

The Energetics of Cyclopropene, 1,4-Cyclohexadiene, and Some of Their Hetero- and/or Exocyclic Derivatives

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The recently defined concept of “ultradiagonal” strain energy is applied to cyclopropene, cyclopropene, and methylenecyclopropene and their respective diaza and diphospha derivatives using ab initio (DFT) calculations. In the relatively few cases where comparisons could be made between theory and either experiment or earlier calculational studies, very good agreement for both energies and structures were found. This gives us confidence for the remaining species. The results were also qualitatively explained, and the concept of ultradiagonal strain gibbs energy is briefly discussed.

Introduction

In a recent study,¹ we defined the “ultradiagonal” strain energy (UDSE) of compounds containing three-membered rings (3MR) as half of the exothermicity of the formal dimerization reaction



where *cyclo*(XYZ)₂ is the unique dimer of a set of six in which both nearest-neighbor and next-nearest-neighbor bonding is conserved; i.e., it has the *cyclo*(XYZXYZ) connectivity. This is taken to be the case for whatever atoms (groups) X, Y, and Z compose the 3MR. For the initial paper,¹ this definition was applied to a set of heterocyclopropanes, *cyclo*(XYZ) = (CH₂)₂E, and of heterodisiliranes, (SiH₂)₂E, wherein E = >CH₂, >NH, >O, and >SiH₂, and shown to give results that seemed reasonable and agreed well with the small bits of experimental information that exist. All of these species were saturated systems; e.g., we recognize the formal dimerization of aziridine and oxirane to form 1,4-dioxane and piperazine and neither of their 1,3- or 1,2-isomers. In the current study, we apply this “ultradiagonal” definition to an understanding of a set of unsaturated 3MR, various derivatives of cyclopropene with the general formula *cyclo*(X₂Z). The choice of X was made to include the parent carbocycle with X = -CH=, Z = >CH₂, and its simplest heterocyclic analogues and derivatives; we recognize the dimers as analogues and derivatives of 1,4-cyclohexadiene and not of the 1,3-isomer with its “extra” double bond–double bond interaction. In particular, we considered only the heterocyclic analogues containing X = -N= and -P= as befits our long-term interest in diagonal and vertical relationships in the periodic table as evidenced by a recent study of boron–silicon and carbon–silicon chemistry;² we note that other such relationships may include carbon, nitrogen, and phosphorus.³ The choice of Z was made to parallel another earlier study of ours⁴ that provided

understanding for a large set of unsaturated alicyclic ring species. It is immediately ledged that experimentally measured thermochemical data are almost totally absent for the current species. We will apply our findings in ref 4 to the present work: all unreferenced enthalpies of formation in the current study are implicitly from that source.

Experimental structure data are lacking for many of the systems considered in the present work, and for the sake of consistency we consider only the energies of the end points of the geometry optimization for all the systems.

Computational Methods

Our calculations were carried out using a density functional approach⁵ using Becke’s three-parameter hybrid exchange functional⁶ with the nonlocal correlation functional by Lee, Yang, and Parr.⁷ In all of our calculations, the 6-31G(d) basis set was used,⁸ resulting in the so-called B3LYP/6-31G* calculational level. At the end point of the optimizations, analytical vibrational frequencies were computed using the same method and level. Thus, all of the stationary points were characterized as either minima or saddle points. Recent systematic studies based on different DFT schemes have demonstrated that this particular functional form performs remarkably well in predicting energies, geometries and vibrational frequencies.⁵ The computer program⁹ GAUSSIAN 94 has been used throughout our project. Table 1 gives the assembled total energies for all of the species studied in this paper.

(3) We note a recently published book emphasizes this carbon/phosphorus similarity explicitly in its title: Dillon, K.; Mathey, F.; Nixon, J. F. *Phosphorus: the Carbon Copy*; Wiley: New York, 1998.

(4) Liebman, J. F.; Skancke, A. *Mol. Phys.* **1997**, *91*, 471.

(5) See, for instance: Seminario, E. D., Ed. *Recent Developments of Modern Density Functional Theory (Theoretical and Computational Chemistry, Vol. 4)*; Elsevier: Amsterdam, The Netherlands, 1996.

(6) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

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






















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(2) Skancke, A.; Liebman, J. F. *J. Mol. Struct.* **1998**, *445*, 29.

