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G3(MP2) Calculations of Enthalpies of Hydrogenation, Isomerization, and Formation of [3]-Radialene and Related Compounds

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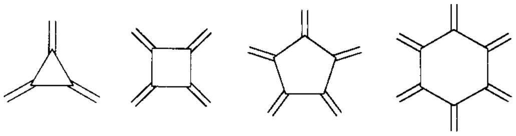
We have carried out a G3(MP2) investigation of the enthalpies of formation, isomerization, and hydrogenation ($\Delta_f H^{298}$, $\Delta_{isom} H^{298}$, and $\Delta_{hyd} H^{298}$), in the gaseous state, of 30 hydrocarbons related, directly or indirectly, to [3]-radialene (tris(methylidine)cyclopropane). The thermochemistry of [3]-radialene and many of the other molecules presented here is dominated by molecular strain. We have discussed the use and limitations of several methods of obtaining an estimate of strain energy (enthalpy). Despite its extraordinarily high $\Delta_f H^{298}$, [3]-radialene (an isomer of benzene) appears to be slightly stabilized by its radial methylene groups, in opposition to the large destabilization brought about by ring strain. Exocyclic conjugative stabilization may be present in an amount less than 5 kcal mol^{-1}, but it is difficult to quantify because there is no rigorous way of separating enthalpic effects due to strain from those due to electron conjugation in these calculations.

The chemistry of radialenes has been reviewed.[1] The simple radialenes [3]-, [4]-, [5]-, and [6]-radialene are very unstable.



They polymerize at room temperature and are unstable in air.[1] The [3]-, [4]-, and [6]-radialenes have been produced at low temperatures,[2] but [5]-radialene has not, to our knowledge, been synthesized. Despite the instability of the parent compounds, many stable derivatives exist. Simple radialenes have considerable theoretical interest because of the possibility of exocyclic aromaticity or conjugation or both.[3] Relative stabilities make it clear that there are no interactions among the double bonds of [3]-radialene that are comparable to the aromaticity of benzene, but because of the instability of simple radialenes, quantitative experimental evidence in support of or in contradiction to a lesser aromaticity, or even antiaromaticity, is lacking.[4]

In this paper, we use the G3(MP2) molecular orbital method[5] to obtain enthalpies of formation, hydrogenation, and isomerization at 298 K ($\Delta_f H^{298}$, $\Delta_{hyd} H^{298}$, and $\Delta_{isom} H^{298}$) to determine the ground-state stability of [3]-radialene along with that of 29 related compounds. Among the radialenes, only [3]-radialene has been the subject of thermochemical experimentation.[4a] Here, we discuss the enthalpic relationships among [3]-radialene, products of its total and partial hydrogenation, and a few of their many structural isomers. We have included work on some simpler related compounds containing the cyclopropane or cyclopropene moiety and some isomers of the [3]-radialene sequential hydrogenation series to look into the enthalpies of isomerization upon going from the highly unstable [3]-radialene series to their stable isomers.

Computational Section

The G3(MP2) method of Curtiss et al.,[5] part of the Gaussian 98 suite of programs,[6] was used throughout. Both theory[7] and methodology[8] have been discussed. G3(MP2) calculations have proven in past studies[5] to be especially well adapted to the study of hydrocarbons, having mean absolute deviations from experiment of <1.0 kcal mol^{-1} for a large data set.

Results

Nomenclature and computed $\Delta_f H^{298}$ values are given in Table 1. Formulas and computed enthalpies of formation of compounds discussed in this paper are shown in Schemes 1−3. Compounds related to [3]-radialene and its hydrogenation products but with fewer side chains are given in Schemes 1 and 2. [3]-Radialene itself and seven products of hydrogenation and partial hydrogenation are given in Scheme 3. Many thermochemical cycles exist connecting the compounds in Schemes 1−3, enabling one to calculate $\Delta_{hyd} H^{298}$ or $\Delta_{isom} H^{298}$ for any desired pair within the same scheme. In Schemes 1−3, italicized numbers are $\Delta_f H^{298}$, numbers above the horizontal arrows are $\Delta_{isom} H^{298}$, and numbers next to the slanting arrows are $\Delta_{hyd} H^{298}$. Computational results for radialene and related compounds are given in Tables 2 and 3. Calculations on simple isomeric molecules and molecules ancillary to the discussion are given in Table 4. Total enthalpies at 298 K, H,^{298} are listed along with zero-point energies, E(ZPE), in Tables 2−4. The thermal correction of the enthalpy from 0 to 298 K, TCH, and the desired $\Delta_f H^{298}$ are given along with an experimental value of $\Delta_f H^{298}$ where one can be found. The mean absolute deviation (MAD) between direct experimental measurements with error bars and calculated results is 0.76 kcal mol^{-1} as compared to an arithmetic mean experimental uncertainty of 0.25 kcal mol^{-1}. The MAD includes 13 values exclusive of the value for [3]-radialene which was estimated from its photoionization pattern.[4a] The mean signed deviation (exp − calc) is −0.24 kcal mol^{-1}, showing no significant trend. If the "derived" values of Liebman and Greenberg[3a] are included, the MAD is 1.29 kcal mol^{-1}. This includes, however, a questionable value for methylenecyclopropene (see endnote 22, ref 3a). Without this value, the remaining MAD is 0.85 kcal mol^{-1}. The total energy $E°$ in hartrees can be obtained by adding TCH to H^{298}, and $\Delta_f E°$ in kcal mol^{-1} can be obtained from $\Delta_f H^{298}$ by subtracting 627.51

