbon bridge (**1** and **2**) leads to much larger destabilization for 1,3 bridging than for 1,2 bridging. On the other hand, a two-carbon bridge (**4** and **5**) leads to larger destabilization for 1,2 bridging than for 1,3 bridging. In the latter case, 1,2 bridging leads to the formation of two small rings rather than one as produced by 1,3 bridging, and this accounts for the difference in energy. In the former case, either type of bridging will lead to two small rings, but the angular deformation is considerably greater with 1,3 bridging.

In comparing the bicyclic compounds, it is sometimes helpful to convert the enthalpies of formation into strain energies.[45] The values are given in Table IV. For **2** and **5**, the strain energies are just the sum of the strain energies of the component rings.[46] The strain energy of **1** is greater than that of two cyclobutane rings, as one might expect due to the large angular distortions. The strain in **4** is 10 kcal/mol greater than that for cyclobutane, which is reasonable in view of the bond angle distortion in the attached five-membered ring. Among the bicyclic compounds, the one having unusually large strain is *trans*-bicyclo[2.2.0]hexane (**6**). This probably results from the factors noted above with regard to its structure.

The relative energies of **5** and **6** are of interest with regard to the question of the stability of **6**. The rearrangement of **5** to 1,5-hexadiene has an activation energy of 36 kcal/mol and is believed to proceed via a chair cyclohexane 1,4-diradical.[25] This diradical may be formed directly from **6**. Since the difference in energy between **5** and **6** is greater than the activation energy

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(41) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

(42) George, P.; Trachtman, M.; Brett, A. M.; Bock, C. W. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1036.

(43) Tables of thermodynamic functions at several temperatures are available as supplementary material.

(44) Wiberg, K. B.; Chen, W. F. *J. Am. Chem. Soc.* **1974**, *96*, 3900.

(45) For a convenient summary of strain energies of small ring compounds, see: Wiberg, K. B. In "Determination of Organic Structures by Physical Methods"; Nachod, F. C., Zuckerman, J. J., Eds.; Academic Press: New York, 1971; Vol. 3, Chapter 4.

(46) This approximation appears to have first been used by Steel, Zand, Hurwitz, and Cohen, ref 22.

Table IV. Relative Energies of Hydrocarbons (kcal/mol)[a]

	basis set/optimization level							
compound	STO-3G/STO-3G	4-31G/4-31G	6-31G+BF/4-31G	6-31G*/4-31G	6-31G*/6-31G*	6-31G**/4-31G	6-31G**/6-31G**	obsd
$2\,CH_4 - H_2$	−18.9	−23.1	−21.5	−21.8	−21.8	−21.2	−21.2	−18.4
$C_2H_2 + 2H_2$	134.9	94.7	90.9	98.7	98.7	96.5	96.5	90.2
$C_2H_4 + H_2$	72.0	42.0	40.5	44.1	44.1	42.8	42.7	39.6
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
cyclopropene + H_2	92.6	71.8	66.3	68.6	68.4	67.5	67.3	60.7
cyclopropane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
bicyclo[1.1.1]pentane	−16.7	34.2		22.7	22.1	23.2	22.6	
bicyclo[2.1.0]pentane	−26.3	20.1		9.0	8.8	9.4		11.2
1,4-pentadiene	0.0	0.0		0.0	0.0	0.0	0.0	0.0
bicyclo[2.2.0]hexene + H_2	111.3	80.5		82.3				
cis-bicyclo[2.2.0]hexane	0.0	0.0		0.0				
bicyclo[2.1.1]hexane	−59.4	−1.3		−8.2				
cis-bicyclo[2.2.0]hexane	−46.0	14.1		6.9				9.2
trans-bicyclo[2.2.0]hexane	16.9	65.6		54.1				
1,5-hexadiene	0.0	0.0		0.0				0.0
windowpane	−164.7	−67.9	−51.7	−60.1	−59.7			
3-cyclopropene	0.0	0.0	0.0	0.0	0.0			
windowpane	19.7	91.0			79.5			
cyclobutene + cyclopentadiene	0.0	0.0			0.0			

[a] Classical energies at 0 K, not corrected for zero-point energies.

