Applications of Potential Energy Calculations to Organic Chemistry. Part 17.[1] Calculations of Highly Strained Cyclopropane Derivatives. Evaluation of Several Solar Energy Storage Systems involving Valence Isomerization of Cyclopropane Rings

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Available computational techniques were critically evaluated for their ability to reproduce and predict heats of valence isomerization of highly strained cyclopropane derivatives. Allinger's MM2 cyclopropane parameters were examined for diverse structures including bicyclo[*n*.1.0]alkanes, spiropentanes, and bicyclopropyls. For the bicyclopropyls, a new parameter set was introduced. Experimental structures and energies of these cyclopropane derivatives were well reproduced by MM2 calculation with these parameters. The standard deviation of the enthalpy calculation for 12 compounds was 0.63 kcal mol^{-1}.† Quadricyclane (1) turned out to be the most difficult to calculate. Neither MM2, MNDO, nor *ab initio* calculations with a minimal basis set and gradient geometry optimization reproduced the heat of isomerization of (1) to norbornadiene (20). A homologous isomerization, tetracyclo[$4.2.0^{2,8}.0^{5,7}$]octane (23) into bicyclo[2.2.2]octadiene (24), is predicted to produce an enthalpy of 30 kcal mol^{-1}, 10 kcal mol^{-1} larger than that of the familiar reaction of (1) to (20). Two other isomerizations, (1*R*,3*R*)-tricyclo-[$3.2.1.0^{1,3}$]oct-6-ene (25) to 5-methylenenorbornene (26), and (1*R*,2*R*)-tricyclo[$4.2.1.0^{1,3}$]non-7-ene (27) to 5-methylenebicyclo[2.2.2]oct-2-ene (28), are predicted to give $\Delta H^{\ddagger}$ 26 kcal mol^{-1}. MM2 is the most convenient method to calculate isomerization of cyclopropane derivatives excepting quadricyclane.

Recent interest in the valence isomerization of highly strained cyclopropane derivatives such as quadricyclane (1) as a means of solar energy utilization [2] has created the need to predict the heat of reaction in these transformations. However, the calculation of strained molecules as big as (1) poses a number of practical problems. They are generally too large for the *ab initio* MO method with an extended basis set and force relaxation, despite the recognized success of this approach in smaller cyclopropane derivatives.[3-7] Semiempirical SCF MO methods such as MNDO [8] often fail with strained polycyclic molecules such as cubane,[8,9] hence their credibility must be checked on a case-by-case basis. In the empirical force field method,[10-12] the cyclopropane ring has been either excluded,[13] regarded as a rigid body,[14-16] or treated as a special system in which ring carbon atoms are given special angle bending and torsional constants.[17,18] Allinger [19] has elaborated the last approach in his latest force field, MM2.[20] In view of the generally high performance of MM2,[11,12,21] it appears desirable to extend this approach to more diverse types of cyclopropane derivatives including (1).

In this paper, we apply *ab initio* with a minimal basis set, MNDO, and MM2 methods to calculate highly strained cyclopropane derivatives constrained in condensed ring systems and critically evaluate their performance.

Calculations

The *ab initio* program package IMSPAK [22] was used to calculate molecules having up to 70 atomic orbitals with the STO-3G basis set combined with geometry optimization by the gradient technique.[23] MNDO [24] and MM2 [19] programs were obtained from QCPE.

Results and Discussion

Examination of Original MM2 Parameters for Cyclopropane.—First, Allinger's original parameter set as given in the MM2 program [19] was tested for its ability to calculate structures and energies of cyclopropanes. Table 1 summarizes key structural parameters calculated for various types of cyclopropanes whose precise structures have been determined experimentally. Agreements between the calculated and observed values are satisfactory not only for simple alkyl derivatives but also for strained bicyclo[*n*.1.0.]alkanes and spiropentanes.

A few comments on bicyclo[2.1.0]pentane (2) and bicyclo-[3.1.0]hexane (3) appear appropriate here in view of recent controversies on the length of the bond between bridgehead carbon atoms of these molecules. Electron diffraction analyses gave abnormally short lengths of 1.43—1.45 Å to (2).[25,26] The same method gave an abnormally long length for the opposite cyclobutane bond (1.622 Å).[25] In contrast, microwave analysis [27] produced more uniform lengths for these bonds. Furthermore, three crystalline derivatives [(4)—(6)] of (2) have been subjected to *X*-ray diffraction analysis [28-30] and consistently gave lengths similar to those from the microwave analysis. These ' statistics ' support a view [27b] that the electron diffraction data of (2) [25] have been interpreted incorrectly. Thus, it is most likely that the C(1)–C(4) bond of (2) is slightly shorter than normal (hence abnomally long for a cyclopropane bond), while C(2)–C(3) bond should have typical cyclobutane length (1.555 Å).[31] It is gratifying to note that MM2 structure of (2) fits well with this picture, as does the structure obtained by *ab initio* calculation with split valence basis set and force relaxation (Table 1).

