Extended Hückel Calculations on Bicyclobutonium and Related Cations

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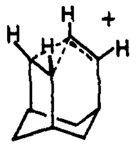
Abstract: Experimental observations have led to a proposed C_s symmetric bicyclobutonium cation as the link between degenerate cyclopropylcarbinyl cations and the juncture accommodating cyclopropylcarbinyl–cyclobutyl rearrangements. Extended Hückel molecular orbital calculations on bicyclobutonium, cyclobutyl, cyclopropylcarbinyl, and tricyclobutonium cations have been performed; the trends in the calculated energies of these ions correlate interestingly with molecular geometry and chemical fact. Energies, self-consistent charge distributions, and overlap populations for selected geometries of $C_4H_7^+$ are given.

Cyclopropylcarbinyl and related cations continue to receive intensive investigation.[3–5] Adequate structural representations for the short-lived reactive intermediates implicated in cyclopropylcarbinyl cation chemistry remain elusive but prized goals.

Three main characteristics of the cyclopropylcarbinyl cation have been known since the early researches of Roberts and Mazur:[6] the ion is formed solvolytically with rate enhancement; it gives rise to cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl products; an isotopic label on one methylene group of the precursor to the carbonium ion is substantially equilibrated among all three methylene groups in the products.

Subsequent work has provided numerous examples of cyclopropylcarbinyl systems giving solvolytic rate enhancements and skeletal rearrangements.[3–5] Recently, a second example of isotopic scrambling among the three potentially equivalent positions of a symmetrically substituted cyclopropylcarbinyl derivative, the 8,9-dehydro-2-adamantyl cation (**1**), was observed.[7–9]



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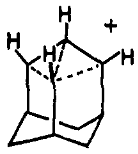

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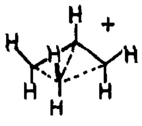

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The experimental results[8,9] led to a postulated C_s symmetric bicyclobutonium ion **2**; the unsubstituted analog **3** was viewed as an important and neglected possibility providing a route for scrambling of labeled cyclopropylcarbinyl cations and for cyclopropylcarbinyl–cyclobutyl interconversions.

Symmetrical bicyclobutonium ions have just received careful and favorable consideration as a possible rationale for data on solvolyses of cyclobutyl systems.[10]

The present article reports extended Hückel (EH) molecular orbital calculations on a variety of C_4H_7 cations. The calculations generate a description of these ions in fair agreement with available chemical fact and the C_s bicyclobutonium ion postulate.

Extended Hückel Method and Parameters

Extended Hückel calculations as developed by Hoffmann[11,12] and a variant in which Coulomb integrals are adjusted with the charge on the atoms were done. The valence-state ionization potentials (VSIP's) were adjusted for charge according to eq 1;[13,14] q is the

$$\mathrm{VSIP}^q = \mathrm{VSIP}^0 - Aq - Bq^2 + C\theta \qquad (1)$$

charge on the atom and θ is the orbital population minus 1 and is included only when $\theta > 0$. The Coulomb integrals, H_{ii}, were set equal to the VSIP's for the particular electron involved. The resonance integrals, H_{ij}, were evaluated by applying the expression 2, with $K = 1.75$, for both σ and π interactions; the S_{ij} are the overlap integrals.

$$H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij} \qquad (2)$$

Iteration proceeded until the difference between each initial and calculated charge was within 0.02. The actual parameters used are given in Table I.[15] Slater

Table I. Parameters for Extended Hückel Calculations

Atom	Orbital	Slater exp	VSIP^0, eV	A, eV	B, eV	C, eV
H	1s	1.00	−13.6	27.2	13.62	0
C	2s	1.625	−21.01	11.9	0	1.7
C	2p	1.625	−11.27	11.9	0	1.5

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[2] National Institutes of Health Predoctoral Fellow, 1966–1967.

[3] P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

[4] M. Hanack and H.-J. Schneider, *Fortsch. Chem. Forsch.*, 8, 554 (1967).

[5] G. A. Olah and P. von R. Schleyer, Ed., "Carbonium Ions," John Wiley and Sons, Inc., New York, N. Y., in press.

[6] J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, 73, 2509, 3542 (1951).

[7] J. E. Baldwin and W. D. Foglesong, *Tetrahedron Letters*, 4089 (1966).

[8] J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.*, **89**, 6372 (1967).

