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Survey of the Heats of Formation of Three-Membered-Ring Species

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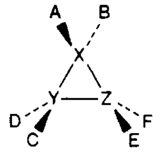
I. Introduction

The organic chemical community has long been fascinated[1] by compounds with three-membered rings. These rings are the smallest of all ring systems, yet they enjoy a high degree of possible chemical functionalization. More precisely, in structure I the ring atoms X, Y, and Z can all be carbons or any or all can be replaced by heteroatoms. Likewise, the groups A–F can be univalent substituents, they can be joined together to form intra- and/or inter-ring multiple bonds, or they can be parts of other rings. Numerous primary articles and secondary reviews have been written on these species, including the recent two-volume set of books on cyclopropanes edited by Rappoport[2] that are part of Patai's continuing series *The Chemistry of Functional Groups*. Numerous aspects of the energetics of three-membered rings are discussed in several chapters[3] in Rapopport's books. The same can be said of various chapters[4] in the new continuing book series *Molecular Structure and Energetics*. We also note the recent review by Kolesov and Kozina[5] (KK) that deals heavily with the thermochemistry of compounds with strained rings, a class of compounds containing numerous three-membered rings.



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Our review will also reflect a strong thermochemical bias. Tables I–IV present an archival collection (all data are through mid-1988) of heats of formation of three-membered-ring species that are carbocyclic or heterocyclic containing nitrogen, oxygen, and sulfur, respectively. Data for species in both their condensed and vapor phase are given whenever available. Square brackets around a value denote that the value is for the solid, and parentheses following a value give its suggested error bars or uncertainty. To aid the general reader all discussion in the text will use the "customary" energy unit kcal/mol. However, following orthodox thermochemical practice and current international scientific convention, we use the energy unit kJ/mol for the tables: recall that the conversion factor is officially exactly defined as 4.184 kJ ≡ 1 kcal. We also discuss many of these numbers in subsequent sections in order to explain how they were obtained, to interrelate diverse molecules, and to expose seemingly erroneous values or unreasonable assumptions. Table V compares the heats of formation of oxiranes and cyclopropanes related by the formal exchange of oxygen and methylene. No apparent regularity arises. Table VI likewise compares thiiranes and cyclopropanes related by the formal exchange of sulfur and methylene. Again, systematic comparison proves evasive.

In the concluding sections of this review, we present a collection of literature experimental data on the norcaradiene–tropylidene equilibrium and that of their

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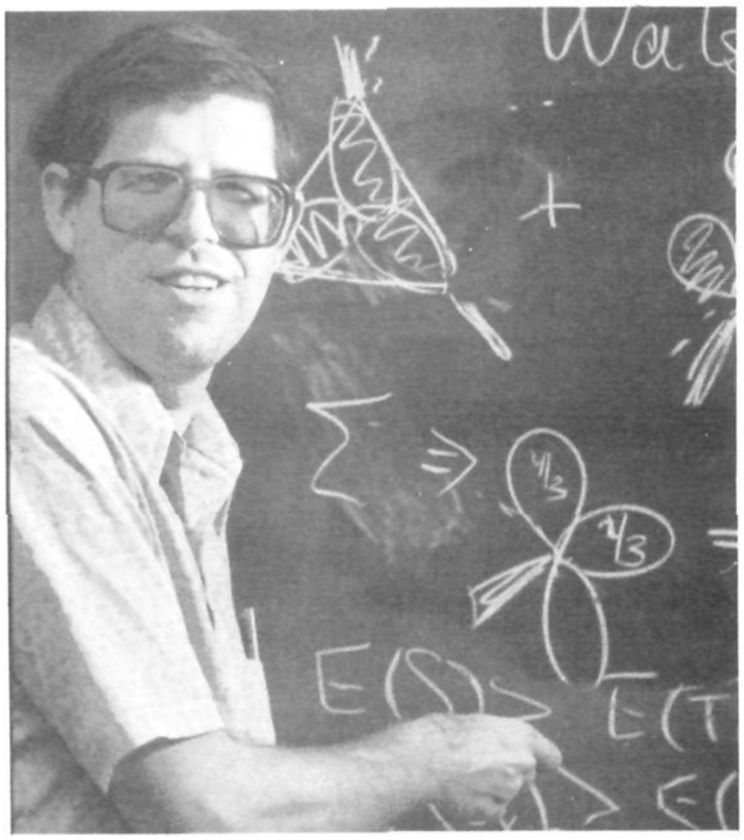


Joel F. Liebman was born in Brooklyn, NY, on May 6, 1947. He received his B.S. in Chemistry from Brooklyn College of the City University of New York in 1967 and his Ph.D. from Princeton University in 1970 with Professor Leland C. Allen, studying the bonding of noble gas and fluorine compounds. From September 1970 through August 1971, he was a NATO Postdoctoral Fellow (and Ramsay Honorary Fellow) at the Departments of Theoretical and Physical Chemistry of Cambridge University with Professors A. David Buckingham and John W. Linnett. He returned to the U.S. as a NRC–NBS Postdoctoral Research Associate with Drs. Thomas D. Coyle and Frederick E. Brinckman of the Inorganic Chemistry Section, National Bureau of Standards—Gaithersburg. In September 1972, he joined the Chemistry Department of the University of Maryland Baltimore County as an Assistant Professor and became a Full Professor in 1982. His research interests are diverse and include studies of the inorganic and organic chemistry of fluorine compounds, the interface of the energetics of gaseous neutral and ionic organic species, the nature of strained organic molecules (cf. this review and the book with Arthur Greenberg *Strained Organic Molecules*), and conceptual regularities in chemical phenomena. He is the author or coauthor of over 100 articles in the primary or review literature and the coauthor or coeditor of more than a dozen books. He coedits with Dr. Greenberg the series of research monographs *Molecular Structure and Energetics*, is consulting editor for *Structural Chemistry*, and actively collaborates on both research and data projects with Dr. Sharon G. Lias and her colleagues at the National Institute for Standards and Technology. He is also an avid poet and punner.