Table 1. Total Energies (in au) for Species 1–18

System	E(B3LYP)/6-31G*	n	EZPE corrected	Symm.	H corrected ^{a)}	G corrected ^{b)}
 (1)	-116.61904	0	-116.56277	C _{2v}	-116.55851	-116.58606
 (2)	-233.41850	0	-233.29594	D _{2h}	-233.28976	-233.32310
 (3)	-148.72055	0	-148.68689	C _{2v}	-148.68293	-148.70989
 (4a)	-297.50071	1	-297.42669	D _{2h}	-297.42160	-297.45352
 (4b)	-297.51173	0	-297.43760	C _{2v}	-297.43215	-297.46459
 (5)	-721.97416	0	-721.94550	C _{2v}	-721.94113	-721.97104
 (6a)	-1443.98511	1	-1443.92591	D _{2h}	-1443.91837	-1443.95657
 (6b)	-1443.99975	0	-1443.93985	C _{2v}	-1443.93188	-1443.97126
 (7)	-154.70131	0	-154.64038	C _{2v}	-154.63539	-154.66533
 (8)	-309.61688	0	-309.48404	D _{2h}	-309.47640	-309.51328
 (9)	-186.78310	0	-186.74538	C _{2v}	-186.74062	-186.77014
 (10a)	-373.69165	1	-373.60807	D _{2h}	-373.60161	-373.63620
 (10b)	-373.69166	0	-373.60808	C _{2v}	-373.60075	-373.63859
 (11)	-760.04961	0	-760.01647	C _{2v}	-760.01117	-760.04357
 (12a)	-1520.16391	1	-1520.09369	D _{2h}	-1520.08456	-1520.12617
 (12b)	-1520.16491	0	-1520.09478	C _{2v}	-1520.08474	-1520.12958
 (12c)	-1520.15261	0	-1520.08354	C _{2v}	-1520.07322	-1520.11779
 (13)	-190.64191	0	-190.60404	C _{2v}	-190.59949	-190.62872
 (14)	-381.45168	0	-381.36633	D _{2h}	-381.35916	-381.39554
 (15)	-222.71248	0	-222.69763	C _{2v}	-222.69338	-222.72205
 (16a)	-445.49409	1	-445.45876	D _{2h}	-445.45260	-445.48698
 (16b)	-445.49974	0	-445.46613	C _{2v}	-445.45876	-445.49625
 (17)	-795.98074	0	-795.97075	C _{2v}	-795.96583	-795.99764
 (18a)	-1591.97803	2	-1591.95604	D _{2h}	-1591.94782	-1591.98813
 (18b)	-1591.98667	0	-1591.96494	C _{2v}	-1591.95492	-1592.00089

^a Sum of electronic and thermal enthalpies (298 K). ^b Sum of electronic and thermal free energies (298 K).

Results

Energetics. We commence with the parent cyclopropene, X = -CH= and Z = >CH₂ (species **1**), for which the dimerization reaction enthalpy, the difference of the enthalpies of formation of two cyclopropenes¹⁰ and one 1,4-cyclohexadiene (CHD, species **2**), is ca. 449 kJ (mol-

(10) All enthalpies of formation and of reaction, and strain energies, in the current paper are in kJ mol⁻¹ where by definition 4.184 kJ mol⁻¹ equals 1 kcal mol⁻¹. All calculated total energies are reported in au where 1 au equals 2625 kJ mol⁻¹.

CHD)⁻¹. Letting "mol⁻¹" refer to the six-membered ring (6MR) species, the value calculated in this paper is 454 kJ mol⁻¹ in very good agreement. Are these values, 449 and 454 kJ mol⁻¹, reasonable? Let us immediately divide these numbers by 2 and thus return to the 3MR strain energies of direct interest.¹¹ The strain energy values obtained, 225 or 227 kJ mol⁻¹, are very close to an archive value¹² for the strain energy of cyclopropene, 228.0 kJ mol⁻¹, and so the calculations are credible. Consider now X = -N= and Z = >CH₂ (diazirine, species **3**). While

there are recommended enthalpies of formation of the relevant parent heterocycle and several other diazirines,¹³ there are apparently no available thermochemical data on the parent 3,6-dihydro-1,2,4,5-tetrazine (**4b**) nor any other tetrazine derivative at all. From our calculations, we find a strain energy of diazirine of 87 kJ·mol⁻¹. The difference of this value and that of cyclopropene is profound—it is all but irrelevant with which value (currently calculated, earlier derived,⁴ or “archival”¹²) is chosen for cyclopropene. This diazirine result is plausible. In the 3MR diazirine the nitrogen lone pairs are splayed out relative to the 6MR and so there is less repulsion. Equivalently, the 3MR is effectively stabilized and has less strain energy. The reader is now alerted to the fact that species **2** is planar while **4b** is not.