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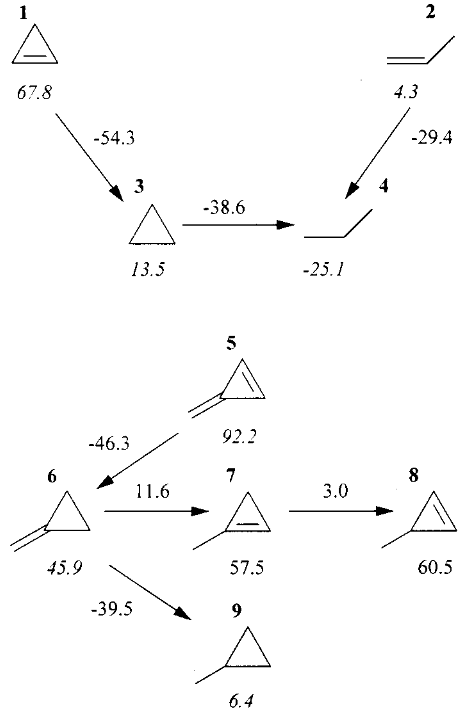
TABLE 1: Nomenclature

no.	compound	G3(MP2)	$\Delta_f H^{298}$
1	cyclopropene	67.8[a]	66.2 ± 0.6[b]
2	propene	4.3[a]	4.8 ± 0.2
3	cyclopropane	13.5[a]	12.7 ± 0.1
4	propane	−25.1[a]	−25.0 ± 0.1
5	methylenecyclopropene	92.2	101[c]
6	methylenecyclopropane	45.9[a]	47.9 ± 0.4
7	1-methylcyclopropene	57.5	58.2 ± 0.3
8	3-methylcyclopropene	60.5	
9	methylcyclopropane	6.4	6.4 ± 0.3[d]
10	dimethylenecyclopropane	76.1	
11	methylmethylenecyclopropene	80.6	
12	methylmethylenecyclopropane	38.8	39.9[c]
13	1,2-dimethylcyclopropene	47.5	44.5[c]
14	1,3-dimethylcyclopropene	50.2	
15	*cis*-dimethylcyclopropane	0.6	0.4[c]
16	*trans*-dimethylcyclopropane	−0.7	−0.9[c]
17	[3]-radialene	103.6	95 ± 3[e]
18	methyldimethylenecyclopropane	68.9	
19	dimethylmethylenecyclopropene	69.5	
20	*cis*-dimethylmethylenecyclopropane	32.7	
21	*trans*-dimethylmethylenecyclopropane	31.7	
22	trimethylcyclopropene	40.2	
23	*cis*-1,2,3-trimethylcyclopropane	−4.5	
24	*trans*-1,2,3-trimethylcyclopropane	−6.6	
25	benzene	18.6[a]	19.7 ± 0.2
26	cyclohexa-1,3-diene	24.9	25.4 ± 0.2
27	cyclohexene	−1.4	−1.2 ± 0.2
28	cyclohexane	−29.3	−27.5 ± 0.2
29	1-butene	−0.4	0.0 ± 0.3
30	*n*-butane	−30.2[a]	-30.0 ± 0.2

