Tetrahedron Vol. 32, pp. 317 to 323. Pergamon Press 1976. Printed in Great Britain

AN ALTERNATIVE APPROACH TO THE PROBLEM OF ASSESSING DESTABILIZATION ENERGIES (STRAIN ENERGIES) IN CYCLIC HYDROCARBONS

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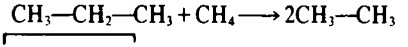
(*Received in USA* 23 *June* 1975; *Received in UK for publication* 23 *September* 1975)

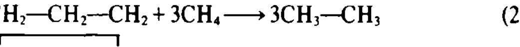
Abstract—Reactions involving no hypothetical structures having averaged group energies or particular bond energy assignments are described, that provide an alternative basis for evaluating strain energies of cyclic hydrocarbons. These reactions match C–C bonds in the sense of having equal number of sp^3-sp^3, sp^3-sp^2, sp^2-sp^2, etc. bonds in reactants and products, while simultaneously matching the various C–H bonds as closely as possible. Such reactions single out those structural features that lead to destabilization of strained ring systems. Theoretical and experimental molecular indices are introduced as a measure of these destabilizing effects, and are compared to conventional ring strain energies.

INTRODUCTION

In their theoretical study of the complete hydrogenation of organic molecules, Hehre *et al.*, broke the process down into two steps. The first consists of a separation reaction in which all the formal bonds between heavy (non hydrogen) atoms are separated into the simplest (parent) molecules with the same type of bond, adding CH_4 as necessary to complete the stoichiometry.† The second consists of the full hydrogenation of the reaction products. They termed the bond separation step an *isodesmic* reaction—one in which there is a retention of the number of bonds of a given formal type (single, double, triple), but a change in the structural relationships between them, e.g.

$$CH_3{-}CH_2{-}CH_3 + CH_4 \longrightarrow 2CH_3{-}CH_3 \qquad (1)$$


$$CH_2{-}CH_2{-}CH_2 + 3CH_4 \longrightarrow 3CH_3{-}CH_3$$
(2)


$$CH_2{-}CH{=}CH + 3CH_4 \longrightarrow 2CH_3{-}CH_3 + CH_2 = CH_2$$
(3)

see their Table II.

From the point of view of thermochemistry the energies of isodesmic reactions measure deviations from the additivity of bond energies. For example, reactions (2) and (3) can be used as bases for defining and evaluating the strain energy of the cyclopropane and cyclopropene rings respectively.[1,2] The experimental strain energy, identified as the enthalpy change in the reactions, is obtained from ΔH_f° data on the reacting molecules and the corresponding theoretical strain energy, defined as the difference in total energy of reactants and products, is obtained from calculations of the ground state energy of the reacting molecules. This formulation,‡ which involves no hypothetical structures having averaged group energies or particular bond energy assignments, treats ring strain as a parameter for a real reaction, thus facilitating an unambiguous comparison of theory and experiment.

However, these particular isodesmic reactions involve quite profound changes in the nature of the C–H and C–C bonds. For example, in reaction (2) it is necessary to convert the six secondary C–H bonds in cyclopropane and the twelve unique C–H bonds in three methane molecules into primary C–H bonds in ethane. Similarly, reaction (3) requires the conversion of two C_{sp^2}–C_{sp^3} bonds into two C_{sp^3}–C_{sp^3} bonds. Structural features of this nature, that have nothing to do with the ring strain, entail energy changes which are reflected in the numerical values of the strain energy obtained from the above procedure.§

It is the purpose of this paper to present alternative reactions with which to assess the strain energy of ring systems. These reactions match the number of each type of C–C bond (sp^3-sp^3, sp^2-sp^3, etc.) and also match the number of each type of C–H bond in reactants and products as closely as possible. Matching in this way minimizes extraneous energy contributions. In a previous paper we have shown how these same features can be incorporated into the design of reactions for the evaluation of stabilization energies that originate in electron delocalization.[3]

GENERAL DEFINITIONS

First, we define an *homodesmotic* reaction as one in which (1) there are equal numbers of C atoms in their various states of hybridization in reactants and products and (2) there are equal numbers of C atoms with zero, one, two, and three H atoms attached in reactants and products. These conditions imply that there are equal numbers of each type of C–C bond (sp^3-sp^3, sp^2-sp^3, etc.), and that the various types C–H bonds are matched as

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†If heteroatoms are included it is necessary to include other hydrides such as NH_3 or H_2O to complete the stoichiometry.[1]

‡This procedure is different from that of Newton and Schulman,[2] whose definition of ring strain involves a hypothetical strain free reference molecule.