Table V. Thermodynamic Functions for Hydrocarbons[a]

compound	ΔE_f[b] (class)	ZPE	ΔH_f (0 K)	ΔH_f (298 K)	ΔF_f (298 K)	$S°$ (298 K)	SE[c] (298 K)	ref
C(s)	0.0	(0.0)	0.0	0.0	0.0	1.4		*e*
hydrogen	0.0	6.0	0.0	0.0	0.0	31.2		*e*
methane	−31.2	27.2	−16.0	−17.9	−12.2	44.5		*d, e*
ethane	−44.1	45.5	−16.5	−20.2	−7.9	54.9		*d, e*
ethylene	−4.6	30.9	14.5	12.5	16.2	54.5		*d, e*
acetylene	46.1	14.3	54.5	54.3	50.2	48.0		*d, e*
cyclopropane	−14.4	49.1	16.8	12.7	24.9	56.8	27.5	*d, f, g*
cyclopropene (9)	46.4	33.8	68.3	66.2	68.7	58.3	52.3	*f, g, h*
bicyclo[1.1.1]pentane (1)	9.2	70.5	55.8	49.6	70.2	62.8	66.6	*g, i, j*
bicyclo[2.1.0]pentane (2)	−4.2	71.7	43.7	37.7	56.8	67.6	54.6	*g, l, m*
1,4-pentadiene (3)	15.4	69.2	29.7	25.3	40.7	79.7		*e*
bicyclo[2.1.1]hexane (4)	−36.8	89.9	23.3	15.3	43.7	69.2	37.3	*k, j, n*
bicyclo[2.2.0]hexene (12)	57.6	74.8	102.6	94.9	122.4	72.0	90.0	*k, j, o*
cis-bicyclo[2.2.0]hexane (5)	−21.7	89.1	37.7	29.9	57.5	71.5	51.8	*k, l, n*
trans-bicyclo[2.2.0]hexane (6)	25.6	90.2	85.9	77.9	106.2	69.4	99.8	*j, k, n*
1,5-hexadiene (7)	−30.5	86.3	26.0	20.1	42.8	82.4		*k, p*
windowpane (8)	82.8	116.8	163.8	154.2	191.0	76.3	177.5	*j, k, n*
cyclobutene (10)	6.3	53.1	41.5	37.5	48.3	62.7	28.4	*d, f, g*
cyclopentadiene (11)	−3.5	57.4	36.1	31.9	42.4	65.5		*d, f, g*

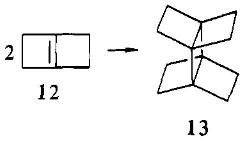
[a] Energies are given in kcal mol^{-1}, entropies in cal deg^{-1} mol^{-1}. The uncertainty in the experimental values of ΔH_f is on the order of 0.3–0.4 kcal/mol. [b] Classical energies of formation in the vibrationless state at 0 K. The values have *not* been corrected for the zero point energy of graphite. [c] Conventional strain energies derived by calculating energies of unstrained models with Franklin group equivalents: CH_2 = −4.926, CH = −1.09, C = 0.80, *cis*-HC=CH = 18.88, C=C = 24.57 (Franklin, J. L. *Ind. Eng. Chem.* 1949, *10*, 1070). [d] The vibrational frequencies were taken from Sverdlov et al. (Sverdlov, L. M.; Kovner, M. A.; Krainov, E. P. "Vibrational Spectra of Polyatomic Molecules"; Halsted Press: New York, 1974). [e] The thermodynamic data were taken from Stull et al. (Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. "The Chemical Thermodynamics of Organic Compounds"; Wiley: New York, 1969). [f] Enthalpies of formation were taken from Cox and Pilcher (Cox, J. D.; Pilcher, G. "The Thermochemistry of Organic and Organometallic Compounds"; Academic Press: London, 1970). [g] The experimental geometries (Table II) were used in calculating the thermodynamic functions. [h] The vibrational frequencies were taken from Eggers and Tum (Eggers, D. F., Jr.; Tum, Y. *J. Phys. Chem.* 1979, *83*, 502). [i] The vibrational frequencies were taken from Wiberg et al. (Wiberg, K. B.; Sturmer, D.; Lewis, T.; Levin, I. W. *Spectrochim. Acta, Part A* 1975, *31A*, 57). [j] The ΔE(class) was obtained from the calculated energies as described in the text. [k] The calculated geometries (6-31G* where available, 4-31G in the other cases) were used, with the C–H bond lengths increased by 0.1 Å to give better agreement with the experimental data. [l] The ΔH_f was based on the enthalpy of hydrogenation (ref 8). [m] The vibrational frequencies were taken from Bragin and Guthals (Bragin, J.; Guthals, D. *J. Chem. Phys.* 1975, *79*, 2139). [n] The vibrational frequencies were taken from a molecular mechanics calculation (see supplementary material). [o] The vibrational frequencies were estimated via a normal coordinate treatment using the force constants obtain in an analysis of cyclobutene (unpublished results, this laboratory). [p] The thermodynamic data were estimated from values for 1,4-pentadiene[e] and the normal increments for one CH_2 group. The difference in ΔH_f (298 K) between 1,4-pentadiene and 1,5-hexadiene corresponds to the normal value.

for the thermolysis of **5**, the energy of the diradical must then be less than that of **6**, and its conversion to this intermediate would be exothermic. This leads to a strong presumption that **6** would rearrange rapidly to **7**. The geometry optimization for **6** was started with a considerably longer central bond than the equilibrium value. Since the geometry optimization leads to shortening of the bond, there may be a significant, but possibly small, barrier separating **6** and **7**.