Arthur Greenberg was born in Brooklyn, NY, on Sept 27, 1946. He received his B.S. in Chemistry from Fairleigh Dickinson University in 1967 and his Ph.D. degree from Princeton University in 1971, studying conformational analysis under the supervision of Professor Pierre Laszlo. The period from July through December 1970 was spent at the Université de Liège in Belgium with Professor Laszlo. From 1972 through 1977 Dr. Greenberg was on the faculty at Frostburg State College, moving in 1977 to the New Jersey Institute of Technology, where he is Professor of Chemistry and Co-Director of the Air Pollution Research Laboratory. Dr. Greenberg's research interests include experimental and theoretical organic chemistry studies, especially on substituted strained molecules and strained bridgehead lactams, as well as environmental chemistry emphasizing polycyclic aromatic hydrocarbons and their derivatives. He is the author or coauthor of 70 research articles, co-author with Joel Liebman of the book *Strained Organic Molecules*, coeditor with Dr. Liebman of the book series *Molecular Structure and Energetics*, and coeditor with Dr. István Hargittai of the journal *Structural Chemistry*. He is an enthusiastic collector of rare chemistry and alchemy books and is patiently awaiting the Dodgers return to Brooklyn.

substituted derivatives (Table VII) and of the norbornadiene–quadricyclane equilibrium (Table VIII) and of their substituted derivatives (Table IX). The absence of reliable data is shown to be a major hindrance to a complete discussion of the roles of heteroatoms, substituent effects, and solvation on the structure and energetics of ground-state species and the transition states that interconnect them.

II. Why Should There Be Another Review?

Despite the problems associated with a continued lack of information and all the earlier reviews, a new review of three-membered rings should still warrant the reader's attention. Three-membered rings are the smallest of all rings and among the smallest of functionalities that introduce strain into organic molecules. Nonetheless, these strained species with three-membered rings allow for considerable diversity of substituents, heteroatoms, and unsaturation. In neutral and charged species alike, three-membered rings also allow for the possibility of aromaticity. Species containing three-membered rings thus are archetypical for much of our understanding of the energetics of organic compounds. Three-membered rings are also common in inorganic chemistry, and their understanding is useful therein as well. However, for the sake of brevity, we only consider the large and significant class of "classical organic compounds" with three-membered rings and limit our attention to only those heats published through mid-1988.[6]

We acknowledge that many of the directly determined values of heats of formation have already been tabulated by KK. We also make use of numerous primary articles as well as the recent thermochemical compendium by Pedley, Naylor, and Kirby[7] (PNK). In case of "conflict" of experimental values between this and Kolesov and Kozina's review, we defer to Kozina's first-hand experimental experience with the thermochemistry of many of the compounds of interest here. Indeed, we generally accept the value KK selected even when it was derived from an estimated heat of vaporization. It should be noted that the heats of formation of most gaseous organic compounds reported in the primary and review literature incorporates a heat of vaporization not corrected either to 25 °C or for nonideality of the vapor.

We also go beyond the studies of KK and PNK to present derived heat of formation results from numerous reaction calorimetry studies. These cases require energetics for the non-three-membered-ring species to be available. Reactions employed include both hydrogenation and dehydrogenation, both addition and extrusion reactions of carbenes, and rearrangement reactions catalyzed by heat, light, or metal ions. Many of these reactions are discussed explicitly, careful attention being given to the not-too-rare cases of contradictory heat of formation values arising from seemingly unequivocal studies. In these cases, the heats of formation are referenced DRV to explicitly denote that they are derived values.

Heats of reaction can also yield useful information even when the heat of formation of the product is unknown. More precisely, careful estimates of the heat of formation of the reaction product also allow one to obtain a reasonable estimate of the heat of formation of the starting material. We thus also report the results of some analyses where we use a literature heat of reaction and estimate the thermochemistry of a "normal" molecule to derive a heat of formation of some interesting compound with a three-membered ring. These values, too, are denoted DRV.

Even without direct derivation of heats of formation, heats of reaction can still be instructive. The thermochemistries of the equilibria between tropylidenes and norcaradienes and between norbornadienes and quadricyclanes provide examples of this. Our study concludes with analyses of these and related reactions with explicit regard to the roles of substituents, heteroatoms, and solvation in modifying and modulating the structures and energies of both ground-state species and the transition states that interrelate them. Compounds containing three-membered rings continue to astonish, to confound, and to educate the chemical community.