§These extraneous energy contributions in general lead to an underestimation of the strain energy, see Figs 1–4 below.

closely as possible.[†] For example cyclopropane can, in principle, react with ethane to yield propane

$$\overline{CH_2-CH_2-CH_2}+3CH_3-CH_3\rightarrow 3CH_3-CH_2-CH_3. \qquad (4)$$

All the C atoms are sp^3 hybridized, and the C–H bonds are matched in that there are equal *numbers* of C atoms with two and three H atoms attached.[‡] Similiar reactions can be drawn up for the other cycloparaffins using only ethane and propane. Other cyclic structures require additional reactant species, as will be discussed later.

It is clearly more appropriate to base measurements and calculations of the strain energy of the cyclopropane ring on reaction (4) rather than reaction (2), since reaction (2) requires additional changes in binding energy, quite unrelated to the strain in the cyclopropane ring. We realize, of course, that the energy change in a reaction of this kind is not due solely to distortion of valence bond angles,[5] nor is it solely a property of the cyclic structure being investigated. In fact it is impossible to write down a chemical reaction involving cyclic and acyclic structures in which the energy difference between reactants and products is due only to bond angle distortion. Homodesmotic reactions minimize, as far as possible, extraneous contributions to strain energy from changes in hybridization,[§] and gross changes in the nature of C–H bonds in reactants and products.

The ethane and propane molecules in reaction (2) simply serve to establish a reference level from which to measure the overall destabilization of the ring. This reference level would be shifted if other molecules (that also meet the homodesmotic criteria) were chosen as reactants. But this in no way detracts from the special advantages of the homodesmotic reaction concept. In fact, all evaluations of strain energy from thermochemical data depend on a choice of comparison molecule, and in the usual procedure in which the averaged or "best" values from either group parameters or bond energy terms are employed, the comparison molecule is by necessity some idealized structure. The homodesmotic reaction concept eliminates the need to introduce such an idealized structure in the definition and evaluation of ring strain.

We now define the homodesmotic destabilization energy (HDE) in terms of the enthalpy change for the appropriate homodesmotic reaction under standard conditions. Such reactions are exothermic, by necessity, on account of the destabilization in the cyclic reactant species. HDE is therefore identified as ΔH° with the sign changed so as to give a positive quantity. HDE is easily obtained once ΔH_f° has been determined for all the reactant and product species.

Finally we define the theoretical molecular orbital destabilization energy (HMODE) as the difference in total energy of reactants and products in the homodesmotic reaction.

The corresponding quantities for an isodesmic reaction are denoted by IDE and IMODE respectively.

For strict comparison between theory and experiment, ΔH°, and thus HDE or IDE, is corrected to 0°K and due allowance made for zero-point energy contributions, the corrected quantities being denoted by subscripts-$\Delta H^\circ_{\text{corr}}$, HDE_{corr} and IDE_{corr}.

COMPARISON OF EXPERIMENTAL AND THEORETICAL DESTABILIZATION ENERGIES, AND CONVENTIONAL RING STRAIN ENERGIES

(a) *Cyclopropane and cyclopropene ab-initio evaluations.* The results of calculations based on the isodesmic reactions (2) and (3), and the homodesmotic reactions (4) and (5),[||]

Table 1. Comparison of experimental[a] and theoretical[b] destabilization energy values for cyclopropane and cyclopropene (kcal/mol)

Cyclopropane		
Isodesmic Reaction	$\overline{CH_2-CH_2-CH_2}+3CH_4\longrightarrow 3CH_3-CH_3$	
	$-\Delta H^\circ_{corr}=IDE_{corr}=23.5^a$	
Base Set	IMODE	$(IMODE-IDE_{corr})$
STO-3G	48.3	24.8
LEMAO-6G	26.2	2.7
4-31G	30.4	6.9
Homodesmotic Reaction:	$\overline{CH_2-CH_2-CH_2}+3CH_3-CH_3$	
	$\longrightarrow 3CH_3-CH_2-CH_3$	
	$-\Delta H^\circ_{corr}=HDE_{corr}=28.0^a$	
Base Set	HMODE	$(HMODE-HDE_{corr})$
STO-3G	46.8	18.8
LEMAO-6G	31.3	3.3
4-31G	30.0	2.0
Cyclopropene		
Isodesmic Reaction:	$\overline{CH_2-CH=CH}+3CH_4\longrightarrow 2CH_3-CH_3+CH_2=CH_2$	
	$-\Delta H^\circ_{corr}=IDE_{corr}=45.2^a$	
Base Set	IMODE	$(IMODE-IDE_{corr})$
STO-3G	66.1	20.9
LEMAO-6G	53.8	8.6
4-31G	58.0	12.8
Homodesmotic Reaction:	$\overline{CH_2-CH=CH}+2CH_3-CH_3+CH_2=CH_2$	
	$\longrightarrow 2CH_3-CH=CH_2+CH_3-CH_2-CH_3$	
	$-\Delta H^\circ_{corr}=HDE_{corr}=-56.7^a$	
Base Set	HMODE	$(HMODE-HDE_{corr})$
STO-3G	75.0	18.3
LEMAO-6G	67.5	10.8
4-31G	67.2	10.5

(a) Values obtained from ΔH_f° data at 298°K corrected to 0°K, with further corrections for zero point energy contributions, from reference 1, Tables I and II.