[9] J. E. Baldwin and W. D. Foglesong, *ibid.*, 90, 4303 (1968).

[10] K. B. Wiberg, G. A. Hess, Jr., and A. J. Ashe, III, in ref 5.

[11] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962).

[12] R. Hoffmann, *ibid.*, **39**, 1397 (1963).

[13] H. Basch, A. Viste, and H. B. Gray, *Theoret. Chim. Acta* (Berlin), 3, 458 (1965).

[14] D. G. Carroll, A. T. Armstrong, and S. P. McGlynn, *J. Chem. Phys.*, **44**, 1865 (1966).

[15] Compare L. C. Cusachs and J. W. Reynolds, *ibid.*, **43**, S160 (1965).

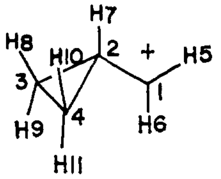
exponents were not adjusted for charge. In trial calculations with such adjustment, qualitatively similar results were obtained; the most striking quantitative differences noted were in the times required for computation by the IBM 7094.

It was found that the total energies calculated by the EH method with and without iteration to constant charge were approximately linearly related for the series of C_4H_7 cations over a range of some 175 kcal/mol and the overlap populations calculated by the two techniques were essentially identical. The charge iteration method produced, however, quite different and "more reasonable" charge densities.

All H–C and C–C bond lengths were taken to be 1.08 and 1.52 Å, respectively, except where noted otherwise.

Results and Discussion

Cyclopropylcarbinyl Cations. The energy difference between a cyclopropylcarbinyl cation in the conformation **4**, locating C(1), H(5), and H(6) in the plane defined by C(2), H(7), and the midpoint of C(3)–C(4), and the conformation **5**, in which this plane bisects the H(5)–C(1)–H(6) angle, has been calculated.[16] Conformation **4** is more stable than **5** by 9 kcal/mol, according to the simple extended Hückel method without charge iteration. Wiberg has applied the self-consistent field modification of the extended Hückel method developed by Pople and coworkers[17,18] and calculated[19] an energy difference of 8 kcal/mol.



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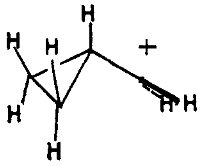

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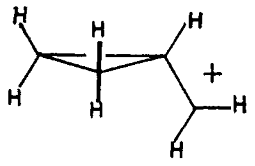
The energy of the favored conformation **4** was found to be insensitive to the H(7)–C(2)–C(1) angle between 120 and 109° 28′ and the H(8)–C(3)–H(9) or H(10)–C(4)–H(11) angles between 120 and 116°.

Displacements of the hydrogens on C(3) and C(4) out of the planes perpendicular to the three-membered ring through these carbons and bisecting the opposite C–C bond (**6**), however, led to considerable destabilization of the ion. It is very slightly cheaper energetically to move "in" the "bottom" protons, H(9) and H(11), than the "top" protons, H(8) and H(10). The difference between these two deformation geometries amounts to only 10 kcal/mol between **7** and **8**, where the distance between the hydrogens brought "in" has been reduced to 1.52 Å. Bringing both pairs of hydrogens "in" to this extent gives a cation calculated to be 130 kcal/mol less stable than the strain-free form, **4**.



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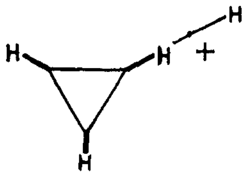

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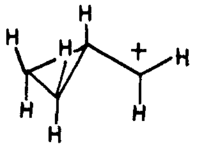

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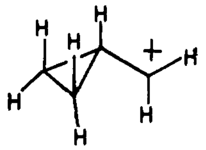

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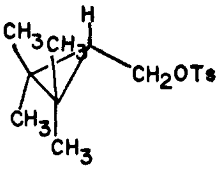
The calculations suggest that similarly substituted but differently distorted cyclopropylcarbinyl derivatives, such as **9** and **10**,[20] should show dramatically different solvolysis rates and are consistent with the slightly faster rates of the *exo* isomers **11** (n = 2, 3) relative to the *endo* isomers **12**,[21] and of **13** to **14**.[22]



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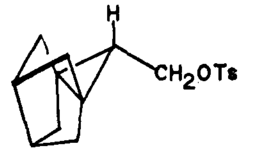