III. Archive of the Heats of Formation of Three-Membered-Ring Compounds

A. Organization of the Data

In the first of our archival tables, the heats of formation of carbocyclic compounds with three-membered rings are presented, while the Tables II–IV are for nitrogen-, oxygen-, and sulfur-containing three-membered rings. While perhaps slightly more "expensive" in length than putting all four tables together, this segregation by the presence and nature of heteroatoms allows for easier internal comparison of many classes of compounds, e.g., oxabicycloalkanes (also known as cycloalkene oxides). In addition, in that the thermochemistry of species containing three-membered rings is dominated by carbocycles, our decision obviates beginning discussion with the rather ill-defined thermochemistry of three diazirines. In all four of these archival tables we employ the following conventions. The first is that we generally name all the compounds using quite proper nomenclature except in those cases when there is a "popular" name, which we also employ. Since systematic names are often cumbersome while trivial names are often nondescriptive, the structure of many species will be given explicitly in a collection of formulas. The second convention is that the tables are all internally arranged according to the *Chemical Abstracts* (Hill) sort scheme. This often results in formally related compounds being quite far apart in the listing but has the advantage that it may immediately be determined if a compound has been studied. The third convention is to append the letters DRV to designate a heat of formation value that has been derived by use of some method other than the direct measurement of heat of combustion—we explicitly admit that these values are of significantly variable reliability. These derived values are discussed at some length in subsequent sections. While it may be argued that only thermochemists will make use of these discussions, we dissent. They are designed also for the experimental organic chemist to maximize use of the admittedly sparse data. Indeed, we are saying to the reader neither "trust us" nor "disregard that datum". Rather, this allows the reader to decide whether to trust an entry and additionally apply the logic to other species of interest or to disregard it.

B. Carbocycles

In Table I, the heats of formation (in kJ/mol) of carbocyclic compounds with three-membered rings are presented.

C. Nitrogen-Containing Rings

In Table II, the heats of formation (in kJ/mol) of compounds with three-membered rings containing nitrogen are presented.

D. Oxygen-Containing Rings

In Table III, the heats of formation (in kJ/mol) of three-membered rings containing oxygen are presented.

E. Sulfur-Containing Rings

In Table IV, the heats of formation (in kJ/mol) of three-membered rings containing sulfur are presented.

IV. Commentary on the Derived Thermochemistry of Carbocyclic Three-Membered-Ring Compounds

In this section, we discuss the derived heats of formation of compounds with carbocyclic three-membered rings. That is, we consider those species that were studied by thermochemical methods other than the direct measurement of heat of combustion. As noted earlier, the commentaries that follow are designed to aid the reader in the use of the currently available data. We emphasize that combustion calorimetry is but one of a variety of ways to obtain desired heats of formation. If the methods that follow are diverse and untested and the accuracy either ill-defined or seemingly insufficient, it is to be noted that heat of combustion experiments are arduous and seemingly becoming a "lost art". It is our conviction that, for better or worse, thermochemical data will increasingly be obtained through unorthodox approaches used by nonthermochemists and *not* corroborated by the more classical combustion calorimetric methods.

A. C_3F_6 through C_7H_6

The general observation that, despite their structural simplicity, three-membered ring carbocyclic compounds are nontrivial to analyze is illustrated by the first compound in Table I. The heat of formation of hexafluorocyclopropane was found[8] by interrelating the ionization potential of this species and the appearance

TABLE I. Heats of Formation of Carbocyclic Compounds with Three-Membered Rings[a]