What is found for 3*H*-diphosphirene, species **5** with X = -P= and Z = >CH₂? The result is hard to disentangle. Recall, “[h]eteroatoms in small heterocyclic rings affect bond angles, bond lengths and bond strengths through a combination of factors, including their intrinsic hybridization, magnitude of covalent radii, angle-bending constants, nonbonding interactions, and long-range electronic effects.”¹⁴ For example, lone pair effects are expected to be smaller because the lone pairs are more s-like, more symmetric, more indifferent to their environment. Furthermore, as shown by amines and phosphines, the “natural” angles around P are smaller than those of N, and so more accommodating to the geometric demands of a 3MR. Our calculations result in a strain energy for **5** of 65 kJ mol⁻¹. This value seems small, perhaps too small, until it is recalled that elemental phosphorus has a white allotrope composed of tetrahedral P₄ molecules, and this is but ca. 10 kJ (mol-P)⁻¹ higher in energy than the seemingly unstrained red and black allotropes.¹⁵ By contrast, 6MR, as seen in species **6**, are not particularly commonplace, special or important in phosphorus chemistry.

We now turn to a comparison of methylenecyclopropene and *p*-xylylene, species **7** and **8**, respectively, with X = -CH= and Z = >C=CH₂. Use of the earlier recommended values¹⁶ results in a strain energy of methylenecyclopropene of 275 kJ·mol⁻¹, while the current study gives 269, again in good agreement. The increased strain energy over cyclopropene itself is consistent with

(11) Admittedly, for some of the species discussed in this paper, e.g., for X = -CH=, Z = >CO (cyclopropenone), there are sources of both destabilization and stabilization; see also: Skancke, A.; Hosmane, R. S.; Liebman, J. F. *Acta Chem. Scand.* **1998**, *52*, 967. We lump all of these destabilization and stabilization effects together and consider for the current paper the net destabilization to be the “strain energy”.

(12) See, for example: Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978; especially p 91ff.

(13) See the discussion in: Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1989**, *89*, 1225.

(14) Greenberg, A.; Liebman, J. F. Reference 12, p 260.

(15) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C₁ and C₂ organic substances in SI units. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2. For a discussion of the preferred thermochemical reference state for phosphorus, namely this P₄ allotrope as opposed to the thermodynamically more stable red and black forms, see: Skancke, A.; Slayden, S. W.; Liebman, J. F. *Struct. Chem.* **1998**, *9*, 429.

(16) We opted for the calculationally consistent enthalpy of formation of methylenecyclopropene from ref 4, not that previously recommended in the literature. We still do not understand the discrepancy between the values derived from theory and experiment. However, it is encouraging that the strain energies for cyclopropene and methylenecyclopropene calculated in the current paper have very nearly the same difference that would be calculated using our “ultradiagonal” approach with the numbers in ref 4.

the destabilizing presence of another trigonal carbon atom¹⁷ ameliorated by some π -stabilization (dare we say en route to “aromaticity”?) in the 3MR.

Consider now the diazirine derivative, species **9**, and its dimer **10**, with X = -N= and Z = >C=CH₂. The strain energy is reduced to 157 kJ mol⁻¹. In other words, the two nitrogens in the 3MR result in a decrease of strain energy of 113 kJ mol⁻¹, where recall we compare all of our currently calculated results with those of the current cyclopropene/cyclohexadiene difference. This self-consistency of the choice of values was expected to facilitate understanding of the results. This is realized. For example, the effect of the two nitrogens in decreasing the strain energy of diazirine from that of cyclopropene is 154 kJ mol⁻¹. Is the effect of the *exo*-methylene, some 157–113 = 44 kJ mol⁻¹, significant? Admitting that less is known about the thermochemistry of compounds containing their “substructures”, both azo compounds¹⁸ and enamines¹⁹ alike, than we would want or expect, we acknowledge the plausibility of the value. From electronegativity reasoning we expect the nitrogens to reduce the cyclopropenium contribution in species **6** relative to that of **7**, and thereby reduce whatever aromatic stabilization we wish to invoke for the carbocyclic methylenecyclopropene ring system.