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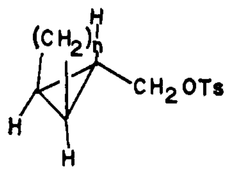

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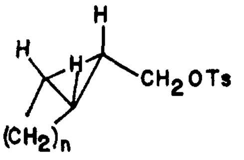

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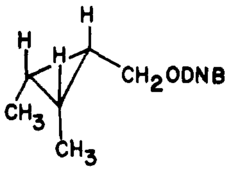

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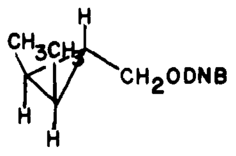

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The calculated sensitivity of energy to cyclopropylcarbinyl cation geometry of substituents at C(3) and C(4), with the C(3)–C(4) bond length constant, suggests an alternative explanation for the trend noted[22] in relative rates for the series **11** (dinitrobenzoates); with n = 2, 3, and 4, the relative rates are 1.3, 40, and 200.[22]

Tricyclobutonium Cations. The two tricyclobutonium cations **15** (γ = 120°) and **16** have already received considerable theoretical attention.[23] The ion **15**, considered to be the theoretically less attractive model, has been predicted to have a triplet ground state and to be of high energy.[23] The EH calculations as a function of the C–C distance at the base of the ion give results consistent with those secured earlier: with decreasing C–C distance, the ion rapidly becomes less stable (Figure 1), but at longer C–C distances, the calculated energy becomes comparable to other forms of the C_4H_7 cation and less than that of the alternative tricyclobutonium ion **16**. Hence, the triplet tricyclobutonium ion need no longer be considered so theoretically disreputable, relative to the singlet ion **16**. Both are of considerably higher energy (~150 kcal/mol) than the unsubstituted cyclopropylcarbinyl cation; neither would be expected

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[16] R. Hoffmann, *J. Chem. Phys.*, 40, 2480 (1964).

[17] J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, 43, 5129 (1965).

[18] J. A. Pople and G. A. Segal, *ibid.*, 43, 5136 (1965); 44, 3289 (1966).

[19] K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968).

[20] P. K. Freeman, V. N. M. Rao, and G. E. Bigman, *Chem. Commun.*, 511 (1965).

[21] K. Wiberg and A. J. Ashe, III, *J. Am. Chem. Soc.*, 90, 63 (1968).

[22] P. von R. Schleyer and G. W. Van Dine, *ibid.*, 88, 2321 (1966).

[23] M. E. H. Howden and J. D. Roberts, *Tetrahedron, Suppl.*, 2, 403 (1963).

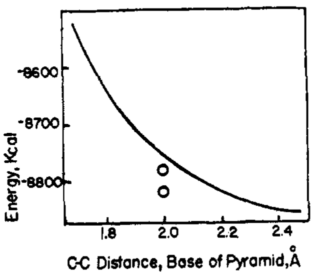
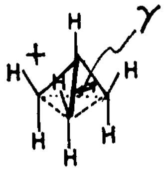


Figure 1. Calculated energies of tricyclobutonium ions without charge iteration. The curved line is based on points for ion **15**; the two points are for ion **16**, with sp^3 (higher energy) and sp^2 hybridization of C(1), C(3), and C(4).

to be involved in unsubstituted cyclopropylcarbinyl cation chemistry.



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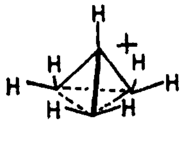

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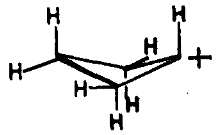
Cyclobutyl Cation. Hoffmann has shown[24] through EH calculations that the puckered cyclobutyl system has a substantial cross-ring bonding interaction in geometry **17**, but not in geometry **18**, thus providing an insight into the observed 10^6–10^8 difference in solvolytic rates exhibited by the bicyclic tosylates **19** and **20**[25,26] (n = 2, 3).