The situation with (3) is more complicated. Among the *X*-ray analyses of derivatives of (3) [(7)—(10)] [30-34] and of heteroatom analogues (11),[35] three of them indicate abnormally short C(1)–C(5) lengths (1.46—1.49 Å), whereas the other three gave slightly longer than normal lengths (1.51—1.52 Å) for the bridgehead–bridgehead bond. Again, MM2 and *ab initio* calculations gave almost identical structure with the C(1)–C(5) bond length of 1.51 Å. In view of the high reliability of *ab initio* calculation with double-zeta type basis set and force geometry optimization in reproducing structures of other strained hydrocarbons,[6] we are inclined to regard the *ab initio* structure as the most reasonable.

The only structural type for which Allinger's cyclopropane

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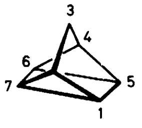
† 1 kcal mol^{-1} = 4.184 kJ mol^{-1}.



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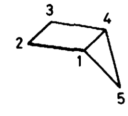

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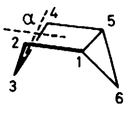

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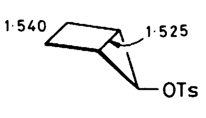

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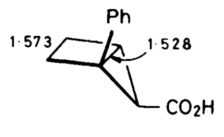

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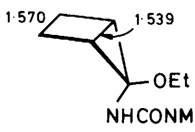

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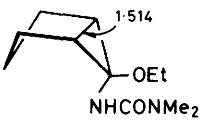

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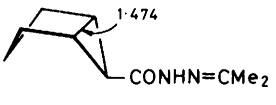

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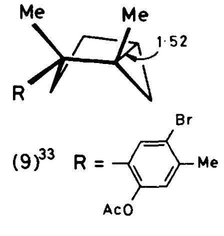

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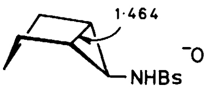

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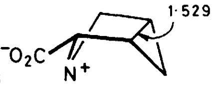
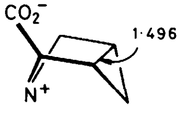


(11a)[35]



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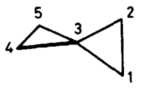

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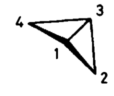

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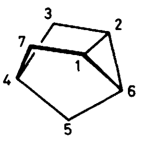

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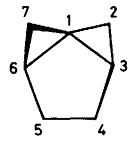

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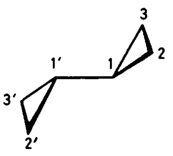

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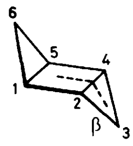

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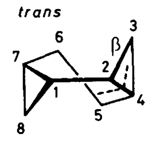

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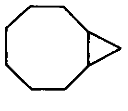

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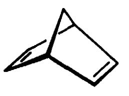

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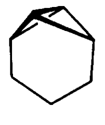

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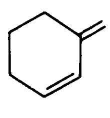

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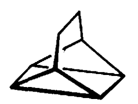

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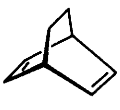

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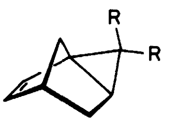

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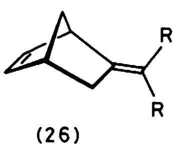

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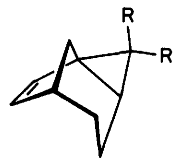

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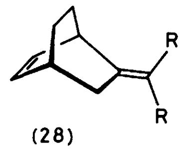


(28)

Bs = 4-bromobenzenesulphonyl

parameter set meets with some difficulty is that of bicyclopropyl. Although Allinger implemented devices for angle bending and torsional parameters in order to distinguish between different cyclopropyl rings when they are joined in the spiro fashion as in spiropentane (12) or fused with each other as in bicyclo[1.1.0]butane (13), no such consideration was given to the bond stretch parameter. Hence, the C–C bond joining two cyclopropyl rings, *e.g.* in *trans*-bicyclopropyl (16), would have been treated simply as the usual endocyclic cyclopropane bond. This bond is known to be abnormally short according to electron diffraction (1.499 Å)[36] and low-temperature *X*-ray diffraction (1.487 Å)[37] analyses, but was calculated to be much longer (1.534 Å) by MM2. We added two natural lengths for bonds that directly connect two cyclopropane rings: one is for the tricyclohexane (17) where the connecting bond is also a cyclobutane bond, and the other is for all other types (Table 3). While the latter, general type may be temporarily fixed at 1.487 Å,[37] it is rather difficult to decide the standard values for the tricyclohexane type. If we give a special atom type (*e.g.* no. 29) to C(1) and C(2) [and to C(4) and C(5)] of (17), not only the C(1)–C(2) [C(4)–C(5)] but also the C(1)–C(5) [C(7)–C(4)] bond become the 29–29 type. The C(1)–C(2) type, which is a cyclobutane bond, appears to change greatly from compound to compound. While electron diffraction of (17) gave only the average lengths,[38] *ab initio* (4-21 G, force relaxation) calculations[39] gave a value (1.504 Å) which is similar to the experimental value of bicyclopropyl.[36,37] However, the corresponding bond in (1) is longer than usual: 1.56—1.57 (electron diffraction)[39] or 1.541 Å (*ab initio*).[40] On the other hand, the C(1)–C(5) [C(2)–C(4)] bond of (17) is predicted to be longer (1.547 Å)[40] than the corresponding bond length of (2) (1.525 Å)[6a] and of (1) (1.524 Å).[40] We place emphasis on reproducing the *ab initio* lengths of (17)[40] and gave two provisional standard lengths for these bonds (Table 2).