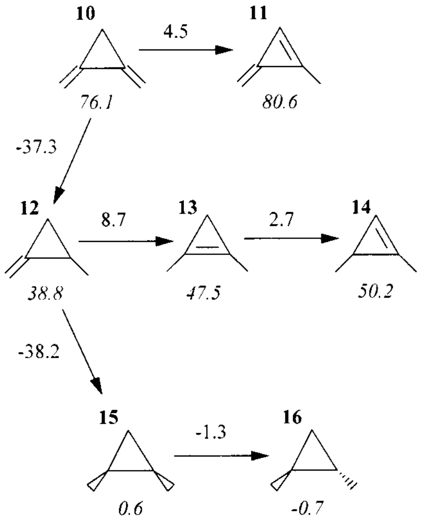
[a] See ref 5. [b] Experimental results are from ref 10 unless otherwise noted. [c] See ref 3a; no experimental uncertainty given. [d] Estimated $\Delta_{vap}H^{298}$; 5.9 kcal mol^{-1}. [e] Experimental value from ref 4a; value not included in mean deviations between experiment and calculation.

SCHEME 1

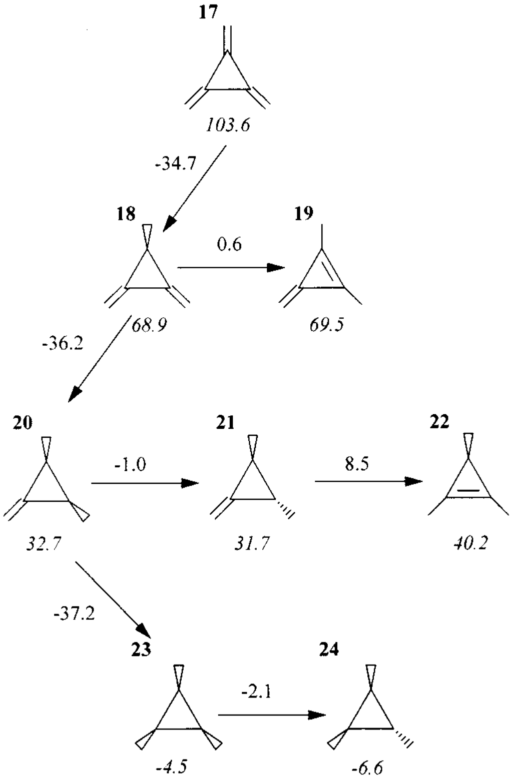


× TCH from $\Delta_f H$.^{298} A simple QBASIC program for routine conversion of $E°$ and H^{298} to $\Delta_f E^0$ and $\Delta_f H^{298}$ is available.[9]

SCHEME 2



SCHEME 3



Discussion

Exo−Endo Stability. The question of exo−endo stability has been of interest to computational chemists for many years.[11] The enthalpy of isomerization from a methylcycloalkene to the corresponding methylenecycloalkane goes (roughly) in the ratio 3:4.5:1 for isomerizations **a**, **b**, and **c** in Figure 1.

Allinger ascribes the enthalpic pattern in reactions **a**, **b**, and **c** to the interplay of torsional strain and bending strain. In a relatively strain-free environment, the more highly substituted double bond is more stable than the less substituted double bond as in reaction **a**. In reaction **b**, torsional strain in the methylene-substituted reaction product is dominant over bond bending in the reactant, leading to an increase in the positive $\Delta_r H^{298}$ relative to reaction **a**. The endocyclic double bond "relieves more torsional strain than it increases bending strain".[11] In reaction **c**, however, the reverse is true. The endocyclic double bond is now distorted to ~90° in the four-membered ring and bending strain in the reactant dominates torsional strain in the product. The enthalpy change is still positive, but $\Delta_r H^{298}$ is smaller in **c** than it is for **a** or **b**.

TABLE 2: Computed Energies and Enthalpies for the Compounds in Schemes 1 and 2[a]

	1	**2**	**3**	**4**
H^{298}	−116.40141	−117.66767	−117.65305	−118.87949
E(ZPE)	0.05403	0.07630	0.07791	0.09873
TCH	0.00427	0.00512	0.00437	0.00557
$\Delta_f H^{298}$	67.82	4.30	13.47	−25.08
$\Delta_f H^{298}$(exp)	66.2 ± 0.6[b]	4.7 ± 0.3[c]	12.7 ± 0.1	−25.0 ± 0.1

	5	**6**	**7**	**8**
H^{298}	154.42246	−155.66119	−155.64277	−155.63786
E(ZPE)	0.05858	0.08191	0.08116	0.08078
TCH	0.00501	0.00526	0.00578	0.00562
$\Delta_f H^{298}$	92.16	45.90	57.46	60.54
$\Delta_f H^{298}$(exp)	101[c]	47.9 ± 0.1[b]	58.2 ± 0.1	