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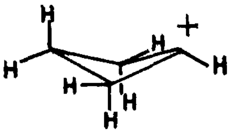

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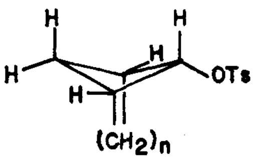

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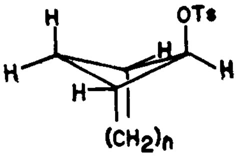

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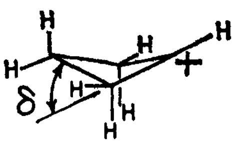
Calculations of the total energy of the cyclobutyl cation (**21**) as a function of the angle of pucker δ



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(Figure 2) show that the energy of the ion decreases as the angle between the C(1)–C(2)–C(3) plane and the C(1)–C(3)–C(4) plane increases from 0° until the cross-ring C–C distance approaches 1.9 Å and the angle between the two planes is greater than 60°.[26a]

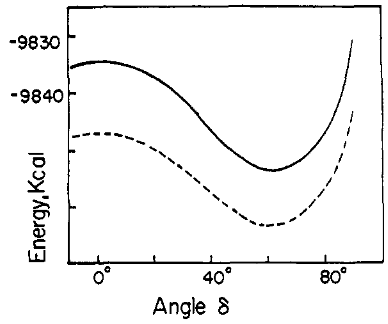


Figure 2. Calculated energies of cyclobutyl cations (**21**) with charge iteration. The assumed C–C bond lengths were 1.52 and 1.58 Å for the upper and lower curves, respectively.

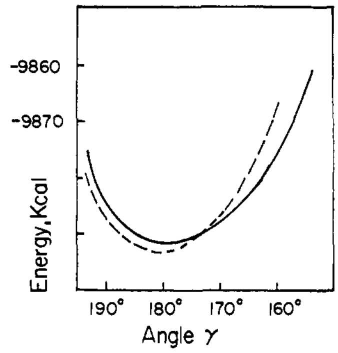
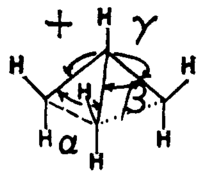


Figure 3. Calculated energies for C_s bicyclobutonium ions (**22**, α = β). The solid line is based on energies calculated without charge iteration and transposed 1000 kcal to lower energies. The broken line is for energies with charge iteration.

Bicyclobutonium Cations. EH calculations on the asymmetrical bicyclobutonium ion **22** for γ = 154° and β = 127, 115, and 103° gave an invariant total energy (±0.5 kcal/mol). Thus, over a wide range, the location of the three planar methylene groups in the bicyclobutonium ion lacking a plane of symmetry is energetically inconsequential. The symmetrical C_s bicyclobutonium ion (**3**; **22** with α = β) has an energy minimum near γ = 180° (Figure 3).



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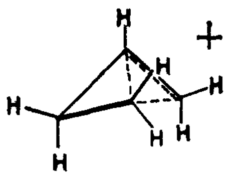

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The bicyclobutonium ion geometry (**23**) which gave the lowest calculated total energy by the approach implemented by Howden and Roberts[23] was found to be about 10 kcal/mol less stable than ion **22** (β = 127°).

Methylene Plus Allyl Cation. Another approach to a geometry akin to that giving the minimum for the C_s bicyclobutonium ion (**3**) would be through a 1 + 3 cycloaddition of nonlinear methylene with an allyl cation. The geometry suggested by this notion (**22**, with C(1) to C(3) and H(5) to H(9) planar, bond angles

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(24) R. Hoffmann, unpublished data.

(25) K. B. Wiberg and R. Fenoglio, *Tetrahedron Letters*, 1273 (1963).

(26) K. B. Wiberg and B. A. Hess, Jr., *J. Am. Chem. Soc.*, **89**, 3015 (1967).

(26a) Note Added in Proof. Recently published EH calculations have been adduced as support for the view that the planar classical cyclobutyl cation is more stable that any folded form [R. E. Davis and A. Ohno, *Tetrahedron*, **24**, 2063 (1968); R. E. Davis, A. S. N. Murthy, and A. Ohno, *Tetrahedron Letters*, 1595 (1968)]. The reason for the different calculated results is still unclear; it may well be associated with different geometrical models for deformation of the cyclobutyl cation.