(b) IMODE taken from Table II, HMODE calculated from the total energies in the various basis sets listed in Table I of the same reference.

[†] While homodesmotic reactions may be regarded as a special case of isodesmic reactions, as defined in Ref. 1, the additional matching of hybridization and bonding characteristics puts them in a class of their own. All homodesmotic reactions are isodesmic, but few isodesmic reactions are homodesmotic. In fact none of the isodesmic reactions of Ref. 1 are homodesmotic.

[‡] Although in reaction (4) the C–H bonds in cyclopropane and ethane are matched as closely as they can be according to chemical type with the C–H bonds in propane, we do not imply that the contributions of these bonds to the total molecular energies are identical since there are undoubtedly conformational differences. But this is beside the point. Adverse interactions between partially (or wholly) eclipsed hydrogen atoms have long been considered one of the factors contributing to the overall destabilization in cyclic structures which, for brevity, is referred to as ring strain.

[§] As we shall show later, the appropriate homodesmotic reaction for cyclopropane, for example, eliminates the conversion of $C_{sp^2}–C_{sp^3}$ bonds into $C_{sp^3}–C_{sp^3}$ bonds inherent in the isodesmic reaction (3) above.

[||] In reaction (5) there are equal numbers of both the $C_{sp^2}–C_{sp^3}$ bonds and the $C_{sp^3}–C_{sp^3}$ bonds in reactants and products in contrast to the isodesmic reaction(3).

$$\overline{CH_2—CH=CH} + 2CH_3—CH_3 + CH_2=CH_2 \longrightarrow 2CH_3—CH=CH_2 + CH_3—CH_2—CH_3 \quad (5)$$

are presented in Table 1, utilizing total energies in the three *ab initio* basis sets STO-3G, LEMAO-6G and 4-31G.[1] In all cases the theoretical calculations overestimate the destabilization energy, as shown by the positive values of ($IMODE-IDE_{corr}$) and $HMODE-HDE_{corr}$) in the third column although for cyclopropane the difference is only 2-3 kcal/mole with LEMAO-6G and 4-31G. Overall, the values based on the homodesmotic reactions are in slightly better agreement, which is a little surprising since the homodesmotic reactions involve three additional heavy atoms in reactants and products, and hence larger total energies. Possibly this potential source of a greater discrepancy is offset by the enhanced cancellation of structural factors inherent in the design of the homodesmotic reactions.

A more important issue, however, is whether the destabilization energy calculated on the basis of the isodesmic reaction, or the homodesmotic reaction, is a better index of ring strain. Comparison with conventional ring strain energies, CRSE, evaluated as the difference between the heat of atomization of a hypothetical cyclic structure with no ring strain (calculated from thermochemical bond energy terms,[4] and the heat of atomization of the real cyclic structure,† shows the agreement to be much closer in the case of HDE values, see Table 2. However, *for comparison with quantum theoretical calculations HDE values have the distinct advantage over CRSE values of relating destabilization to the total energy of real molecules, with their own unique physical properties and not hypothetical structures whose energy depends on bond energy assignments and some unspecified geometry.* When real molecules are employed there is a causal connection imposed by nature between structure and total molecular energy, which is absent when hypothetical structures are used.

Table 2. Comparison of the destabilization energies of cyclopropane and cyclopropene based on isodesmic and homodesmotic reactions, with conventional ring strain energies (kcal/mol)

Compound	IDE[a]	HDE[a]	CRSE[b]
Cyclopropane	19.8 ± 0.7	26.5 ± 0.9	27.5
Cyclopropene	40.6 ± 1.2	53.2 ± 0.9	53.8

(a) Calculated from ΔH_f^o data at 298°K selected by Cox and Pilcher [4].

(b) Calculated from the thermochemical bond energy term values (Laidler parameters) recommended by Cox and Pilcher reference 4, Table 50, p.592.

(b) *Three-, four-, five- and six membered ring systems—semi-empirical calculations.* Baird and Dewar[5] using a semi-empirical SCF MO treatment—the MINDO approximation-obtained values for the heat of formation at 25°C (ΔH_f^o) for a number of hydrocarbons, from which values of HMODE and IMODE can be calculated for some 22 cyclic structures (see Table 3).