It is known that single determinant Hartree–Fock calculations do not correctly represent bond breaking and lead to large energies for this process.[47] It was possible that **6** is not a discrete species but would be found to dissociate to **7** without a potential barrier if this problem could be eliminated. Here, the generalized valence bond (GVB)[48] formalism appeared to be particularly useful, since it assigns a wave function to each electron in the specified bonds and leads to correct dissociation. Thus, a geometry optimization was carried out with the GVB perfect pairing approximation for the central bond and the 4-31G basis. The results are shown in Table II. The central bond now is somewhat longer, but the species still represents a minimum in the potential energy surface. We shall at a later time attempt to estimate the activation energy for the conversion of **6** to **7**.

Finally, we may examine the energy of bicyclo[2.2.0]-1(4)-hexene (**12**). The enthalpy of hydrogenation is calculated to be 65 kcal/mol (Table V), which may be compared with 54 kcal/mol for the hydrogenation of cyclopropene (**9**). It is clear that **12** has a considerably higher strain energy than **9**. This is in good accord with its remarkable chemical reactivity.[27] The dimerization to the highly strained propellane **13** is estimated to be exothermic by 88 kcal/mol!

The preceding discussion has been concerned largely with the geometries and energies derived from the calculations. The wave functions potentially contain much information concerning intramolecular interactions, changes in electron density distribution with changes in structure, etc. A quantum topological[49] analysis of the wave functions will be presented at a later time.



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Registry No. 1, 311-75-1; **2**, 185-94-4; **3**, 591-93-5; **4**, 285-86-9; **7**, 592-42-7; **8**, 40220-30-2; **9**, 2781-85-3; **10**, 822-35-5; **11**, 542-92-7; **12**, 30830-20-7; hydrogen, 1333-74-0; methane, 74-82-8; ethane, 74-84-0; ethylene, 74-85-1; acetylene, 74-86-2; cyclopropane, 75-19-4; bicyclo[2.2.0]hexane, 186-04-9.

Supplementary Material Available: Tables of atomic coordinates and thermodynamic data for compounds **1**–**12** (10 pages). Ordering information is given on any current masthead page.

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CIDNP Studies of Photoinitated Electron-Transfer Reactions. Sensitized Isomerization of an Electron Acceptor Norbornadiene

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Abstract: Chemically induced dynamic nuclear polarization (CIDNP) has been observed on irradiation of dimethylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**3**) in the presence of aromatic electron-donor sensitizers in acetonitrile. Nuclear polarization is detected for selected protons of **3** (emission) and its quadricyclene valence isomer **4** (enhanced absorption). The complementary CIDNP effects are rationalized in terms of the quenching of hydrocarbon singlests via electron transfer, intersystem crossing between resultant singlet and triplet radical-ion pairs, and competition between singlet and triplet ion recombination. The energetics of recombination allow that triplets of either **3** or the sensitizers may be populated. A distinction is made between pairs in which the sensitizer triplet level is above or below that of **3**. The CIDNP effects are discussed in terms of other photochemical results regarding the electron-transfer photosensitized isomerization, **3** → **4**.

The photochemical interconversion of norbornadiene (**1**) and its valence isomer, quadricyclene (**2**), has been known for some time.[1] For the forward reaction the mechanism involving triplet–triplet energy transfer is well understood and has recently attracted attention as a relatively efficient means for driving a photochemical energy storage system.[2] Due to the unusual electron donor properties of the strained isomer **2**, the back reaction can also be photoinduced by using electron acceptors as sensitizing agents[3] to promote electron transfer. A new mechanism for the **1** → **2** isomerization was recently proposed,[4] also involving electron transfer which was based on the observation of chemically induced dynamic nuclear polarization (CIDNP) effects on irradiation of **1** in the presence of a singlet sensitizer, 1-cyanonaphthalene. An examination of ion-pair energies suggested the role of electron donor for **1** in the quenching of cyanonaphthalene fluorescence in acetonitrile. The data further provided that geminate ion pairs once formed as singlets may intersystem cross to triplet ion pairs of sufficient energy to populate, through back electron transfer, the triplet state of either reactant. Deposition of excitation energy in **1** through triplet recombination[5] finally leads to isomerization as expected. The different options offered to singlet vs. triplet ion pairs are responsible for opposite nuclear spin polarization in reactant and product isomers.[4]

In a separate paper[6] we have reported that the isomerization of the norbornadiene derivative **3** can be successfully carried to

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