Table II. Energies, Overlap Populations, and Charge Distributions[a]

Structure	Energy, kcal/mol	Net charge on carbon				Reduced overlap populations					
		C(1)	C(2)	C(3)	C(4)	12	13	14	23	24	34
4	−9909	0.179	0.147	0.089	0.089	0.990	−0.031	−0.031	0.550	0.550	0.688
22, $\beta = 127°$ $\gamma = 154°$	−9880	0.197	0.133	0.062	0.100	0.915	−0.048	0.017	0.683	0.574	0.376
22, $\alpha = \beta$ $\gamma = 178°$	−9892	0.110	0.132	0.110	0.141	0.797	−0.05	0.207	0.797	0.569	0.207
22, $\gamma = 180°$ ∠ C(1)–C(2)–C(3) = 120°	−9898	0.099	0.153	0.099	0.131	0.842	−0.075	0.267	0.842	0.376	0.267
21, $\delta = 60°$	−9863	0.089	0.196	0.089	0.111	0.767	−0.134	0.571	0.767	0.100	0.571
23	−9870	0.112	0.131	0.071	0.154	1.142	−0.101	0.035	0.671	0.238	0.717
Methylcyclopropane		−0.062	−0.033	−0.054	−0.054	0.726	−0.064	−0.064	0.656	0.656	0.609

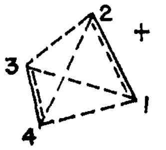
[a] After iteration to constant charge.

120°, and C(4) 1.52 Å from the C(1)–C(2)–C(3) plane) does in fact give a lower total energy for the C_s bicyclobutonium ion.

This conception also leads to a simple MO bonding scheme for the C_s symmetrical bicyclobutonium ion; the two highest energy filled orbitals are derived by mixing the lowest two MO's of the allyl π system with the two nonbonding atomic orbitals of nonlinear methylene. Each component would contribute one orbital symmetric and one antisymmetric with respect to reflection through the H(7)–C(2)–C(4)–H(10)–H(11) plane.

Calculated energies, overlap populations, and charge distributions for several of the cations considered above are presented in Table II.

Two points deserve special comment. First, the C_s bicyclobutonium ion **3** or **2** effectively distributes positive charge onto all four carbon atoms. Second, representations of the cyclopropylcarbinyl cation including dotted lines connecting C(1) with C(3) and C(4) as in **24** are unsatisfactory. There have always been subjective criteria for the difference between the scientifically justified and the unconscionable profligate usage of dotted lines as components of structural representations; now there is an objective one, namely, consideration of whether overlap populations are positive or negative. Bonding and antibonding interactions ought not to be depicted by the same style of dotted lines in a single structure.



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Conclusions

The experimental results with the 8,9-dehydro-2-adamantyl cation (**1**) led[8,9] to three suggested modes of formation for the C_s bicyclobutonium ion. All three are now seen, on the basis of the EH calculations, to be energetically feasible.

As the cyclobutyl cation **21** is folded about the C(1)–C(3) axis, the energy of the ion drops until the system approaches the geometry reached by the symmetrical distortion of **15** (Figure 2).

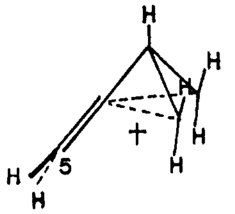
As the angle γ in the tricyclobutonium ion **15** increases, destroying the C_{3v} symmetry of that species but preserving a plane of symmetry, the energy of the $C_4H_7^+$ system decreases until $\gamma = 180°$ (Figure 3).

As one cyclopropylcarbinyl cation rearranges to another by swinging a methylene group of the three-membered ring, the ion passes through geometries appropriate to a model C_s bicyclobutonium ion and, when midway between the other two methylenes, a C_s bicyclobutonium ion. This path is predicted, on the basis of the approximate EH calculations for the particular geometrical parameters selected, to be one characterized by a low activation energy—neither an energy valley nor an insuperable barrier.

Another way of viewing this process is as a thermal 1,3-suprafacial migration of a CH_2^+ substituent from one to the other end of an allylic system, occurring with inversion of configuration at the migrating carbon atom.[27] This description does not do justice to the subtle and extensive mutual interdependence of these two units in such $C_4H_7^+$ ions, but it does point out the congruence between the stereochemical aspects of degenerate cyclopropylcarbinyl cation interconversions with recent experiment[27] and theory.[28]

Thus, the suggested C_s bicyclobutonium ion seems to pass the basic tests for a reasonable structural postulate that can be run with EH calculations. The merit and suitability of the symmetric bicyclobutonium ion proposal will, of course, be settled through experimentation;[29] with sufficient experimental evidence, one may be in a better position to consider[30] the view that the EH method is "incorrect in principle" and "no significance can be attached to the results of such calculations."[31]

The EH method may, of course, be applied equally reliabily to related cations. For instance, we calculate an energy preference of 40 kcal/mol for ion **25**, analogous to the C_s bicyclobutonium ion, over the vinyl cation form **26**.[32] Could the dimethyl derivative of **25**



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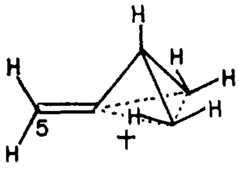

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or **26** be generated and observed in the nmr, there should be two identical rather than two different methyl absorptions.