The calculated structural parameters of bicyclopropyl

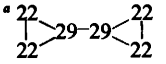
Table 1. Experimental and calculated structural parameters of cyclopropane derivatives [a]

Compound	Parameter	Experimental [b]		Calculated		
		E.d.	Other	MM2 [c]	HF (d.z.) [d]	HF (6—31G*) [d]
Cyclopropane	R(CC)	1.509 [e]	1.512 [f]	1.508	1.509 [g]	1.497 [h,i]
	R(CH)	1.088	1.083	1.088	1.072	1.076
	θ(HCH)	115.1	114.0	115.2	114.9	114.0
	θ(CCH)	117.6		117.7		
Methylcyclopropane	R[C(1)C(2)]	1.509 [j]		1.512		
	R[C(1)C(4)]	1.517		1.520		
trans-1,2-Dimethylcyclopropane	R[C(1)C(2)]	1.508 [j]		1.515		
	R[C(1)C(4)]	1.519		1.521		
Bicyclo[1.1.0]butane (13)	R[C(1)C(2)]		1.498 [k]	1.510	1.497 [l]	1.488 [m]
	R[C(1)C(3)]		1.497	1.486	1.481	1.463
	φ [n]		122.7	126.5	120.0	120.7
	θ[C(1)C(3)H]		128.4	126.8	132.5	131.7
Bicyclo[2.1.0]pentane (2)	R[C(1)C(2)]	1.543 [o]	1.528 [p]	1.537	1.521 [l]	1.528 [i]
	R[C(1)C(4)]	1.439	1.536	1.524	1.525	1.513
	R[C(1)C(5)]	1.521	1.507	1.509	1.500	1.494
	R[C(2)C(3)]	1.622	1.565	1.555	1.555	1.558
	φ	109.4	112.7	121.5	112.4	
2-*endo*-Methyl-(2)	R[C(2)C(6)]		1.535 [q]	1.527		
	θ[C(3)C(2)C(6)]		119.9	115.0		
	θ[C(1)C(2)C(6)]		120.1	117.0		
2-*exo*-Methyl-(2)	R[C(2)C(6)]		1.519 [q]	1.528		
	θ[C(3)C(2)C(6)]		115.0	114.5		
	θ[C(1)C(2)C(6)]		114.8	115.5		
Bicyclo[3.1.0]hexane (3)	R[C(1)C(2)]	1.543 [r]		1.524	1.512 [l]	
	R[C(1)C(5)]	1.454		1.511	1.505	
	R[C(1)C(6)]	1.515		1.511	1.502	
	R[C(2)C(3)]	1.543		1.541	1.540	
	φ	109.4		112.8	111.4	
	α [s]	154.8		150.4	152.5	
Nortricyclene (14)	R[C(1)C(2)]	1.515 [t]		1.512		
	R[C(1)C(7)]	1.527		1.525		
	R[C(3)C(4)]	1.554		1.550		
	θ[C(1)C(2)C(3)]	107.0		107.3		
	θ[C(1)C(7)C(4)]	96.9		95.6		
Spiropentane (12)	R[C(1)C(2)]	1.519 [u]		1.534		
	R[C(1)C(3)]	1.469		1.480		
	θ[C(1)C(3)C(4)]	137.2		137.0		
Tricyclo[4.1.0.0^{1,3}]heptane (15)	R[C(1)C(2)]	1.465 [v]		1.468		
	R[C(1)C(3)]	1.519		1.485		
	R[C(2)C(3)]	1.526		1.545		
	R[C(3)C(4)]	1.521		1.528		
	R[C(4)C(5)]	1.572		1.550		
	θ[C(2)C(1)C(7)]	162.4		150.1		