In the isodesmic reactions, methane is again employed as a reactant to bring about the separation of all formal bonds between the heavy (non hydrogen) atoms into the simplest parent molecules with the same type of bond, e.g. ethane and ethylene.[1] In the homodesmotic reactions, several new product species are required to furnish the appropriate type of sp^3 or sp^2 C atom bonded to one H atom, or none at all, in order to match the corresponding atoms in the reactant species. The simplest molecules for this purpose, e.g. those with the smallest number of heavy atoms, are isobutane and neopentane $(CH_3)_3CH$ and $(CH_3)_4C$, in the case of paraffinic structures, and isobutene $(CH_3)_2C = CH_2$ in the case of the olefinic structures. These other molecules, along with ethane, propane and propene establish the reference levels for the evaluation of destabilization energies for these more complicated structures, just as ethane and propane alone do for the simpler cycloparaffins. Values of IDE, HDE and CRSE have also been calculated, using experimental ΔH_f^o data.[4,5]

Comparison of the experimental and theoretical values, HDE with HMODE, and IDE with IMODE, shows again that the differences are less for the homodesmotic reactions—in 15 of the 22 cases. The average difference is 3·0 for the homodesmotic reactions compared to 3·3 for the isodesmic reactions—a marginal distinction quantitatively, in view of the approximations involved. Yet, as before, larger discrepancies would be expected for the homodesmotic reactions because of the greater structural complexity of reactant and product species. This better agreement with the homodesmotic reactions is suggestive again of the enhanced calcellation of extraneous structural features inherent in the design of this kind of reaction.

Turning to the comparison of HDE and IDE values with conventional ring strain energies several features call for comment. First, while there is close agreement between HDE and CRSE for cyclobutane, cyclobutene, cyclopentane, cyclopentene and cyclohexane, the values of IDE become progressively more negative as the ring size increases. However the value −15·4 for cyclohexane suggests in no way the (almost) complete lack of strain which is generally believed to characterize this 6-membered ring.[6] Secondly, while the HDE and CRSE values are very much alike for the unsubstituted and Me-substituted rings, the IDE values are systematically and substantially more negative—the dimethyl derivatives more so than the monomethyl derivatives. No such diminution in the strain energy upon the introduction of substituents into the ring has been envisaged in conformational analysis, nor does there appear to be any evidence for it in the magnitude of other physical properties.[6] On the contrary, substitution is understood to lead to an increase in strain energy because of the greater likelihood of adverse interactions between non-bonded atoms or groups—an extreme case being the destabilization that characterizes axial substitution in cyclohexane.

A far more likely explanation of this otherwise curious anomaly is the necessity in the isodesmic reactions for methyl derivatives to include additional methane molecules as reactants with the concomitant formation of additional ethane molecules as products. For example, in the case of cyclobutane and methylcyclobutane,

$$\overline{CH_2—CH_2—CH_2—CH_2} + 4CH_4 \longrightarrow 4CH_3—CH_3 \quad (7)$$

$$\overline{CH_2—CH(CH_3)—CH_2—CH_2} + 5CH_4 \longrightarrow 5CH_3—CH_3 \quad (8)$$

this introduces extraneous energy contributions that have

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†The conventional ring strain energy, although not widely recognized as such, is a reaction parameter, namely $\Delta H°$ for the reaction

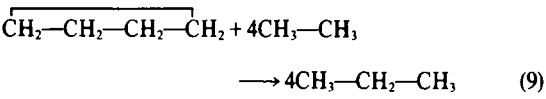
Hypothetical cyclic structure (no strain) ⟶ Real cyclic structure. (6)