We are not aware of any experimental energy data for species **11** and its dimers **12a–c** with X = -P= and Z = >C=CH₂, wherein system **12b** is the lowest energy species. However, a recent study on benzene valence isomers and their phosphorus analogues gives an interesting example of a related species with a P–P one-electron π bond.²⁰ The strain energy of **11** is but 82 kJ mol⁻¹, the exomethylene resulting in a small increase for 3*H*-diphosphirene **5** as opposed to that for cyclopropene **1**, compatible with phosphorus having a somewhat lower electronegativity than carbon.

Let us turn to cyclopropenone, species **13**, *p*-benzoquinone, **14**, and their relatives with X = -CH= and Z = >CO. The currently calculated strain energy is 210 kJ mol⁻¹, while from the previous results we would have found a value of 211 kJ mol⁻¹. Again, the current and previous sets of calculational results are encouragingly consistent.¹⁶ The strain energy is less than that of cyclopropene. This seems unreasonable until it is remembered that cyclopropenones are usually considered to be aromatic²¹ and correcting for its ca. 80 kJ mol⁻¹ of aromatic stabilization results in an altogether reasonable 60 kJ mol⁻¹ of >C=O or trigonal carbon-induced destabilization.¹⁷

The penultimate species to be discussed are **15** and **16** with X = -N= and Z = >CO. A strain energy of 94 kJ mol⁻¹ is found for species **15**. Because the electronegativity of nitrogen is higher than carbon, we expect greater aromatic stabilization for cyclopropenone than its diaza analogue. This is indeed found. The decrease of strain

(17) Wiberg, K. B.; Fenoglio, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3395. Also, see: Liebman, J. F. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: Chichester, UK, 1995; Vol. 2.

(18) Liebman, J. F.; Afeefy, H. Y.; Slayden, S. W. In *The Chemistry of Hydrazo, Azo and Azoxy Groups*; Patai, S., Ed.; Wiley: Chichester, UK, 1997; Vol. 2.

(19) Liebman, J. F.; Perks, H. M. In *The Chemistry of Enamines*; Rappoport, Z., Ed.; Wiley: Chichester, UK, 1994.

(20) Canac, Y.; Bourissou, D.; Baceiredo, A.; Gornitzka, H.; Schoeller, W. W.; Bertrand, G. *Science* **1998**, *279*, 2080.

(21) Steele, W. V.; Gammon, B. E.; Smith, N. K.; Chickos, J. S.; Greenberg, A.; Liebman, J. F. *J. Chem. Thermodyn.* **1985**, *17*, 505.

Table 2. Calculated Strain Energy of *cyclo*-(X₂Z) Species (in kJ mol⁻¹)

Z =	X =		
	-CH=	-N=	-P=
>CH ₂	227	87	65
>C=CH ₂	269	157	82
>CO	210	94	31

energy on going from cyclopropene to the ketone is 17 kJ·mol⁻¹, while for diazirine the strain energy increases by 7 kJ mol⁻¹.

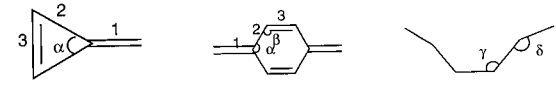
We conclude this section with a brief discussion of diphosphirenone, **17**, and its dimer **18b** with X = -P= and Z = >CO. The strain energy of the 3MR is 31 kJ mol⁻¹. Essentially low for a 3MR—see summary Table 2—it is altogether plausible in terms of the already low value for the parent heterocycle **6** and its diminution because of the aromaticity and electronegativity effects already documented but less strongly for the 3-methylenediphosphirene, species **11**. As seen from the behavior of the carbocyclic methylenecyclopropene and cyclopropenone and their diaza analogues, we expect **17** to enjoy greater stabilization and less strain energy than **11**.

It is seen that the calculated results for most of the species X₂Z we have investigated are internally consistent but experimentally uncorroborated—we await further theoretical and experimental investigations corroborating and extending our findings.

Structural. The focus in the present work has been on energy differences between ground-state species rather than on structural detail. However, since DFT methods have been far less used in structural determination and understanding than, for instance, Møller–Plesset perturbation analysis, the quality of the method and basis set employed here is of interest.