[a] Distances are reported in Ångstrom and angles in degrees. [b] E.d. = electron diffraction, M.w. = microwave analysis, R.a. = Raman spectroscopy, X = *X*-ray diffraction. [c] Present study. [d] *Ab initio* C–C bond lengths (R_E) are scaled to experimental (E.d., R_G) lengths according to Schaefer.[40b] [e] O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, 1964, **17**, 538. [f] R.a., R. J. Butcher and W. J. Jones, *J. Mol. Spectrosc.*, 1973, **47**, 64. [g] 3—21G basis set, ref. 7, no. 6626. [h] Ref. 7, no. 1104. [i] Ref. 6*b*. [j] A. W. Klein and G. Schrumpf, *Acta Chem. Scand.*, 1981, **A35**, 425. [k] M.w., K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, 1969, **50**, 1976. [l] 4—31G basis set, ref. 6*a*. [m] Ref. 6*a*. [n] Dihedral angle between the two component planes of bicyclic system. [o] Ref. 25. [p] M.w., ref. 27. [q] M.w., M. D. Harmony, C. S. Wang, K. B. Wiberg, and K. C. Bishop, III, *J. Chem. Phys.*, 1975, **63**, 3312. [r] E.d.–M.w. combined method, ref. 26. [s] Dihedral angle between the plane C(1)C(2) · · · C(4)C(5) and the plane C(2)C(3)C(4). [t] R. K. Bohn, K. Mizuno, T. Fukuyama, and K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 1395. [u] G. Dallinga, R. K. Van der Draai, and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas*, 1968, **87**, 897. [v] Z. Smith, B. Andersen, and S. Bunce, *Acta Chem. Scand.*, 1977, **A31**, 557.

Table 2. Additional MM2 parameters for bicyclopropyl inner carbon (atom type no. 29) [a]

	Bond		Force const. (mdyn Å^{-1})	Natural length (Å)	
Stretch	29–29	(Acyclic)	4.4	1.487	
		(3-Ring) [b]	4.4	1.530	
		(4-Ring) [c]	4.4	1.503	
	Angle	Force const. (mdyn Å^{-1} rad^{-2})	Natural angle (°)	NH [d]	
Bend	1–22–29	0.60	118.2	0	
	1–22–29	0.60	110.4	1	
	5–29–29	0.36	112.6		
	5–29–22	0.36	111.7		
	Bond	Normal kcal mol^{-1}	Strainless kcal mol^{-1}		
Heat [e]	29–29	−0.710	1.090		

[a] 

Other atom types used in this Table: 1 = sp^3 carbon, 5 = hydrogen, 22 = cyclopropyl carbon. [b] In three-membered ring, *e.g.* C(1)–C(7) of (1). [c] In four-membered ring, *e.g.* C(1)–C(5) of (1). [d] Number of hydrogen atoms attached to the central atom. [e] Bond increment for the calculation of heats of formation.

derivatives are compared with experimental and *ab initio* values in Table 3. The agreement is only moderate for (1) as expected, albeit the experimental structures of ethano-bridged bicyclopropyl (18)[41] were quite satisfactorily reproduced. Whereas Braun and Traetteberg[41] expected strong repulsion between the 3- and 8-methylene groups and the consequently distorted six-membered ring in *cis*-(18), our calculations indicate no severe crowding between the *cis*-cyclopropane rings (3-H ··· 7-H 2.32 Å) and no significant ring distortion in this isomer compared to *trans*-(18) (ω_{2456} −28.9° for *cis versus* −28.1° for *trans*, ω_{4567} 52.50° for *cis versus* 42.84° for *trans*).

Having surveyed the structural aspects, we now turn to the energy. Only one type of bond increment parameter (29–29) had to be devised and this was used such that the heat of formation and strain energy of bicyclopropyl (16) are exactly reproduced (Table 2). Table 4 summarizes the calculated heats of formation of 15 compounds whose heats of formation have been experimentally determined. Two structures having the bicyclo[1.1.0]butane skeleton [(13) and 1,3-dimethyl-(13)] at first gave heats of formation *ca.* 8 kcal mol^{-1} higher than those observed, indicating that the central cyclopropane bond (−7.429 kcal mol^{-1})[20] must be counted twice in the calculation of heat increments. When this measure was taken, our calculation gave reasonable agreement with experimental values.