Table 3. Experimental and theoretical destabilization energies at 25°C

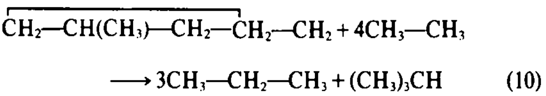
COMPOUND	CRSE[a]	HDE[b]	HMODE[c]	IDE[b]	IMODE[c]
A. Six-Membered Ring					
Cyclohexane	0	-2.0 ± 1.7	2.0	-15.4 ± 1.3	-12.0
Methylcyclohexane	-0.5	-1.9 ± 2.0	0.4	-20.5 ± 1.6	-18.1
B. Five-Membered Ring					
Cyclopentane	6.2	4.5 ± 1.5	4.4	-6.7 ± 1.2	-7.2
Methylcyclopentane	6.3	5.3 ± 1.5	4.4	-11.2 ± 1.3	-11.8
Cyclopentene	5.7	4.5 ± 1.4	5.5	-12.7 ± 1.2	-13.8
1-Methylcyclopentene	5.9	4.8 ± 1.8	6.4	-19.2 ± 1.6	-21.7
Methylenecyclopentane	6.5	5.2 ± 1.5	5.9	-15.8 ± 1.3	-18.3
C. Four Membered Ring					
Cyclobutane	26.5	25.1 ± 1.2	30.3	16.2 ± 0.9	20.9
Methylcyclopentane	22.8	22.1 ± 1.5	30.3	7.9 ± 1.5	16.5
Cyclobutene	30.0	29.1 ± 0.9	33.5	14.2 ± 1.1	16.5
1-Methylcyclobutene *	29.3	28.5 ± 2.0	33.9	6.8 ± 2.0	8.2
1,2-Dimethylcyclobutene*	33.0	32.3 ± 1.5	34.5	3.8 ± 1.6	0.1
D. Three-Membered Ring					
Cyclopropane	27.5	26.5 ± 0.9	30.6	19.8 ± 0.7	23.6
Methylcyclopropane*	27.2	26.9 ± 1.3	30.2	14.9 ± 1.3	18.7
Methylenecyclopropane	41.8	41.1 ± 1.2	42.3	24.6 ± 1.2	22.8
Cyclopropene	53.8	53.2 ± 0.9	54.5	40.6 ± 1.2	39.9
1-Methylcyclopropene	54.9	54.4 ± 1.1	53.8	34.9 ± 1.0	30.5
1,2-Dimethylcyclopropene*	52.1	51.7 ± 1.3	53.6	25.5 ± 1.4	21.5
E. More Complicated Three Membered Ring Systems					
Dicyclopropyl	54.1	53.4 ± 2.6	61.5	29.5 ± 2.3	38.5
Spiropentane	64.0	62.4 ± 1.7	61.4	40.5 ± 1.4	38.9
Bicyclobutane	65.2	65.2 ± 1.3	64.9	45.8 ± 1.2	46.5
1,3-Dimethylbicyclobutane*	69.9	68.7 ± 2.4	61.1	38.3 ± 2.4	30.0

(a) Calculated using thermochemical bond energy terms (Laidler parameters) recommended by Cox and Pilcher, Ref. 4, Table 50, p. 592. (b) Calculated from the experimental ΔH_f° data selected by Cox and Pilcher,[4] with the exception of the compounds marked by asterisks for which the values were adopted from Baird and Dewar.[5] For methylcyclobutane, ΔH_f° for the liquid, $-10{\cdot}63 \pm 0{\cdot}33$,[4] has been taken together with an estimated ΔH_v° of 6·8, to give ΔH_f° for the gas of $-3{\cdot}83 \pm 0{\cdot}5$. For methylenecyclopentane, ΔH_f° for the liquid, $-4{\cdot}80 \pm 0{\cdot}21$, has been taken together with ΔH_v° for methylcyclopentane, $7{\cdot}58 \pm 0{\cdot}01$, to give ΔH_f° for the gas of $+2{\cdot}78 \pm 0{\cdot}22$.

nothing to do with the underlying energetics of the ring fission process. There is no built-in cancellation of energy terms relating to the substituent group. On the other hand, in the corresponding homodesmotic reactions,



$$CH_2{-}CH_2{-}CH_2{-}CH_2 + 4CH_3{-}CH_3 \longrightarrow 4CH_3{-}CH_2{-}CH_3 \qquad (9)$$



$$CH_2{-}CH(CH_3){-}CH_2{-}CH_2{-}CH_2 + 4CH_3{-}CH_3 \longrightarrow 3CH_3{-}CH_2{-}CH_3 + (CH_3)_3CH \qquad (10)$$

the same number of ethane molecules are required as reactants, there are the same number of product molecules and the methyl substituent in the ring is matched, in its structural setting, by the methyl sidechain in isobutane.

The following survey of HDE, IDE and CRSE values for homologous series of ring structures bears out the above conclusion that HDE is a better index of destabilization than IDE.

(c) *Cycloparaffins, cyclo-olefins, bicyclo*[n, 1, 0] *parafins and spiroparaffins—HDE, IDE and CRSE values.* The general homodesmotic and isodesmic reactions for the evaluation of destabilization energies for these four classes of cyclic hydrocarbons are set out in Table 4. HDE, IDE and CRSE values are compared in Figs. 1–4 in terms of ΔH° for the homodesmotic and isodesmic reactions, and for reaction (6) in the reverse sense following the same sign convention.† We choose to

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†The homodesmotic reactions, as written, are almost all exothermic on account of the destabilization in the reactant cyclic hydrocarbon. The conversion of the real cyclic structure into an hypothetical cyclic structure with no strain would be the corresponding exothermic process.