A number of the compounds discussed in the present text are well-characterized species; this is especially true for *p*-benzoquinone (**14**) and methylenecyclopropene (**7**). The former is the archetypical example in a vast and ubiquitous series of compounds, the quinones;²² the latter is an example of a class of well-characterized strained molecules. Hence, we use these examples as test cases for the employed level of sophistication and note that an early electron diffraction study²³ of *p*-benzoquinone gave a *D*_{2h} (planar) form with the >C=O (denoted 1 in Table 3) of 1.225 ± 0.002 Å, the >C=C< bond (denoted 3 in Table 3) of 1.344 ± 0.003 Å and the C–C bond (denoted 2 in Table 3) of 1.481 ± 0.002 Å. As shown in Table 2, our results are in very good agreement with these data. Furthermore, there is additional support in the nearly identical results from an early X-ray structural determination.²⁴

Methylenecyclopropene (**7**) may be considered the simplest of the fulvene systems. There is an exceptionally high polarity in this molecule with an experimentally determined dipole moment of 1.90 ± 0.2 D. Our computed value was 2.0 D, and hence the electron flow from the ring is well accounted for. Moreover, theory gave structural results in very good agreement with the literature results from microwave spectroscopy²⁵ that gave an

Table 3. Distances (in Å) and Angles (in deg) Obtained from B3LYP/6-31G* Optimization


system	distance 1	distance 2	distance 3	α	β	γ	δ
1		1.509	1.205	50.8			
2		1.506	1.335	112.9	123.6	180.0	
3		1.478	1.228	49.1			
4a		1.429	1.431	110.7	124.6	180.0	
4b		1.479	1.242	112.0	115.7	140.8	
5		1.879	2.026	65.2			
6a		1.881	2.037	130.7	114.6	180.0	
6b		1.887	2.048	118.2	105.5	121.4	
7	1.330	1.446	1.320	54.3			
8	1.354	1.461	1.350	116.0	122.0	180.0	180.0
9	1.316	1.406	1.267	53.6			
10a	1.347	1.416	1.264	123.1	118.3	180.0	180.0
10b	1.347	1.416	1.264	122.6	118.3	170.7	178.1
11	1.330	1.813	2.055	69.1			
12a	1.356	1.834	2.049	133.1	113.5	180.0	180.0
12b	1.354	1.835	2.050	128.9	110.9	173.6	177.8
12c	1.336	1.806	2.380	78.5	98.2	100.6	179.1
13	1.207	1.436	1.346	55.9			
14	1.225	1.487	1.343	117.2	121.4	180.0	
15	1.192	1.386	1.311	56.5			
16a	1.200	1.459	1.254	122.3	118.9	180.0	
16b	1.028	1.396	1.254	125.2	116.1	145.2	
17	1.199	1.831	2.100	70.0			
18a	1.216	1.907	2.051	134.2	112.9	180.0	
18b	1.210	1.911	2.056	123.7	104.5	122.0	

exocyclic bond of 1.332 ± 0.006 Å, a C–C bond of 1.441 ± 0.006 Å, and a ring C=C bond of 1.323 ± 0.003 Å in very good agreement with experiment.

Thus, the geometric framework is well reproduced by our computations. We note that MP2/6-31G*-optimized calculations in ref 25 also gave very good agreement for the geometric parameters, but the dipole moment was calculated to be 2.33 D.

Conformational preferences are issues for the six-membered ring systems being investigated. For 1,4-cyclohexadiene (**2**) itself the preferred conformation has been the source of some controversy,²⁶ but the most recent findings from X-ray analysis²⁷ and others' ab initio calculations²⁸ agree on planarity along with our calculations.

These specimen examples suggest that B3LYP/6-31G* is at least as good as MP2/6-31G* for structure determination, and since a much larger portion of the correlation energy is included, energy comparisons with density functional theory should be more trustworthy²⁹ than second-order Møller–Plesset theory.

Many of the systems (most of the N-containing species and, indeed, all of the P-containing species) reported in Table 3 are unknown experimentally to our knowledge. The quality of the data reported in Table 3 is thus more difficult to appraise.