Two other structures, *trans*-bicyclo[6.1.0]nonane [*trans*-(19)] and (1), gave discrepancies with experiment of larger than 3 kcal mol^{-1}. The experimental heat of formation of *trans*-(19) was reported by Corbally[42] together with that of the corresponding *cis*-isomer, and he proposed that bicyclo[6.1.0]nonane is the smallest bicycloalkane for which the *trans*-isomer is more stable than the corresponding *cis*-derivative (Table 4). We believe that the reported heat of formation of *cis*-(19) is correct but that of *trans*-(19) incorrect for the following three reasons. First, the three reported experimental heats of formation of *cis*-(19) agree among each other as well as with our calculated value (Table 4). Hence, it is very likely that *cis*-(19) has a heat of formation of 7.5 kcal mol^{-1}. Second, it is more likely that *trans*-(19) will be thermodynamically less stable than *cis*-(19). In the analogous olefin, cyclo-octene, the *trans*-isomer is 10—11 kcal mol^{-1} less stable than the corresponding *cis*-isomer.[43] Finally, SCF MO MNDO calculations[8,24] also accorded higher stability to *cis*-(19) compared with *trans*-(19) (Table 4). Furthermore, whereas Corbally[42] states that the experimental heats of formation of the isomers of (19) agree with force field calculations, the Engler force field[13] that they employed has not been parameterized for cyclopropanes, and therefore the agreement should be considered accidental. In our calculations of (19), an extensive search was carried out for the global energy minimum conformation of the *trans*-isomer, starting from a conformation obtained by adding methylene to the well known C_2 global minimum conformer[10] of *trans*-cyclo-octene, and the starting conformation was confirmed to have the lowest energy (see Appendix). Based on this result, the global minimum conformation of *cis*-(19) was obtained by combining the C_1 global minimum structure of *cis*-cyclo-octene with a methylene group.[44]

We have not found the right way to correct for the calculated heat of formation of (1) which was 14.4 kcal mol^{-1} too high. The reason for the overestimation is probably related to our failure to reproduce its structure with a satisfactory level of precision. Clearly, (1) cannot be regarded as a molecular mechanical extension of (14). Thus, excluding (1), (16), and *trans*-(19), the standard deviation of the calculated heats of formation among the remaining 12 structures in Table 4 is 0.63 kcal mol^{-1}, which should be regarded as falling within the practicable range. For comparison, the corresponding standard deviation of the original MM2 for 42 hydrocarbon molecules is 0.42 kcal mol^{-1}.[20]

Molecular mechanics usually perform less satisfactorily in energy than in structural calculations.[10–13,45] Table 5 gives a few examples which demonstrate some difficulties in reproducing small energy changes accompanied by conformational processes such as *trans*-to-*gauche* interconversions. The errors in these cases are *ca.* 1 kcal mol^{-1}, which one would expect from the magnitude of the standard deviation in energy calculations.

Heats of Valence Isomerization of Strained, Polycyclic Cyclopropane Derivatives.—Three available methods of computation of molecular energies, namely molecular mechanics, and semi- and non-empirical SCF molecular orbital calculations, gave diverse heats of reaction for the quadricyclane $\longrightarrow$ norbornadiene isomerization (Table 6).[46,47] Since all the computations performed in this work involve complete geometry optimization,[23,24,49] the failure of computation should reflect inherent properties of the methods. The excessive heat of reaction obtained by MM2 is due to the overestimation of strain in (1) as mentioned above. MNDO well reproduces the energy of (1), but overestimates the norbornadiene energy by 8 kcal mol^{-1}. The performance of STO-3G gradient calculation is certainly disappointing.

The valence isomerization (21) $\longrightarrow$ (22), for which the heat of reaction has been determined,[49] was overestimated by MNDO. This MO method overestimates the enthalpy of bicyclo[1.1.0]butane (13) by 17 kcal mol^{-1},[8] and hence should be particularly unsuitable for the calculation of this isomerization. The MM2 enthalpy of (21) and MNDO enthalpy of (22) are perhaps correct, since the combination of these reproduces the observed heat of reaction.* For a hypothetical interconversion of homoquadricyclane (23) to bicyclo[2.2.2]-octadiene (24), the three computational methods gave close

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* The reported experimental value pertains to the liquid phase, and may be a few kcal mol^{-1} too high. See ref. 46 for discussion.

Table 3. Experimental and calculated structural parameters of bicyclopropyl and derivatives[a]