Table 4. General reactions for the evaluation of destabilization energies

Cycloparaffins.	
homodesmotic:	$(CH_2)_n + nC_2H_6 \longrightarrow nCH_3CH_2CH_3$
isodesmic:	$(CH_2)_n + nCH_4 \longrightarrow nC_2H_6$
Cyclo-olefins.	
homodesmotic:	$\overline{(CH_2)_{n-2} - CH = CH} + C_2H_4 + (n-1)\ C_2H_6$ $\longrightarrow 2CH_3CH = CH_2 + (n-2)\ CH_3CH_2CH_3$
isodesmic:	$\overline{(CH_2)_{n-2} - CH = CH} + nCH_4$ $\longrightarrow C_2H_4 + (n-1)\ C_2H_6$
Bicyclo [n,1,0] Paraffins.	
homodesmotic:	$C_{n+3}H_{2n+4} + (n + 4)\ C_2H_6$ $\longrightarrow 2(CH_3)_3CH + (n + 1)\ CH_3CH_2CH_3$
isodesmic:	$C_{n+3}\ H_{2n+4} + (n + 5)\ CH_4 \longrightarrow (n + 4)\ C_2H_6$
Spiroparaffins.	
homodesmotic:	$C_nH_{2n-2} + (n + 1)\ C_2H_6$ $\longrightarrow (CH_3)_4\ C + (n-1)\ CH_3CH_2CH_3$
isodesmic:	$C_nH_{2n-2} + (n + 2)\ CH_4 \longrightarrow (n + 1)\ C_2H_6$

make the comparison in terms of $\Delta H°$ directly, instead of HDE and IDE (i.e. $\Delta H°$ with change of sign), because it is the exothermicity of a reaction—in which the ring structure is disrupted, but the bonding remains substantially the same—that is evocative of destabilization.

Curves (a) and (b) in Fig. 1 for the cycloparaffins show how closely $\Delta H°$ for the homodesmotic reactions corresponds to -CRSE as an index of destabilization. The exothermicity is large for C_3 and C_4: low at C_5: about zero for C_6, i.e. no destabilization: it rises again between C_6 and C_{12}, with a maximum at about C_9: and it is then effectively zero for the larger rings. The somewhat anomalous values for C_{14} and C_{17} are probably due to experimental error. These changes correlate extremely well with what is known of the conformation of these compounds.[6]

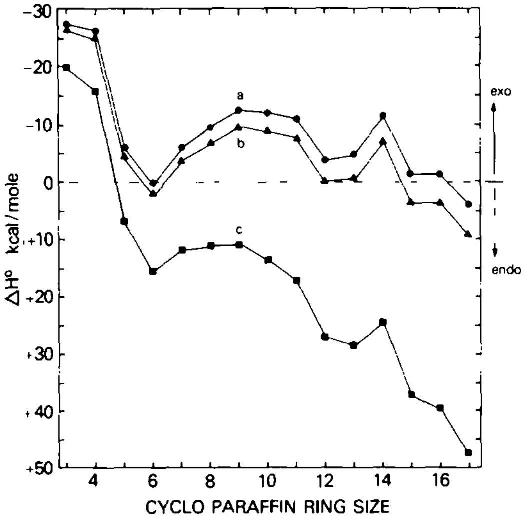

Fig. 1. Plot of $\Delta H°$ as a function of ring size for the cycloparaffins (a) for the conversion of the real cyclic structure into an hypothetical cyclic structure with no strain, i.e. -CRSE, (b) and (c) for the homodesmotic and isodesmic reactions set out in Table 4, i.e. -HDE and -IDE respectively.

Although similar variation is perceptible in the $\Delta H°$ values for the isodesmic reactions, see curve (c), it is superimposed on a steady trend toward more endothermic values, so much so that there is no longer any correlation between the numerical values and the presence or absence of destabilization. All the values, except those for C_3 and C_4 are endothermic, and the physical significance of exothermicity as the index of strain is thereby lost. Moreover, $\Delta H°$ for C_6 is endothermic to the extent of 15 kcal/mole, and for C_{12} to the extent of 27 kcal/mole, numbers which give no indication that there is very little destabilization in either of these structures.[6] As in the case of Me substitution discussed above, this steady trend toward greater endothermicity is attributable to a mismatch in the C–H bonds in the reactants and products, that becomes more significant as the ring size increases and more CH_4 molecules are required as reactants, and more C_2H_6 molecules are formed as products.