	9	**10**	**11**	**12**
H^{298}	−156.88916	−193.67294	−193.66575	−194.90409
E(ZPE)	0.10485	0.08636	0.08564	0.10890
TCH	0.00570	0.00620	0.00665	0.00670
$\Delta_f H^{298}$	6.40	76.07	80.58	
$\Delta_f H^{298}$(exp)	6.4 ± 0.3[c]			39.9[d]

	13	**14**	**15**	**16**
H^{298}	−194.88346	−194.87923	−196.12326	−196.12535
E(ZPE)	0.10821	0.10782	0.13180	0.13164
TCH	0.00741	0.00725	0.00717	0.00714
$\Delta_f H^{298}$	47.52	50.17	0.58	−0.73
$\Delta_f H^{298}$(exp)	44.5[d]	0.4[d]	−0.9[d]	

[a] Units are hartrees and kcal mol^{-1}. The total energy E^0 can be obtained by subtracting TCH from H^{298}, and $\Delta_f E^0$ can be obtained from $\Delta_f H^{298}$ by subtracting 627.51 (TCH) from $\Delta_f H^{298}$. [b] Experimental values from ref 10. [c] Estimated $\Delta_{vap} H^{298}$; 5.9 kcal mol^{-1}. [d] Reference 3a; no uncertainty given.

TABLE 3: G3MP2 Enthalpies of Formation of [3]-Radialene and Its Hydrogenation Products in Scheme 2

	17	**18**	**19**	**20**
H^{298}	−231.68880	−232.90927	−232.90821	−234.13195
E(ZPE)	0.09112	0.11335	0.11263	0.13589
TCH	0.00715	0.00774	0.00838	0.00826
$\Delta_f H^{298}$	103.65	68.85	69.52	32.67
$\Delta_f H^{298}$(exp)	95.3 ± 3[a]			

	21	**22**	**23**	**24**
H^{298}	−234.13355	−234.11989	−235.35627	−235.35957
E(ZPE)	0.13577	0.13479	0.15878	0.15849
TCH	0.00826	0.00899	0.00874	0.00874
$\Delta_f H^{298}$	31.67	40.24	−4.54	−6.61
$\Delta_f H^{298}$(exp)				

[a] Experimental value from ref 4a.

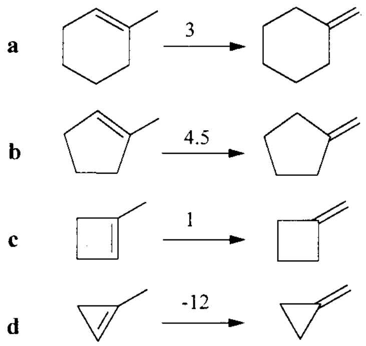


Figure 1. Enthalpy changes for endo−exo isomerization.

Upon looking at this pattern, the natural expectation is that reaction **d**, isomerization **7** → **6** in Scheme 1, would be less endothermic still, possibly becoming exothermic, because of the increase in bending strain on going from a four-membered ring in reactant **c** to the three-membered ring in reactant **d**, 1-methylcyclopropene. Indeed, this expectation is fulfilled at the bottom reaction of Figure 1. What is remarkable about this reaction is the magnitude of the exothermic reaction enthalpy, nearly −12 kcal mol^{-1}. The same argument holds a fortiori for reaction **8** → **6** which is exothermic to an extent of nearly −15 kcal mol^{-1}.

In Scheme 2, the "escape enthalpy", $\Delta_{isom} H^{298}$, for the endocyclic double bond in methylmethylenecyclopropene (**11** → **10**) to the corresponding dimethylene compound is only −4.5 kcal mol^{-1}, less than half the corresponding escape enthalpy (**7** → **6**) in Scheme 1. Escape enthalpies to the methylmethylenecyclopropane in the second row of Scheme 2 are also reduced relative to the simpler compounds in Scheme 1 but they are still large, −9 to −11 kcal mol^{-1} for the isomerizations **13** → **12** and **14** → **12**.

In Scheme 3, isomerization of the endocyclic **19** to **18** is essentially nil, and in row 3 of Scheme 3, exothermic isomerization takes place with evolution of about 8 kcal mol^{-1}. Escape enthalpies for the double bond from endocyclic to the exocyclic position are favorable throughout Schemes 1−3, but they are diminished with the number of methyl groups.

Triplet States. Throughout Schemes 1−3, agreement between calculated results and experimental results, where available, along with consistency of calculated thermochemical results with one another argue against existence of triplet ground states among the molecules studied. The debatable exception is [3]-radialene itself, for which there is disagreement between the experimental value, 95 ± 3 kcal mol^{-1}, and the computed value, 103.6 kcal mol^{-1}.