		ΔH_f, kJ/mol			
formula	name	[ΔH_f(s)] or ΔH_f(l)	ref	ΔH_f(g)	ref
C_3F_6	hexafluorocyclopropane			−978	9DRV
$C_3H_2F_4$	1,1,2,2-tetrafluorocyclopropane			−590 (42)	DRV
C_3H_4	cyclopropane			277.1 (2.5)	5
$C_3H_4Cl_2$	1,1-dichlorocyclopropane	−27.2 (1.2)	15	42	DRV
C_3H_4O	cyclopropane			16 (4)	DRV
C_3H_5Br	bromocyclopropane	27.6 (4.4)	21DRV		
C_3H_6	cyclopropane (1a)			53.5 (0.5)	5
C_3H_7N	cyclopropylamine	45.8 (0.5)	7	77.0 (0.7)	7
C_4H_4	methylenecyclopropene			423	DRV
C_4H_5N	cyanocyclopropane	140.8 (0.8)	7	181.8 (1.0)	7
C_4H_6	methylenecyclopropane			200.5 (1.8)	5
C_4H_6	1-methylcyclopropene			243.6 (1.1)	5
C_4H_6	bicyclobutane (**2a**)	193.7 (1.2)	7	217.2 (0.8)	5
$C_4H_6O_2$	cyclopropanecarboxylic acid	[−415 (8)]	25		
C_4H_8	methylcyclopropane	1.7 (0.6)	5	24.3	5
C_5H_5N	1-cyanobicyclobutane (**3a**)	258.8 (1.2)	7	304.6 (1.3)	7
C_5H_6	ethynylcyclopropane	261.1 (0.8)	5	292.0 (1.7)	5
C_5H_6	bicyclo[2.1.0]pent-2-ene (**4a**)			334 (4)	DRV
C_5H_6	tricyclo[1.1.1.$0^{1,5}$]pentane (**5a**) ([1.1.1]propellane)	326 (4)	29DRV	351 (4)	29DRV
$C_5H_6F_2$	1,1-difluoro-2-vinylcyclopropane			−242	DRV
$C_5H_6O_4$	cyclopropane-1,1-dicarboxylic acid	[−803]	31		
$C_5H_6O_4$	*cis*-cyclopropane-1,2-dicarboxylic acid	[−799]	31		
C_5H_8	vinylcyclopropane	102.5 (0.8)	5	127.2 (1.3)	30DRV
C_5H_8	ethylidenecyclopropane			161	DRV
C_5H_8	1,2-dimethylcyclopropene			186	DRV
C_5H_8	2-methyl-1-methylenecyclopropane			167	DRV
C_5H_8	spiropentane (**6**)	147.5 (1.3)	5	175.0 (1.3)	5
C_5H_8	bicyclo[2.1.0]pentane (**2b**)	130.7 (1.3)	5	158.7 (1.3)	5
$C_5H_8Cl_2$	*cis*-1,1-dichloro-2,3-dimethylcyclopropane	−86.9 (0.9)	5	−47.2	5
$C_5H_8Cl_2$	*trans*-1,1-dichloro-2,3-dimethylcyclopropane	−90.2 (1.1)	5	−50.7	5
C_5H_8O	acetylcyclopropane	−154.7 (1.0)	5	−115.3 (1.0)	5
$C_5H_8O_2$	methyl cyclopropanecarboxylate	−346.0 (1.5)	30a		
C_5H_{10}	ethylcyclopropane	−24.8 (0.8)	5	3.4	5
C_5H_{10}	1,1-dimethylcyclopropane	−33.3 (0.7)	5	−8.2 (1.2)	5
C_5H_{10}	*cis*-1,2-dimethylcyclopropane	−26.3 (0.6)	5	1.7	5
C_5H_{10}	*trans*-1,2-dimethylcyclopropane	−30.7 (0.8)	5	−3.8	5
$C_5H_{10}O_2$	1,1-bis(hydroxymethyl)cyclopropane	−436	31		
$C_5H_{11}N$	1,1-aminocyclopropylethane	−23	31[b]		
C_6H_6	trimethylenecyclopropane (**7**) ([3]-radialene)			396 (12)	37DRV
C_6H_6	tricyclo[3.1.0.$0^{2,6}$]hexene (**8a**) (benzvalene)	331.6 (1.4)	38DRV	363	DRV
C_6H_7N	1-cyanobicyclo[2.1.0]pentane (**9a**)	227.8 (1.1)	7	272.1 (1.2)	7
C_6H_8	1-vinylbicyclobutane (**3b**)	221.2 (5.4)	5		
C_6H_8	bicyclo[3.1.0]hex-3-ene (**10**)	120.6 (2.9)	5		
C_6H_8	1,3,3-trimethylcyclopropene	137.7 (0.8)	5	164.5 (1.9)	5
C_6H_8	tricyclo[3.1.0.$0^{2,6}$]hexane (**11a**)			228.0	39DRV
$C_6H_8F_2$	1,1-difluoro-2-[(*E*)-1-propenyl]cyclopropane				
$C_6H_8F_2$	*cis*-1,1-difluoro-2-methyl-3-vinylcyclopropane				
$C_6H_8O_2$	methyl bicyclobutane-1-carboxylate (**3c**)	−203.1 (0.6)	7	−164.6 (0.7)	7
C_6H_{10}	bicyclopropyl (**12**)	95.8 (3.3)	5	129.3 (3.6)	5
C_6H_{10}	bicyclo[3.1.0]hexane (**2c**)	5.1 (2.1)	5	38.6 (2.1)	5
C_6H_{10}	isopropenylcyclopropane	61.2 (1.3)	5	89.6 (1.3)	5
C_6H_{10}	[(*E*)-1-propenyl]cyclopropane			96.5 (1.3)	DRV
C_6H_{10}	*cis*-1-methyl-2-vinylcyclopropane			95.1 (1.0)	DRV
C_6H_{10}	dimethylmethylenecyclopropane	−32	31[b]		
C_6H_{10}	1,3-dimethylbicyclobutane			255	DRV
C_6H_{12}	1,1,2-trimethylcyclopropane	−96.2 (0.8)	5	−65.7	5
C_6H_{12}	isopropylcyclopropane	−46	31		
$C_6H_{12}O_6$	trimethyl *cis,cis*-cyclopropane-1,2,3-tricarboxylate	[−1106.5 (0.9)]	30a		
		−1075.2 (1.6)	30a		
$C_7H_2N_4$	1,1,2,2-tetracyanocyclopropane	[591.7 (10.5)]	7	680 (45)	41DRV
C_7H_6	1,1-diethynylcyclopropane	500.9 (0.8)	5	538.5	5
C_7H_6	benzocyclopropene (**18**)	329 (4)	42DRV	367 (4)	42DRV
$C_7H_6O_8$	cyclopropane-1,1,2,2-tetracarboxylic acid	[−1592]	31		
C_7H_8	tetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane (**14**) (quadricyclane)	[302.2 (2.3)]	5DRV[c]	339.1 (2.3)	5DRV[c]
C_7H_8	bicyclo[4.1.0]hepta-2,4-diene (**15**) (norcaradiene)	163	DRV[c]	202	DRV[c]
C_7H_9N	1-cyanobicyclo[3.1.0]hexane (**16a**)	98.5 (1.8)	7	142.1 (1.8)	7
C_7H_{10}	tricyclo[4.1.0.$0^{2,6}$]heptane (**17a**) (nortricyclene)	31.1 (2.1)	5	70.4 (1.5)	5
C_7H_{10}	5,5-dimethylbicyclo[2.1.0]pent-2-ene (**4b**)			267 (4)	DRV
C_7H_{10}	3-cyclopropyl-1,2-butadiene	195.8 (1.8)	5	233.5	5
C_7H_{10}	bicyclo[4.1.0]hept-2-ene (**18**)	74.7 (2.8)	5	116.2 (3.0)	5
C_7H_{10}	*anti*-tricyclo[4.1.0.$0^{2,4}$]heptane (**19**)	112.8 (1.3)	5	149.3 (1.4)	5
C_7H_{10}	tricyclo[4.1.1.$0^{2,7}$]heptane (**11b**)			185.8	39DRV
$C_7H_{10}O_4$	dimethyl cyclopropane-1,1-dicarboxylate	−718	31		
C_7H_{12}	2-cyclopropyl-1-butene	83	31		