There is exactly the same contrast in the case of the cyclo-olefins, the bicyclo [*n*, 1, 0] paraffins and the spiroparaffins between $\Delta H°$ for the homodesmotic reaction and -CRSE on the one hand, and $\Delta H°$ for the isodesmic reaction on the other (see Figs. 2–4). Notably the $\Delta H°$ values for the isodesmic reactions of all but the C_3 and C_4 cyclo-olefins are substantially endothermic (Fig. 2) likewise for the C_9, C_{10} and C_{11} spiroparaffins (Fig. 4). Moreover the $\Delta H°$ values for the isodesmic reactions of the [4, 1, 0], [5, 1, 0] and [6, 1, 0] bicycloparaffins are nearly zero (Fig. 3), which gives no indication of the destabilization that is undoubtedly present in these structures on account of the 3-membered ring. However, as in the case of the cycloparaffins, the $\Delta H°$ values for the homodesmotic reactions reflect the traditional conventional ring strain energies very faithfully.

(d) *Cubane and tetracyclopentadiene—HDE, IDE and CRSE values.* As might be expected the contrast is even more accentuated with polycyclic structures in which a greater proportion of the carbon atoms are bonded to two H atoms or only one. Two examples will suffice. In Table 5, values are presented for cubane (six 4-membered rings) and the addition polymer of cyclopentadiene, tetracyclopentadiene (seven 5-membered rings, two mono-olefinic and five paraffinic). Again the ΔH° values for the homodesmotic reactions agree very closely with the -CRSE values,† whereas the ΔH° values for the isodesmic reactions are more endothermic by as much as 60 and 120 kcal/mole respectively.

DISCUSSION

It is abundantly clear from sections 3(a-d), that while the isodesmic reduction of cyclic hydrocarbons by methane to give ethane can serve as a useful and meaningful bond separation step in the complete reduction of the cyclic structure to fully hydrogenated products, neither the sign

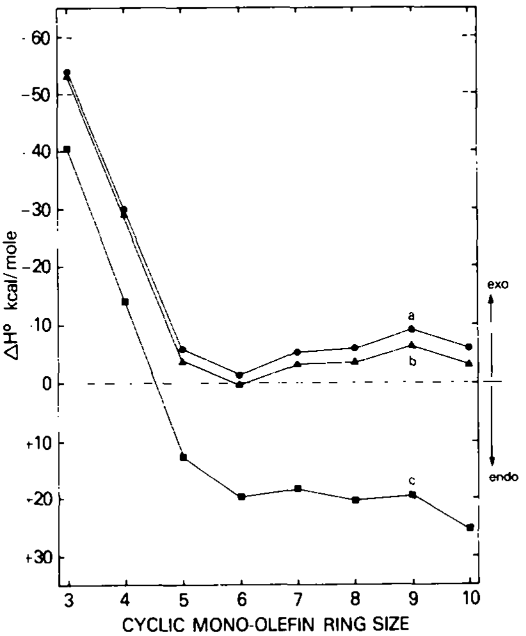

Fig. 2. Plot of ΔH° as a function of ring size for the cyclic mono-olefins (a) for the conversion of the real cyclic structure into an hypothetical cyclic structure with no strain, i.e. -CRSE, (b) and (c) for the homodesmotic and isodesmic reactions set out in Table 4, i.e. -HDE and -IDE respectively.

Table 5. Reactions for the evaluation of destabilization energies for cubane and tetracyclopentadiene

Cubane

(i) Ring Strain Reaction

C_8H_8 (real molecule) $\longrightarrow$ C_8H_8 (hypothetical molecule: no strain)

$\Delta H^\circ = -162.7$ kcal/mol (-CRSE)

(ii) Homodesmotic Reaction

$C_8H_8 + 12C_2H_6 \longrightarrow 8(CH_3)_3CH$

$\Delta H^\circ = -165.1 \pm 3.5$ kcal/mol (-HDE)

(iii) Isodesmic Reaction

$C_8H_8 + 16CH_4 \longrightarrow 12C_2H_6$

$\Delta H^\circ = -105.3 \pm 3.6$ kcal/mol (-IDE)

Tetracyclopentadiene[a]

(iv) Ring Strain Reaction

$C_{20}H_{24}$ (real molecule) $\longrightarrow$ $C_{20}H_{24}$ (hypothetical molecule: no strain)

$\Delta H^\circ = -66.0$ kcal/mol (-CRSE)

(v) Homodesmotic Reaction

$C_{20}H_{24} + 2C_2H_4 + 24C_2H_6$

$\longrightarrow 4CH_3CH = CH_2 + 12(CH_3)_3CH + 4(CH_3)_2\ CH_2$

$\Delta H^\circ = -67.8 \pm 8.5$ kcal/mol (-HDE)

(vi) Isodesmic Reaction

$C_{20}H_{24} + 32CH_4 \longrightarrow 2C_2H_4 + 24C_2H_6$

$\Delta H^\circ = +51.7 \pm 8.0$ kcal/mol (-IDE)

(a) Sublimation heat estimated to be 30 kcal/mol, which, with ΔH°_f for the solid of $+ 29.9 \pm 2.7$ [4] gives $\Delta H^\circ_f = + 59.9 \pm 2.7$ for the gaseous compound.