Use of the **stable** keyword[12] in Gaussian 98 indicates an RHF → UHF instability but optimization of the triplet state for [3]-radialene gives energies that are of the order of 80−90 kcal mol^{-1} higher than the singlet. Evidence that the D_{3h} triplet is not the ground state is Jahn−Teller distortion of the triplet from the D_{3h} structure to a high energy C_{2v} structure which is a second-order saddle point leading to lower symmetry conformations. Existence of a second-order saddle point in addition to the Jahn−Teller distortion from the D_{3h} conformation both argue against a ground-state triplet in [3]-radialene. We conclude, on energetic and symmetry grounds, that the triplet structure is implausible as the ground state of [3]-radialene and is not responsible for the disagreement between experiment and calculation for $\Delta_f H^{298}$.

Strain Enthalpies. Certainly, strain energy plays a dominant role in the thermochemistry of [3]-radialene and substituted cyclopropenes and cyclopropanes. Unfortunately, there are several methods of calculating strain energy, none of which is unique or clearly preferable over any other and all of which give different answers. Accordingly, we believe that strain energies should be used in a semiquantitative way and that trends and relative values of strain energies calculated by the same method are more useful than absolute values. (In this context, the distinction between enthalpy and energy is not important, and the two terms appear to be used synonymously in the literature.)

Hydrogenation. One method of estimating approximate strain enthalpies is through enthalpies of hydrogenation $\Delta_{hyd} H^{298}$. From G3(MP2) calculations on cyclopropene, cyclopropane, propene, and propane,[4] we find a difference of 24.9 kcal mol^{-1} between $\Delta_{hyd} H^{298}$(cyclopropene) = −54.3 kcal mol^{-1} for saturation of the double bond without ring opening and $\Delta_{hyd} H^{298}$(propene) = −29.4 kcal mol^{-1}. The experimental results,[10] $\Delta_{hyd} H^{298}$(cyclopropene) = −53.5 ± 0.6 kcal mol^{-1} and $\Delta_{hyd} H^{298}$-

TABLE 4: G3(MP2) Computed and Experimental Results for Benzene, Cyclohexa-1,3-diene, Cyclohexene, Cyclohexane, 1-Butene, and *n*-Butane[a]

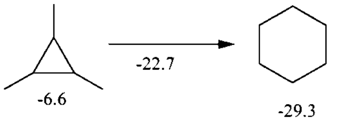
	25	**26**	**27**	**28**	**29**	**30**
H^{298}	−231.82430	−232.97931	234.18629	−235.39571	−156.90003	−158.11243
E(ZPE)	0.09614	0.11755	0.14025	0.16288	0.10382	0.12604
TCH	0.00545	0.00627	0.00661	0.00688	0.00633	0.00688
$\Delta_f H^{298}$	18.63	24.90	−1.43	−29.28	−0.42	−30.15
$\Delta_f H^{298}$(exp)	19.7 ± 0.2	25.4 ± 0.2	-1.2 ± 0.2	-29.5 ± 0.2	0.0 ± 0.3	-30.0 ± 0.2

[a] Experimental values from ref 10.

(propene) = −29.8 ± 0.2 kcal mol^{-1}, are in substantial agreement with computed values. Taking $\Delta_{hyd}H^{298}$(propene) to represent hydrogenation of an unstrained double bond, the difference $\Delta_{hyd}H^{298}$(cyclopropene) − $\Delta_{hyd}H^{298}$(propene) is an approximation to the release of strain energy on going from cyclopropene to cyclopropane, i.e., the strain enthalpy of cyclopropene relative to cyclopropane. Although we can obtain very accurate experimental data for the hydrogenation reactions, the result is still an approximation because we do not know that the bond enthalpies transfer. For example, a C−H bond in cyclopropane does not have precisely the same enthalpy as a C−H bond in propane.

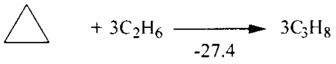
The hydrogenation thermochemistry of methylcyclopropene is very similar to that of cyclopropene (see Table 1) with comparable agreement between calculated and experimental values of $\Delta_{hyd}H^{298}$. Dimethylcyclopropene is somewhat stabilized by its methyl groups but so is the branched reaction product (Scheme 2), so $\Delta_{hyd}H^{298}$ is little affected.