		Experimental[b]		Calculated	
Compound	Parameter	E.d.	Other	MM2	HF (d.z.)[c]
trans-Bicyclopropyl (16)	*R*[C(1)C(1′)]	1.499[d]	1.487[e]	1.492	
	R[C(1)C(2)]	1.507	1.501	1.505	
	R[C(2)C(3)]	1.507	1.510	1.511	
	θ[C(1′)C(1)C(2)]	120.9	120.0	120.5	
	θ(HCH)	116.1	113.0	115.0	
	θ[C(1′)C(1)H]	110.5	113.0	116.2	
trans-Tricyclo[5.1.0.0^{2,4}]octane (18)[f]	*R*[C(1)C(2)]	1.447[g]		1.487	
	R[C(2)C(4)]	1.510		1.505	
	R[C(5)C(6)]	1.562		1.537	
	θ[C(1)C(2)C(4)]	122.1		121.3	
	θ[C(2)C(4)C(5)]	115.1		115.7	
	θ[C(4)C(5)C(6)]	114.7		116.6	
	β[h]	108.9		109.7	
	ω[C(4)C(2)C(1)C(7)]	16.7		14.4	
	ω[BCP][i]	55.6		57.4	
cis-Tricyclo[5.1.0.0^{2,4}]octane (18)	*R*[C(1)C(2)]	1.455[g]		1.491	
	R[C(2)C(4)]	1.513		1.507	
	R[C(5)C(6)]	1.559		1.536	
	θ[C(1)C(2)C(4)]	122.4		119.5	
	θ[C(2)C(4)C(5)]	113.8		115.7	
	θ[C(4)C(5)C(6)]	114.3		115.8	
	β[h]	109.7		108.9	
	ω[C(4)C(2)C(1)C(7)]	17.9		18.8	
	ω[BCP][i]	17.9		19.2	
anti-Tricyclo[3.1.0.0^{2,4}]hexane (17)	*R*[C(1)C(2)]			1.511	1.504[k]
	R[C(1)C(5)]	$(1.508)_{av}$[j]		1.545	1.547
	R[C(1)C(6)]			1.503	1.512
	θ[C(2)C(1)C(6)]	109.9		122.7	109.6
	θ[C(2)C(3)C(4)]			61.9	61.5
	θ[C(3)C(2)C(4)]			59.1	59.2
	β[h]	113.0		129.0	
(1)[l]	*R*[C(1)C(2)]	(1.512)[n]	1.503[m]	1.504	1.523[k]
	R[C(1)C(5)]	1.569	1.562	1.503	1.541
	R[C(1)C(7)]	1.517	1.518	1.549	1.524
	R[C(2)C(3)]	1.537	(1.560)[n]	1.555	1.510
	θ[C(5)C(1)C(7)]			90.0	90.0
	θ[C(2)C(1)C(7)]			59.0	60.0
	θ[C(2)C(1)C(5)]	104.6	105.2	108.8	104.3
	θ[C(1)C(2)C(3)]	110.5	110.2	103.0	110.5
	θ[C(2)C(3)C(4)]	98.3	97.5	105.3	99.4
	ω[C(1)C(2) · · · (C4)C(6)]	62.8	63.1	66.0	62.2
	ω[C(5)C(1)C(7)C(2)]	106.5	107.7	112.1	106.6

[a] Distances are reported in Ångstrom and angles in degrees. [b] See footnote *b* of Table 1. [c] See footnote *d* of Table 1. [d] Ref. 36. [e] X, ref. 37. [f] Favoured conformer with H(1) and H(2) in diequatorial disposition. [g] Ref. 41. [h] Dihedral angle between the plane C(1)C(2)C(4)C(5) and the plane C(2)C(3)C(4). [i] Dihedral angle between two cyclopropyl planes. [j] Ref. 38. [k] 4—21G, ref. 40. [l] Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane. [m] Ref. 39. [n] Assumed.

estimates of *ca.* 30 kcal mol^{-1} for the heat of reaction. We tend to believe this coincidence, because no unusual and difficult features are involved in the structures of (23) and (24), and the calculations probably worked well for this reason. If so, it is interesting to note that this series produces *ca.* 10 kcal mol^{-1} more energy than the familiar (1) → (20) system. The predominant contributor to the increased heat of reaction is the high stability of (24) compared with (20): the enthalpy difference between (20) and (24) (20 kcal mol^{-1}) is much larger than the heat increment of methylene group (5.9 kcal mol^{-1}),[13] and the enthalpy difference between (1) and (23) is only 10 kcal.

For the reactions (25) → (26) and (27) → (28),[51] MNDO gave much higher heats of reaction than MM2. The cyano-group appears to increase the heat of reaction. Both MM2 and MNDO predict that the use of (27), a homologue of (25), decreases the heat of reaction, in contrast to the (1) → (20) system. However, it may be noted that even the

Table 4. Experimental and calculated heats of formation and strain energies of cyclopropane derivatives (kcal mol^{-1})

Compound	Heat of formation			Strain	
	Experimental [a]	Calculated [b]	Difference	Lit. [c]	MM2 [b]
Cyclopropane	12.74	13.37	0.63	28.13, 27.5 [d] 30.8 [e]	28.24
cis-1,2-Dimethylcyclopropane	1.3 [f]	1.47	0.17	30.85	27.86
Ethylcyclopropane [g]	1.1 [f]	−0.29	−1.39	28.7	27.67
(13)	51.9	52.39 [h]	0.49	66.5	66.77
1,3-Dimethyl-(13)	39.3	41.42 [h]	2.12	70.0, 65.9 [i]	66.82
(2)	37.6, 37.0 [i]	36.30	−0.70	57.3, 54.6 [d] 64.9,[e] 56.1 [i]	55.94
(3)	9.07, 9.3 [i]	8.60	−0.70	33.91, 33.5 [i]	33.99
1,3,5-Trimethyl-(3) [j]	−15.5 [c]	−15.39	0.11	30.6	31.42
Bicyclo[4.1.0]heptane [k]	0.32, 0.4 [i]	1.21	0.81	30.29, 29.6 [i]	32.36
Nortricyclene (14)	28.8, 19.7 [f] 19.6,[l] 20.2 [m]	19.48	−0.72	47.0	43.96
cis-Bicyclo[6.1.0]nonane (19) [n]	−7.42, −7.6 [i] −7.29 [o]	−7.69 (−8.57) [p]	−0.4	32.81, 31.8 [i]	34.98
trans-Bicyclo[6.1.0]nonane (19)	−9.49 [o]	−5.75 (−4.45) [p]	3.72		36.92
(12)	44.23	43.96	−0.27	65.05	63.61
(16)	31.0 [q]	31.0 [r]	0.0 [r]	55.8	55.80 [r]
(1)	79.5 [m]	93.87	14.4	95,[d] 108.6 [e]	110.34