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†The close correspondence between HDE and CRSE values noted in this paper, on average to within about 1 kcal/mole, simply reflects the extent to which the experimental heats of atomization of the reference molecules-ethane, ethylene, propane, etc.—agree with values calculated on the basis of the thermochemical bond energy terms employed to evaluate CRSE.

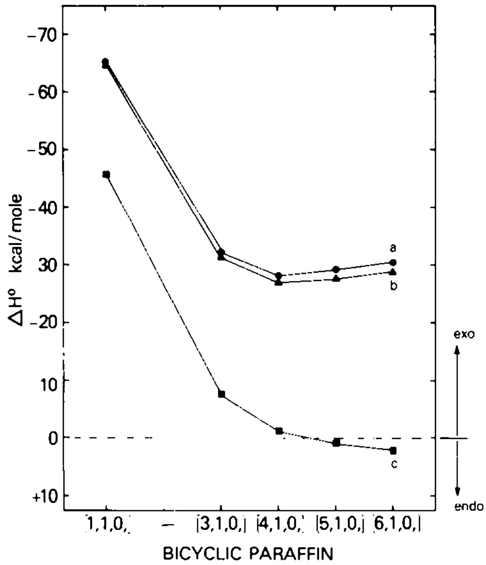

Fig. 3. Plot of $\Delta H°$ for the $[n, 1, 0]$ bicyclic paraffins (a) for the conversion of the real bicyclic structure into an hypothetical bicyclic structure with no strain, i.e. -CRSE, (b) and (c) for the homodesmotic and isodesmic reactions set out in Table 4, i.e. -HDE and -IDE respectively.

nor the magnitude of $\Delta H°$ for these reactions reflect in any way destabilization energies characteristic of the ring systems. To be sure, $\Delta H°$ values calculated from theory can be compared with experimental values (preferably corrected to 0°K, with allowance made for zero-point contributions) but any reaction can be used for this purpose, e.g. the formation reaction from the elements.[5]

The point at issue is the design of reactions for which the $\Delta H°$ values are a meaningful index of destabilization. Homodesmotic reactions, in which states of hybridization of the C-atoms and the number of C–H bonds of each type are matched as far as possible in reactants and products, provide just such indices, corresponding very closely to conventional ring strain energies. For comparison with theory, however, HDE values have an advantage over CRSE values in that they relate destabilization to the total energy of real molecules, with their own unique physical properties, and not to some hypothetical structure whose total energy depends on an assignment of values for bond energy terms and some unspecified molecular geometry. For real molecules there is a causal relationship imposed by nature between structure (and conformation) and the total molecular energy or a similiar fundamental property, e.g. $\Delta H_f°$, which is not present in the other case.

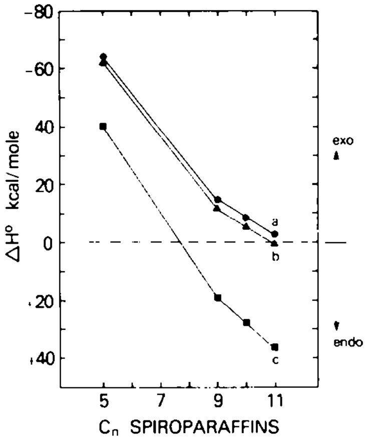

Fig. 4. Plot of $\Delta H°$ for spiropentane, spiro [5, 5] nonane, spiro [5, 6] decane and spiro [6, 6] undecane (a) for the conversion of the real spiro structure into a hypothetical spiro structure with no strain, i.e. -CRSE, (b) and (c) for the homodesmotic and isodesmic reactions set out in Table 4, i.e. -HDE and -IDE respectively.

REFERENCES

[1] W. J. Hehre, R. Ditchfield, L. Radom and J. A. Pople, *J. Am. Chem. Soc.* **92**, 4796 (1970).
[2] M. D. Newton and J. M. Schulman, *Ibid.* **94**, 767 (1972).
[3] P. George, M. Trachtman, C. W. Bock, and A. M. Brett, *Theoret. Chim. Acta* **38**, 121 (1975).
[4] J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds.* Academic Press, New York (1970).
[5] N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.* **50**, 1262 (1969).
[6] E. L. Eliel, *Stereochemistry of Carbon Compounds*, especially Chaps. 7–10. McGraw-Hill, New York (1962).