Isomerization. A very simple method of estimating strain energy in more complicated molecules is through the enthalpy of isomerization to an isomer defined as a "strain-free" reference point. In the case of perhydro[3]-radialene (trimethylcyclopropane), the necessary isomer comes readily to mind in cyclohexane. *trans*-Trimethylcyclopropane has $\Delta_{isom}H^{298}$ = −22.7 kcal mol^{-1} to cyclohexane. The result is smaller than that for cyclopropane suggesting stabilization of the cyclopropane moiety by the methyl groups. We shall take up this issue in greater detail in a later section.



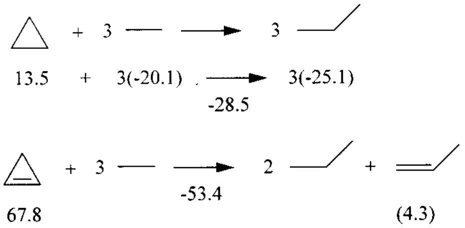
Homodesmotic Reactions. Isodesmic reactions were defined long ago by Hehre[13] and were discussed in relation to cyclopropanes and other strained systems by Dill et al.[14] as reactions, hypothetical or real, in which the number of bonds is conserved and only the relationships among them change. Homodesmotic reactions[15] are a subclass of isodesmic reactions defined by the further constraint that the hybridization of C−H bonds is conserved in the reaction and there is a matching of the number of hydrogen atoms joined to carbon atoms in reactant and product.[15] Isodesmic, homodesmotic, and similar reaction schemes are discussed in detail in ref 16. Briefly, the object of these and similar reaction schemes is to see that unwanted bond enthalpy changes or hybridization enthalpy changes cancel so as to concentrate on a selected aspect of the reaction such as a change in strain or electron conjugation enthalpy. We shall use the term "conjugation enthalpy" to cover effects such as resonance, aromaticity, antiaromaticity, etc., treated in the literature quantum mechanically, as distinct from effects such as mechanical strain which can be treated classically.

Walker et al.[17] used homodesmotic reactions to find 27.4 kcal mol^{-1} for the strain energy of cyclopropane, and we have obtained strain enthalpies for cyclopropenyl compounds in Schemes 1−3 using homodesmotic reaction sets 1−4.



In applying this method to unsaturated hydrocarbons, one may encounter the complication that the strain and conjugation enthalpies appear together in the enthalpy of homodesmotic reaction, which would be zero in their absence. There are numerous other cases, however, in which either strain enthalpy or conjugation enthalpy does not appear or tends to a negligible value. If this is true, the homodesmotic reaction gives the remaining enthalpy without interference. A case in point is that of strained saturated hydrocarbons, for which the conjugation enthalpy can be taken as zero, so that the homodesmotic reaction yields a pure strain energy.[17] In other cases, we set up our homodesmotic reaction so as to minimize strain to the point that it can be ignored, permitting us to regard the enthalpy change of the reaction as expressing a "pure" conjugation effect.

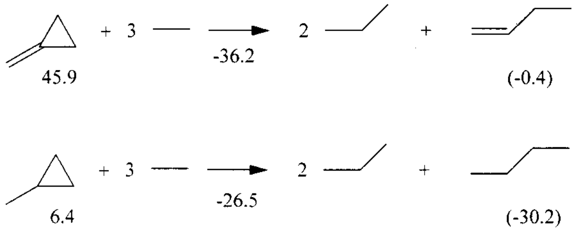
In reaction pair 1 below, cyclopropane undergoes a hypothetical reaction with three molecules of ethane (symbolized by a short horizontal line) to produce three molecules of propane (symbolized by two lines at an oblique angle). The reaction enthalpy obtained by Hess' law addition of $\Delta_f H^{298}$ of the component species is the enthalpy released upon going from a thermochemical system consisting of a strained molecule plus three unstrained molecules to a thermochemical system consisting of three unstrained molecules. The result, using G3(MP2) computed $\Delta_f H^{298}$ values, indicates a strain energy of 28.5 kcal mol^{-1} for cyclopropane, in good agreement with the result of 27.4 kcal mol^{-1} by Walker's G2 calculation.[17]



(1)

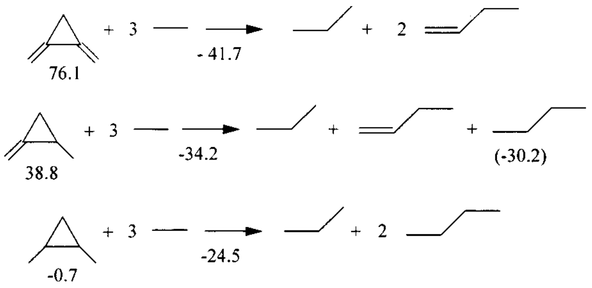
The second homodesmotic reaction in 1 shows a remarkable increase of 24.9 kcal mol^{-1} on comparing cyclopropene to cyclopropane, in agreement with the strain energy in cyclopropene relative to cyclopropane found from its experimental $\Delta_{hyd}H^{298}$.