[a] Unless otherwise noted taken from S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279. [b] This work. [c] Unless otherwise noted taken from P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Am. Chem. Soc.*, 1970, **92**, 2377. [d] Ref. 6*b*. [e] Ref. 40*b*. [f] R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, jun., and M. Pomerantz, *J. Am. Chem. Soc.*, 1968, **90**, 4315; K. B. Wiberg and R. A. Fenoglio, *ibid.*, p. 3395. [g] Methyl group is *gauche* to an edge of cyclopropane ring. Alternative conformation (C_s) with ethyl group bisecting cyclopropane plane is excluded since it was calculated to have a steric energy 3 kcal mol^{-1} higher than the *gauche*-form. [h] The central bond of the bicyclo[1.1.0]butane skeleton is counted twice for calculating the heat increment of the endocyclic cyclopropane C–C bond contribution. See text. [i] S. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *J. Am. Chem. Soc.*, 1970, **92**, 3109. [j] Boat conformation with equatorial 3-methyl. [k] The predominant conformation of bicyclo[4.1.0]heptane has its six-membered ring in the half-chair conformation, A. Aumelas, E. Casadevall, and A. Casadevall, *J. Chem. Res.* (*S*), 1981, 111; *J. Chem. Res.* (*M*), 1981, 1360. Our optimized geometry indeed gave a half-chair six-membered ring for this molecule, with the following endocyclic dihedral angles starting from the fused bond: −2.8, 18.4, −49.5, 64.5, −49.6, 19.0°. [l] W. V. Steele, *J. Chem. Thermodyn.*, 1978, **10**, 919. [m] Ref. 47. [n] Global energy minimum conformation was assumed in analogy with the global minimum conformation of *cis*-cyclo-octene oxide which has a chair-boat cyclo-octane moiety, K. L. Servis and E. A. Noe, *J. Am. Chem. Soc.*, 1973, **95**, 171. Optimized dihedral angles along the eight-membered ring of *cis*-(19) are, starting from the fused bond: 3.8, −84.6, 76.0, −70.4, 105.3, −58.3, −52.2, 89.9°. [o] Ref. 42. [p] By MNDO. [q] A. E. Beezer, W. Lüttke, A. de Meijere, and C. T. Mortimer, *J. Chem. Soc. B*, 1966, 648. [r] Normal and strainless heat increments (Table 2) for the 29–29 type bond are given to reproduce the reported heat of formation and strain energy of (14).

Table 5. Experimental and calculated conformational enthalpies of several cyclopropane derivatives (kcal mol^{-1})

		Experimental	Calculated
(16)	*trans-gauche*	0.17 [a]	−0.93
trans-(18)	Unfavoured [b] − favoured [c]	1.1 [d]	2.04
Isopropylcyclopropane	*gauche-trans*	0.72 [e]	2.35

[a] H. Braun and W. Lüttke, *J. Mol. Struct.*, 1975, **28**, 391. [b] Unfavoured *trans*-(18) has H(1) and H(2) in diaxial disposition. See ref. 41. [c] See footnote *f* of Table 1. [d] Estimated based on the 13% composition of unfavoured conformer in *trans*-(18) obtained by E.d. analysis.[41] [e] T. Schaefer, R. Sebastian, and R. E. Wasylishen, *Can. J. Chem.*, 1982, **60**, 845.

minimum predicted heat of reaction for (25) ⟶ (26) is the largest known among the solar energy storage systems.

Conclusions

Highly strained cyclopropanes are generally difficult to calculate by available versions of molecular orbital methods. Molecular mechanics (MM2) is most suitable for this purpose, although the enthalpy and structure of quadricyclane (1) is badly reproduced by this method. MM2 gives good results for various types of cyclopropane derivatives except for (1). The accuracy of MM2 in calculating energies of cyclopropanes is high, but errors may amount to ±1 kcal mol^{-1}. A homologue (23) of quadricyclane is predicted to produce 10 kcal mol^{-1} more energy than (1) in the valence isomerization to tricyclic diene.