TABLE I (Continued)

formula	name	ΔH_f, kJ/mol			
		[ΔH_f(s)] or ΔH_f(l)	ref	ΔH_f(g)	ref
C_7H_{12}	2-cyclopropyl-2-butene	62	31		
C_7H_{12}	bicyclo[4.1.0]heptane (**2d**) (norcarane)	−27.2 (1.2)	5	11.6 (1.3)	5
C_7H_{12}	1-methylbicyclo[3.1.0]hexane (**16b**)	−33.1 (1.2)	5	1.5 (1.3)	5
C_7H_{12}	5,5-dimethylbicyclo[2.1.0]pentane (**9b**)			92 (5)	DRV
C_7H_{14}	1,1,2,2-tetramethylcyclopropane	−119.8 (0.8)	5	−86.2	5
C_7H_{14}	1,1-dimethyl-2-ethylcyclopropane	−90.2 (0.8)	5	−56.7	5
C_7H_{14}	2-cyclopropylbutane	−75	31		
C_7H_{14}	*cis*-1,2-diethylcyclopropane	−79.9 (1.3)	5	−44.5 (1.5)	5
C_7H_{14}	*trans*-1,2-diethylcyclopropane	−83.3 (1.2)	5	−49.0 (2.3)	5
C_8H_8	tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (**20**) (semibullvalene)			308 (1)	47DRV
C_8H_{10}	*cis*-7-methylenebicyclo[4.1.0]hept-2-ene (**18b**)	208.6 (1.0)	5	252.0	5
C_8H_{12}	tricyclo[3.2.1.0^{1,5}]octane (**5b**) ([3.2.1]propellane)	−218	48DRV		
C_8H_{14}	bicyclo[5.1.0]octane (**2e**)	−60.3 (1.3)	5	−16.8 (1.5)	5
C_8H_{14}	1-methylbicyclo[4.1.0]heptane (**21a**)	−59.9 (1.5)	5	−20.4 (1.5)	5
C_8H_{14}	2-cyclopropyl-3-methyl-1-butene	13	31		
C_8H_{14}	2-cyclopropyl-1-pentene	−29	31		
C_8H_{14}	2-cyclopropyl-2-pentene	−8	31		
C_8H_{16}	1,1-dimethyl-2-propylcyclopropane	−116.0 (1.7)	5	−77.1	5
C_8H_{16}	2-cyclopropyl-3-methylbutane	−62	31		
C_8H_{16}	2-cyclopropylpentane	−62	31		
C_9H_{10}	phenylcyclopropane	100.3 (0.9)	5	150.5 (0.9)	5
C_9H_{12}	bicyclo[6.1.0]nona-2,4-diene (**23**)	210	DRV	258	DRV
C_9H_{12}	bicyclo[6.1.0]nona-3,5-diene (**24**)	221	DRV	269	DRV
C_9H_{14}	*cis*-spiro(tricyclo[3.2.1.0^{2,4}]octane-6,1′-cyclopropane (**25**)	122.6 (1.6)	5	170.6 (1.6)	5
C_9H_{16}	*cis*-bicyclo[6.1.0]nonane (**2f**)	−70.0 (1.5)	5	−20.6 (1.7)	5
C_9H_{16}	*trans*-bicyclo[6.1.0]nonane (**26**)	−67.9 (1.5)	5	−18.5 (1.7)	5
C_9H_{16}	1,3,5-trimethylbicyclo[3.1.0]hexane (**21b**)	−102.0 (2.1)	5	−60.5	5
C_9H_{16}	5-ethyl-1-methylbicyclo[3.1.0]hexane (**21c**)	−98.2 (2.1)	5	−55.4	5
C_9H_{18}	cyclohexylcyclopropane	−314.6 (4.2)	5[d]		
$C_{10}H_{10}$	pentacyclo[3.3.2.0^{2,4}.0^{3,7}.0^{6,8}]dec-9-ene (**27**) (snoutene)	[246.4 (2.1)]	5		
$C_{10}H_{10}$	tricyclo[3.3.2.0^{2,8}]deca-3,7,9-triene (**28**) (bullvalene)	[262.3 (3.0)]	5	334.1 (3.3)	5
		279	53		
$C_{10}H_{10}$	dicyclopropylbutadiyne	505.3 (1.7)	5	563.4 (2.0)	5
$C_{10}H_{10}O_2$	*cis*-2-phenylcyclopropanecarboxylic acid	−320.9 (2.1)	5	−217.6 (2.2)	5
$C_{10}H_{10}O_2$	*trans*-2-phenylcyclopropanecarboxylic acid	−332.1 (2.1)	5	−227.4 (2.1)	5
$C_{10}H_{12}$	(1*rH*,2*tH*,3*cH*,5*cH*,6*tH*,7*cH*)-tetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-ene (**29**)			322	DRV
$C_{10}H_{12}$	1-cyclopropyl-2-methylbenzene	75.4 (1.2)	5	127.4	5
$C_{10}H_{14}$	tetracyclo[3.3.1.1^{3,1}.0^{1,5}]decane (**30**) (1,3-dehydroadamantane)	24	48DRV		
$C_{10}H_{16}$	1,1,7-trimethyltricyclo[4.1.0.0^{2,6}]heptane (**17b**) (tricyclene)	[−71]	31		
$C_{10}H_{16}$	3,7,7-trimethylbicyclo[4.1.0]hept-2-ene (**18b**) (2-carene)	−22.6 (2.3)	5	25.2	5