Reaction pair 2 shows a strain enthalpy for methylcyclopropane that is consistent with cyclopropane slightly stabilized by the methyl group. There is an increase in ring strain of 10 kcal mol^{-1} upon comparing the methylene cyclopropane with methylcyclopropane. The new molecule involved in the homodesmotic reaction is 1-butene with $\Delta_f H^{298}$ = −0.4 kcal mol^{-1} and a symbol that is self-evident from the previous reactions. This strain can be thought of as torsional, imposed by the rigidity of the planar methylene group.



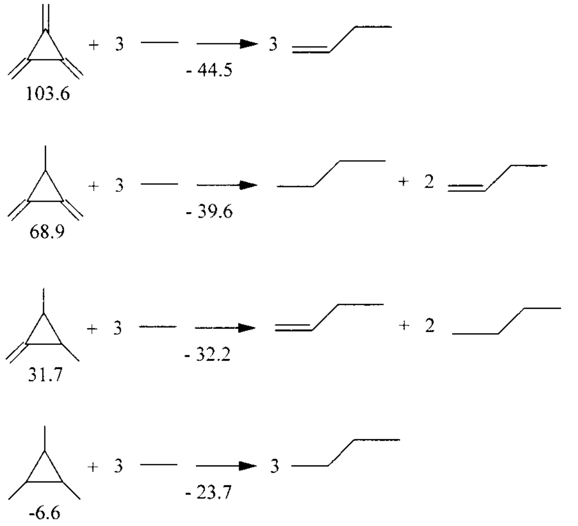
(2)

Reaction group 3 shows a similar 10 kcal mol^{-1} increase in calculated strain enthalpy upon imposing one methylene group on the ring. Imposition of the second methylene group in dimethylenecyclopropane increases strain by about 7.5 kcal mol^{-1}. Two methyl groups in dimethylcyclopropane stabilize the ring, bringing about a 2.0 kcal mol^{-1} reduction in strain enthalpy.



(3)

Reaction group 4 shows an increase in strain enthalpy in the ring upon substitution of one, two, and three methylene groups for methyl groups of 8.5, 7.4, and 4.9 kcal mol^{-1}, respectively. Note also the agreement between the strain energy of perhydro-[3]-radialene calculated by homodesmotic reaction $\Delta_rH^{298} = -23.7$ kcal mol^{-1} and its enthalpy of isomerization to cyclohexane $\Delta_{isom}H^{298} = -22.7$ kcal mol^{-1}



(4)

Sequential substitution of zero, one, two, and three methylene groups on cyclopropane (compounds **3**, **6**, **10**, and **17**) brings about a sequential increase in strain enthalpy of 28.5, 36.2, 41.7, and 44.5 kcal mol^{-1}. Strain enthalpy in the cyclopropane ring diminishes with methylene substitution. Strain energies of the saturated compounds in reaction groups 1−4 (compounds **3**, **9**, **16**, and **24**) are 28.5, 26.5, 24.5, and 23.7 kcal mol^{-1}.

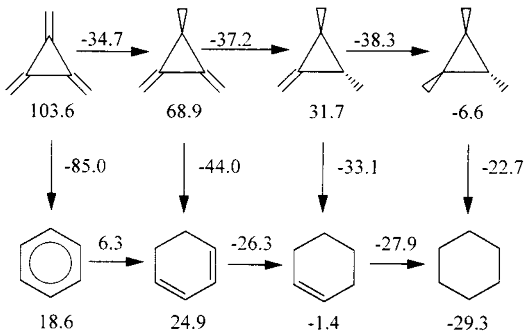


Figure 2. Isomerization and hydrogenation enthalpies for the [3]-radialene system.

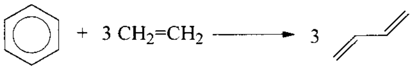
Hydrogenation−Isomerization Cycle. Of the many hydrogenation and isomerization cycles that can be written connecting the component molecules in Schemes 1−4, perhaps the most interesting is the sequential hydrogenation of [3]-radialene itself parallel with the sequential hydrogenation of its isomer, benzene (Figure 2).