Appendix

Torsional Energy Surface Coverage of trans-*Bicyclo*[6.1.0]-*nonane* trans-(19).—In order to search the energy surface as extensively as possible, five sets of three-dimensional energy surface were drawn up by using highly automated two-bond

Table 6. Heats of formation of some cyclic dienes and their photoisomers and isomerization enthalpies (kcal mol^{-1})

	MM2	MNDO	STO-3G [a]	Experimental
(1)	93.87 [b]	81.88	(−266.414 51) [c]	79.5,[d] 80.9 [e]
Norbornadiene (20)	55.24	65.30	(−266.422 65) [c]	57.4,[d] 59.1 [e]
$\Delta\Delta H_F$	38.63	16.58	5.11	22.1,[d] 21.8 [e]
Tricyclo[4.1.0.$0^{2,7}$]heptane (21)	45.27	52.91		
3-Methylenecyclohexene (22)	(14.28)	14.28		
$\Delta\Delta H_F$	(30.99)	38.63		29.99 [f]
Tetracyclo[4.2.0.$0^{2,8}$.$0^{5,7}$]octane (23)	66.72	70.46	(−304.985 12) [c]	
Bicyclo[2.2.2]octadiene (24)	37.31	36.55	(−305.037 52) [c]	
$\Delta\Delta H_F$	29.41	33.91	32.88	

	R = H	R = H	R = CN
(1*R*,3*R*)-Tricyclo[3.2.1.$0^{1,3}$]oct-6-ene (25)	81.26	109.20	183.02
5-Methylenenorbornene (26)	44.03	47.38	109.78
$\Delta\Delta H_F$	37.22	61.82	73.24
(1*R*,3*R*)-Tricyclo[4.2.1.$0^{1,3}$]non-7-ene (27)	54.91	68.85	145.24
5-Methylenebicyclo[2.2.2]oct-2-ene (28)	29.08	25.14	89.35
$\Delta\Delta H_F$	25.83	43.71	55.89

[a] *Ab initio* calculation with minimal basis set and geometry optimization with gradient method. [b] Overestimated by 14 kcal mol^{-1}. See Table 4. [c] Total energy in atomic units. [d] Ref. 47. [e] Ref. 48. [f] Ref. 50.

Table 7. Torsional and valence angles (°) along the eight-membered ring portion of four energy minimum conformations of *trans*-bicyclo[6.1.0]nonane (19)

Atom no.	M1 [a]		M3		M2		M4	
	Torsion [b]	Valence [c]	Torsion	Valence	Torsion	Valence	Torsion	Valence
1	−128.9	112.7	−122.8	110.6	−129.4	112.3	−120.9	111.2
2	87.1	112.7	77.3	111.5	53.2	112.3	95.8	111.2
3	−55.0	111.0	−66.3	111.3	43.1	113.4	−31.5	110.7
4	81.4	114.7	95.9	114.8	−90.6	115.7	−56.8	116.3
5	−115.3	116.2	−42.4	118.5	91.0	117.0	120.3	115.8
6	81.3	116.2	−62.0	120.6	−90.6	117.0	−56.8	115.8
7	−55.0	114.7	54.4	117.1	43.1	115.7	−31.5	116.3
8	87.1	111.0	53.9	112.4	53.2	113.4	95.8	110.7
Point group	C_2		C_1		C_2		C_2	
ΔH_F/kcal mol^{-1}	−5.75		−2.38		−2.03		−0.37	

[a] M1—M4 refer to the corresponding conformers of *trans*-cyclo-octene.[52] [b] Torsional angles at atom *n* means that of (*n* − 1)*n*(*n* + 1)(*n* + 2) four-atom unit. For atoms 1, 7, and 8, angles refer to 8–1–2–3, 6–7–8–1, and 7–8–1–2, respectively. [c] Valence angle at atom *n* means that of (*n* − 1)*n*(*n* + 1) three-atom unit. For atoms 1 and 8, angles refer to 8–1–2 and 7–8–1, respectively.

driver option of MM2,[51] with the following combination of dihedral angles and ranges:

	ω_A	Start (°)	Finish (°)	ω_B	Start (°)	Finish (°)
1	2 345	−90	90	6 781	−105	90
2	2 345	−75	75	5 678	−120	105
3	3 456	−135	120	6 781	−105	75
4	3 456	−120	105	5 678	−120	105
5	4 567	−135	135	6 781	−105	75

Each surface contained three to five energy minima. Re-minimization of these gave four unique energy minima (Table 7). As expected, there exists a close relation between (19) and *trans*-cyclo-octene. Ermer[52] has detected five energy minima for the latter, of which the lowest four correspond to those of (19). Although the relative stability of M2 and M3 is reversed in (19), the global energy minimum conformation M1 is common to both molecules.

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