$C_{10}H_{16}$	3,7,7-trimethylbicyclo[4.1.0]hept-3-ene (**31**) (3-carene)	−29.6 (1.8)	5	18.7 (3.6)	5
$C_{10}H_{16}O$	1-isopropyl-4-methylbicyclo[3.1.0]hexan-3-one (**16c**) (3-thujanone)	−226	31		
$C_{10}H_{18}$	1-isopropyl-4-methylbicyclo[3.1.0]hexane (**16d**) (thujane)	−193	31		
$C_{10}H_{18}$	*cis*-3,7,7-trimethylbicyclo[4.1.0]heptane (**32a**) (*cis*-carane)	−116.0 (2.3)	5	−68.9 (2.9)	5
$C_{10}H_{18}$	*trans*-3,7,7-trimethylbicyclo[4.1.0]heptane (**32b**) (*trans*-carane)	−118.5 (2.5)	5	−70.4 (2.4)	5
$C_{10}H_{18}O$	*cis*-3,7,7-trimethylbicyclo[4.1.0]heptan-2-ol (**32c**) (*cis*-caran-2-ol)	−307.5 (2.3)	5	−230.3	5
$C_{10}H_{18}O$	*cis*-3,7,7-trimethylbicyclo[4.1.0]heptan-3-ol (**32d**) (*cis*-caran-3-ol)	[−329.0 (3.0)]	5	−249.7 (3.3)	5
$C_{10}H_{18}O$	*trans*-3,7,7-trimethylbicyclo[4.1.0]heptan-3-ol (**32e**) (*trans*-caran-3-ol)	[−343.5 (2.4)]	5	−259.2 (2.5)	5
$C_{10}H_{18}O$	*cis*-3,7,7-trimethylbicyclo[4.1.0]heptan-4-ol (**32f**) (*cis*-caran-4-ol)	−312.1 (2.8)	5	−234.1 (4.3)	5
$C_{10}H_{20}$	1,1-dimethyl-2-pentylcyclopropane	−167	31		
$C_{11}H_8$	naphtho[*b*]cyclopropene (**33**)	[360 (1)]	42DRV	435	42DRV
$C_{11}H_{10}$	tricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene (**34**) (dinorcaradiene, [4.4.1]propellatetraene)	279	DRV	338	DRV
$C_{11}H_{14}$	1-cyclopropyl-2,4-dimethylbenzene	36.4 (1.3)	5	91.4	5
$C_{11}H_{14}$	tricyclo[4.4.1.0^{1,6}]undeca-3,8-diene (**35**)	35.0	58		
$C_{11}H_{14}O_8$	tetramethyl cyclopropane-1,1,2,2-tetracarboxylate	[−1432]	31		
$C_{11}H_{16}$	*exo*-tetracyclo[6.2.1.0^{2,7}.0^{3,5}]undecane (**36**)	3.4 (2.1)	5	58.6 (2.2)	5
$C_{11}H_{22}$	1,1-dimethyl-2-hexylcyclopropane	−193.0 (1.7)	5	−144.4	5
$C_{12}F_{18}$	hexakis(trifluoromethyl)tricyclo[3.1.0.0^{2,6}]hexene (**8b**) (hexakis-(trifluoromethyl)benzvalene)	−3644	DRV		
$C_{12}F_{18}$	hexakis(trifluoromethyl)tetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane (**37a**) (hexakis-(trifluoromethyl)prismane)	−3541	DRV		
$C_{12}H_{14}O_2$	ethyl *cis*-2-phenylcyclopropanecarboxylate	−299.9 (1.2)	5	−229.2 (1.3)	5
$C_{12}H_{14}O_2$	ethyl *trans*-2-phenylcyclopropanecarboxylate	[−337.2 (1.2)]	5	−240.3 (1.3)	5
$C_{12}H_{16}$	1-cyclopropyl-2,4,6-trimethylbenzene	5.2 (2.1)	5	63.7	5
$C_{12}H_{16}$	1-cyclopropyl-4-isopropylbenzene	14.2 (1.7)	5		
$C_{12}H_{18}$	hexamethyltetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane (**37b**) (hexamethylprismane)	317	DRV		
$C_{13}H_{20}$	1-cyclohexylbicyclo[4.1.0]heptane (**21d**)	−158.9 (3.2)	5	−108.5	5
$C_{14}H_{18}$	*exo*-hexacyclo[10.1.1^{4,7}.0^{1,12}.0^{2,10}.0^{3,8}.0^{9,13}]tetradecane (**38**) (*exo*-RJ5)	[28]	66	104 (2)	66
$C_{14}H_{18}$	*endo*-hexacyclo[10.1.1^{4,7}.0^{1,12}.0^{2,10}.0^{3,8}.0^{9,13}]tetradecane (**39**) (*endo*-RJ5)	[58]	66	135 (4)	66
$C_{15}H_{10}O$	diphenylcyclopropenone	[197.9 (2.1)]	70–2[e]	316.7 (8.2)	70–2[e]
$C_{15}H_{14}$	1,1-diphenylcyclopropane	185.5 (3.3)	5	250.9	5
$C_{15}H_{14}$	*cis*-1,2-diphenylcyclopropane	178.7 (2.1)	5		
$C_{15}H_{14}$	*trans*-1,2-diphenylcyclopropane	166.2 (3.2)	5	232.8	5