The chemical instability of [3]-radialene, as evidenced by the difficulty experienced in its synthesis and purification, is reflected in a remarkable difference in enthalpy between the most energetic and least energetic members of this sequence, 22 kcal mol^{-1} per C atom. Isomerization of perhydro[3]-radialene (*trans*-trimethylcyclopropane) to cyclohexane gives a ring strain enthalpy of 23 kcal mol^{-1}. Isomerization of tetrahydro[3]-radialene to cyclohexene involves a decrease in enthalpy of 33 kcal mol^{-1}. Substitution of a methylene group for a methyl group increases the isomerization enthalpy by about 10 kcal mol^{-1}. The methylene carbon atom at the apex of the cyclopropanyl triangle has a nominal bond angle of 120°. In tetrahydro[3]-radialene, compromise is struck with the normal triangular bond angle of 60° at the expense of 10 kcal mol^{-1} in strain enthalpy. Dihydro[3]-radialene has an isomerization enthalpy to cyclohexa-1,3-diene that is 11 kcal mol^{-1} greater than that of the tetrahydro compound. Here conjugation enthalpies may exist in reactant and product, but they appear to be approximately equal. If conjugative enthalpies exist in reactant and product, one would expect conjugative stabilization of cyclohexa-1,3-diene to be greater than that of dihydro[3]-radialene and so it is, but the difference is too small to be of much significance.

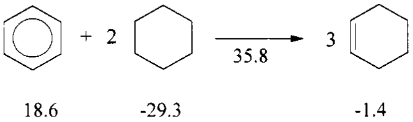
Resonance Energy. Given the unique enthalpic and chemical stability of benzene, and the stability that the benzene moiety confers upon larger molecules, one would like to know whether any part of the "aromaticity" of benzene is retained in its isomer [3]-radialene. The immediate answer would appear to be that [3]-radialene is not aromatic, on the grounds of its chemical instability and high enthalpy of formation per C atom. Indeed, from its chemical behavior, [3]-radialene might even be antiaromatic.

On the basis of information we have so far, judgment is hard to make, because, in the presence of severe molecular strain, correlation stabilization or destabilization might easily be overlooked. The question becomes one of separating mechanical destabilization from electronic influence on molecular enthalpy and stability.

One solution that has been proposed for this problem is to place yet another restriction on the isodesmic reactions, trying to determine conjugation enthalpies by use of homomolecular homodesmotic reactions.[16] Homomolecular homodesmotic reactions are a subclass of isodesmic reactions having all of the constraints of homodesmotic reactions plus the condition that the molecules involved in the reaction shall be as structurally similar as possible. For example, the isodesmic reaction

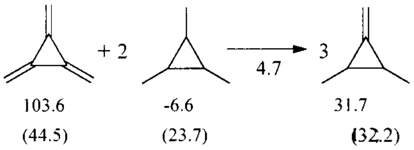


is homodesmotic and the reaction



is homomolecular homodesmotic (and can be shown to be equivalent to Kistiakowski's well-known method[16] of subtracting 3 times $\Delta_{\mathrm{hyd}}H^{298}$(cyclohexene) from $\Delta_{\mathrm{hyd}}H^{298}$ (benzene)).

Applying the homomolecular homodesmotic reaction method to [3]-radialene, we have a 4.7 kcal mol^{-1} enthalpy increase



(5)

for the reaction, implying a like amount of stabilization of the radialene relative to tetrahydro-[3]-radialene. Applying Hess's law to the strain enthalpies in reaction group 4, we can calculate a 4.7 kcal mol^{-1} decrease in strain energy for reaction 5. This is circular reasoning, however, because the "strain free" enthalpies in reaction group 4 cancel; the calculated stabilization enthalpies are not independent. We are left with a stabilization enthalpy that may be due to exocyclic conjugation or strain relaxation in reaction 5 or some mixture to the two. For those who like to say that benzene has 36 kcal mol^{-1} of resonance energy, the same reasoning leads one to say that [3]-radialene, despite the strain imposed by three methylene groups radiating from a cyclopropane ring, has 4.7 kcal mol^{-1} of exocyclic conjugation stabilization.

Conclusion

Sequential addition of one, two, and three methylene groups to cyclopropane brings about an increase in molecular strain. Sequential addition of methyl groups to cyclopropane brings about a small but regular reduction in energy. The thermochemistry of methylene substituted cyclopropane, [3]-radialene, is dominated by angular and torsional strain with not more than 5 kcal mol^{-1} contribution from exocyclic conjugative effects.

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