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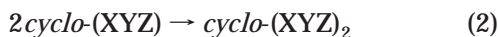
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Table 4. Calculated Strain Gibbs Energy (UDSG) of *cyclo*-(X₂Z) Species (in kJ mol⁻¹)

Z =	X =		
	-CH==	-N=	-P=
>CH ₂	198	59	38
>C=CH ₂	240	129	56
>CO	181	68	7

Comparing the conformations of 1,4-cyclohexadiene and its tetraaza and tetraphospha derivatives (species **2**, **4**, and **6**, respectively) gives a preference for the *C*_{2v} form over the *D*_{2h} form of 0, 28, and 36 kJ·mol⁻¹ and increasingly nonplanarity as shown by deviation from 720° for the sum of all six internal angles of the hexagonal ring. Comparing the related bis *exo*-methylene species, *p*-xylylene and its tetraaza and tetraphospha derivatives (species **8**, **10**, and **12**, respectively), is somewhat complicated. **8** is a true energy minimum. Although **10b** is a true minimum and **10a** is a transition state, these two species have virtually the same energy and geometry. For species **12**, our search for potential surface minima resulted in two nonplanar structures, one slightly nonplanar (**12b**) with a planarization energy of under 1 kJ mol⁻¹ and a high energy form (**12c**), which is more correctly described as two loosely connected three-membered rings. As such, this latter form is akin to the recently reported tetraphosphabenzene valence isomer²⁰ with its two interacting PPC moieties. As mentioned above, *p*-benzoquinone (**14**) is planar. The tetraaza derivative (**16b**) is almost as planar, while the tetraphospha compound (**18b**) is significantly nonplanar. It would appear that even with conjugation of the P=P double bond with the keto group, the P-C-P angle cannot open wide enough to compensate for the small angles around phosphorus to allow for planarity of the entire six-membered ring.

Free Energy. It is relatively rare to discuss strain gibbs energy as opposed to the strain energy or strain enthalpy. By analogy to eq 1, we could define the "ultradiagonal" strain gibbs energy (UDSG) of compounds containing three-membered rings (3MR) as half of the exoergicity of the formal dimerization reaction



Again, *cyclo*-(XYZ)₂ is taken to be the unique dimer of a set of six in which both nearest-neighbor and next-

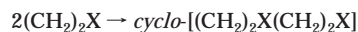
nearest-neighbor bonding is conserved, i.e., *cyclo*-(XYZX-YZ), and X, Y, and Z are arbitrary. Table 4 presents the UDSG values for the various species of interest.

Experiment is all but moot for comparison with theory. However, it is perhaps most telling to note that the calculated UDSG value for all of the three-membered rings we studied differs by some ca. 27 ± 3 kJ mol⁻¹ from the earlier value for the corresponding UDSE value. We are optimistic that this near constancy will be useful in our thermochemical understanding and future studies.

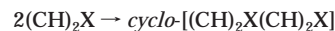
Acknowledgment. This project has received support from the computer center at the University of Tromsø. A.S. wishes to thank them for their support. The United States National Institute of Standards and Technology is also thanked for partial support of the thermochemical studies of J.F.L. We also thank the reviewer for his/her concern about the various schemes for strain energy.³⁰

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(30) We acknowledge that our definition of strain energy is not unique—that ultradiagonal strain energies provide but one approach. One of the reviewers explicitly mentioned one of the simplest approaches for comparison, that of homodesmotic reactions. The current approach provides a unified model for the strain energy of saturated and unsaturated three-membered rings. For formally identically "decorated" cyclopropanes and cyclopropenes, (CH₂)₂X and (CH)₂X, we have the formally identical dimerization reactions



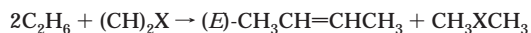
and



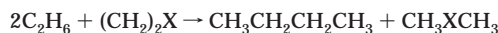
For the cyclopropanes, the homodesmotic reaction is



while for cyclopropenes, the homodesmotic reaction is different



Corresponding to the latter reaction, we may construct for cyclopropanes the new reaction



Since the enthalpy of formation difference of *n*-butane and propane, and propane and ethane, are nearly identical, the two reactions for the cyclopropane have nearly identical enthalpies. Suppose, however, we were studying derivatives of the still-hypothetical cyclopropanedione, (CO)₂X, and comparing them with (CH₂)₂X and (CH)₂X. The ultradiagonal reference species would uniquely be derivatives of 1,2,4,5-cyclohexanetetraone. Would the homodesmotic comparison entail CH₃-COCOCH₃ and C₂H₆ or 2CH₃COCH₃ and 2C₂H₆? Unlike the above situation, the difference of the enthalpies of formation of biacetyl and acetone, and of acetone and ethane, are not nearly identical: they differ by over 20 kJ mol⁻¹.