TABLE I (Continued)

formula	name	ΔH_f, kJ/mol [ΔH_f(s)] or ΔH_f(l)	ref	ΔH_f(g)	ref
$C_{16}H_{20}N_2$	tetracyclopropylsuccinonitrile	[426.8 (2.5)]	74	537.2	74
$C_{20}H_{30}$	hexacyclopropylethane	[357.3 (3.8)]	75	466.5	75
$C_{20}H_{36}$	tetra-*tert*-butyltricyclo[1.1.0.0^{2,4}]butane (**40**) (tetra-*tert*-butyltetrahedrane)	[−45.6 (7.9)]	76	25.9 (8.8)	76
$C_{28}H_{48}O$	(6β)-methoxy-3,5-cyclocholestane (**41**)	[−628.0 (5.5)]	7		

[a] Those data in square brackets are for species in their solid state. Literature citation numbers are given for the majority of compounds. However, all species without such a number, and many with, are discussed at some length in the text. Explicit referencing is given there. [b] This species has an ambiguous name as noted by its reference source. [c] The energetics of the parent species quadricyclane and norbornadiene are discussed in section IV.B, while that of their substituted derivatives is deferred to section VIII. [d] Contradictions in the energetics of this superficially simple species is discussed in section IV.C. [e] The heat of formation given for diphenylcyclopropenone is a composite of directly measured and derived numbers. See the discussion in section IV.E.

TABLE II. Heats of Formation of Three-Membered Rings That Contain Nitrogen

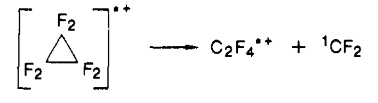
formula	name	ΔH_f, kJ/mol ΔH_f(l)	ref	ΔH_f(g)	ref
CH_2N_2	diazirine (**42a**)			265 (11)	77DRV
$C_2H_3N_2Br$	3-bromo-3-methyldiazirine (**42b**)			291 (18)	78DRV
$C_2H_3N_2Cl$	3-chloro-3-methyldiazirine (**42c**)			243 (24)	78DRV
C_2H_5N	aziridine (**1b**) (ethylenimine)	91.9 (0.6)	7	126.5 (0.9)	7

TABLE III. Heats of Formation of Three-Membered Rings That Contain Oxygen[a]