Acknowledgments. We thank Dr. Donald H. Dugre and Mr. Jon A. Kapecki for valuable consultation on the EH method and the programs employed.

Heats of Hydrogenation. VIII. Compounds with Three- and Four-Membered Rings[1]

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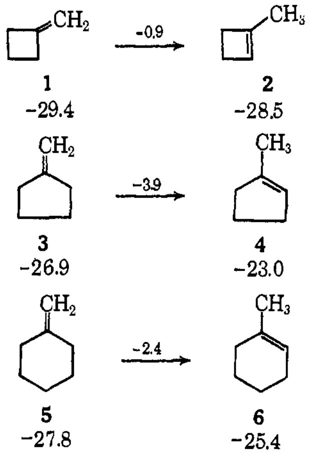
Abstract: The heats of catalytic hydrogenation of methylenecyclobutane, 1-methylcyclobutene, 1,2-dimethylcyclobutene, 1,3-dimethylenecyclobutane, 1-methyl-3-methylenecyclobutene, benzocyclobutene, bicyclo[4.2.0]-octa-2,4-diene, 1,2-dimethylcyclopropene, 1,2-dimethyl-3-carbomethoxycyclopropene, 1-methyl-2-methylenecyclopropane, ethylidenecyclopropane, bicyclo[2.1.0]pentane, 1,3-dimethylbicyclo[1.1.0]butane, and quadricyclene have been measured in solution at 25°. Total strain energies can be estimated for certain of these substances: dimethylcyclopropene, 45 kcal/mol; bicyclopentane, 54 kcal/mol; dimethylbicyclobutane, 67 kcal/mol; quadricyclene, 95 kcal/mol.

For several years we have been interested in the quantitative aspects of steric strain and have already noted a spread of more than 15 kcal/mol in the heats of hydrogenation of two *cis*-disubstituted olefins, *cis*-cyclodecene (−20.7 kcal/mol)[4] and *cis*-di-*t*-butylethylene (−36.2 kcal/mol).[5] This difference serves to emphasize the important influence of strain, both in the starting olefin (*cis*-di-*t*-butylethylene) and in the saturated reduction product (cyclodecane). The enthalpy differences of 9.2 kcal/mol between *cis*- and *trans*-cyclooctenes[4] and of 9.3 kcal/mol between *trans*- and *cis*-di-*t*-butylethylenes[5] serve as further calibration points on the scale of stress effects in highly strained systems.

In the present paper, we report the results of an investigation of the heats of hydrogenation of various small-ring compounds in which steric strain is expected to be high. The data are listed in Table I.

The first two compounds, methylenecyclobutane (**1**) and 1-methylcyclobutene (**2**), comprise a pair of *exo*-*endo* isomers which extends the data previously published for such systems[6] to the four-membered ring.[2] The heat of isomerization of methylenecyclobutane (**1**) into 1-methylcyclobutene (**2**) is −0.9 kcal/mol which is compared with values of −3.9 kcal/mol and −2.4 kcal/mol, respectively, for the corresponding five- and six-membered ring pairs.[5] Since the change in degree of double bond substitution from disubstituted to trisubstituted accounts for about 1.5 kcal/mol[7] in the heat of isomerization, the value for the isomerization of **1** into **2**, corrected for the substitution effect, is +0.6 kcal/mol. Therefore, *exo*cyclic unsaturation in four-membered ring compounds is intrinsically slightly more stable (on an enthalpy basis) than *endo* unsaturation. This situation contrasts with that demonstrated for the five- and six-ring members of the series.[6] The result is not unexpected, since the change from one to two trigonal atoms in the four-membered ring should lead to enhancement of angular strain, but the size of the effect is less than anticipated.



From its heat of combustion[8] cyclobutane is estimated to possess internal strain amounting to 26.2 kcal/mol or 6.55 kcal per methylene group[9] relative to a methylene group of the cyclohexane type as zero. If any substantial part of this strain energy arises from

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[1] Some portions of this work have been published previously in preliminary form.[2,3]

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