formula	name	ΔH_f, kJ/mol [ΔH_f(s)] or ΔH_f(l)	ref	ΔH_f(g)	ref
C_2H_4O	oxirane (**1c**) (ethylene oxide)	−77.6 (0.6)	7	−52.6 (0.6)	7
C_3H_5ClO	(chloromethyl)oxirane (epichlorohydrin)	−148.4 (0.5)	7	−107.8 (4.2)	7
C_3H_6O	methyloxirane (propylene oxide)	−122.6 (0.6)	7	−94.7 (0.6)	7
$C_3H_6O_2$	(hydroxymethyl)oxirane (**43a**) (glycidol)	−298.2 (0.9)	7		
C_4H_8O	ethyloxirane	−168.9 (2.6)	7		
C_5H_8O	6-oxabicyclo[3.1.0]hexane (**44**) (cyclopentene oxide)	−130.8 (6.4)	80	−97.1 (7.0)	80
$C_5H_{10}O$	2,2,3-trimethyloxirane	−257	31		
$C_5H_{10}O_2$	(ethoxymethyl)oxirane (**43b**) (glycidyl ethyl ether)	−296.5 (1.8)	81		
$C_6H_6O_{13}N_4$	cyclohexene oxide 3,4,5,6-tetranitrate (**45a**) (3,4,5,6-alloinositol tetranitrate, A-epoxyconduritol-E tetranitrate)	[−444.1 (2.5)]	7		
$C_6H_{10}O$	*cis*-7-oxabicyclo[4.1.0]heptane (**45b**) (cyclohexene oxide)	−166.0 (1.1)	80	−125.5 (1.1)	80
$C_6H_{10}O_5$	cyclohexene oxide 3,4,5,6-tetraol (**45c**) (1,2-anhydro-3,4,5,6-alloinositol, A-epoxyconduritol-E)	[−906.2 (1.7)]	7		
$C_6H_{12}O$	2,2-diethyloxirane	−249	31		
$C_6H_{12}O$	2,3-diethyloxirane	−258	31		
$C_6H_{12}O_2$	(propoxymethyl)oxirane (**43c**) (glycidyl propyl ether)	−321.2 (2.2)	81	−272.6 (2.3)	81
$C_6H_{12}O_2$	(methylethoxy)methyloxirane (**43d**) (glycidyl isopropyl ether)	−342.9 (2.2)	81	−298.8 (2.7)	81
$C_7H_{10}O$	8-oxatricyclo[3.2.1.0^{1,5}]octane (**46**)	−9.5 (1.0)	5	26.9	5
$C_7H_{10}O$	3-oxatricyclo[3.2.1.0^{2,4}]octane (*exo*-norbornene oxide)	[−98.0 (2.5)]	80	−53.9 (2.6)	80
$C_7H_{10}O_3$	oxiranemethanol methylpropenoate (**43e**) (glycidyl methacrylate)	−454.4 (2.6)	81	−394.2 (2.7)	81
$C_7H_{12}O$	*cis*-8-oxabicyclo[5.1.0]octane (**48**) (cycloheptene oxide)	−197.5 (3.1)	80	−152.3 (3.1)	80
$C_7H_{12}O_3$	oxiranemethanol butanoate (**43f**) (glycidyl butyrate)	−560.4 (2.7)	81	−501.7 (2.6)	81
$C_7H_{14}O$	2,2-diethyl-3-methyloxirane	−298	31		
$C_7H_{14}O_2$	(*n*-butoxymethyl)oxirane (**43g**) (glycidyl butyl ether)	−345.2 (2.6)	81	−291.9 (2.7)	81
$C_7H_{14}O_2$	((2-methylpropoxy)methyl)oxirane (**43h**) (glycidyl isobutyl ether)	−357.7 (2.5)	81	−306.8 (2.6)	81
$C_7H_{14}O_2$	((2,2-dimethylethoxy)methyl)oxirane (**43i**) (glycidyl *tert*-butyl ether)	−339.9 (2.6)	81	−319.7 (2.7)	81
$C_7H_{14}O_3$	(((2,2-dimethylethyl)peroxy)methyl)oxirane (**43j**) (glycidyl *tert*-butyl peroxide)	−321.3 (2.7)	81	−267.5 (2.8)	81
$C_8H_{14}O$	*cis*-9-oxabicyclo[6.1.0]nonane (**49**) (cyclooctene oxide)	[−212.5 (2.1)]	80	−165.1 (2.4)	80
$C_8H_{16}O_2$	((pentyloxy)methyl)oxirane (**43k**) (glycidyl amyl ether)	−368.6 (2.9)	81		
$C_8H_{16}O_2$	(((3-methylbutyl)oxy)methyl)oxirane (**43l**) (glycidyl isopentyl ether)	−384.0 (2.9)	81		
$C_8H_{16}O_2$	((1,1-dimethylpropoxy)methyl)oxirane (**43m**) (glycidyl *tert*-pentyl ether)	−392.5 (2.5)	81		
C_9H_8O	6,6a-dihydro-1a-oxireno[*a*]indene (**50**) (indene oxide)	−8	31		
$C_9H_{10}O$	(phenoxymethyl)oxirane (**43n**) (glycidyl phenyl ether)	−182.0 (2.1)	81	−116.4 (2.1)	81
$C_{10}H_{12}O_2$	((phenylmethoxy)methyl)oxirane (**43o**) (glycidyl benzyl ether)	−209.0 (3.5)	81	−138.0 (3.6)	81
$C_{10}H_{16}O$	1,4,4-trimethyl-*anti*-8-oxatricyclo[5.1.0.0^{3,5}]octane (**51**) (α-3-carene oxide)	−156.5 (1.5)	5	−106.9	5
$C_{10}H_{16}O$	1,4,4-trimethyl-*syn*-8-oxatricyclo[5.1.0.0^{3,5}]octane (**52**) (β-3-carene oxide)	−148.0 (1.6)	5	−97.8	5
$C_{10}H_{20}O_2$	(((1,1-dimethylpentyl)oxy)methyl)oxirane (**43p**)	−442.2 (3.7)	81		

[a] Those data in square brackets refer to the solid state. Literature citation numbers are given for all of the compounds.

potential for the formation of the radical cation of tetrafluoroethylene (accompanied by neutral difluoromethylene) upon photofragmentation (eq 1). Comparison was also made[8] with the corresponding energetics of its sole isomer, the acyclic hexafluoropropene, as well as the interconversion processes of the two forms of neutral and cationic C_3F_6. In the current case, the molecular ion fragmentation is conceptually straightforward because there are only these two C_3F_6 isomers and one form of C_2F_4 and of singlet CF_2. Nonetheless,



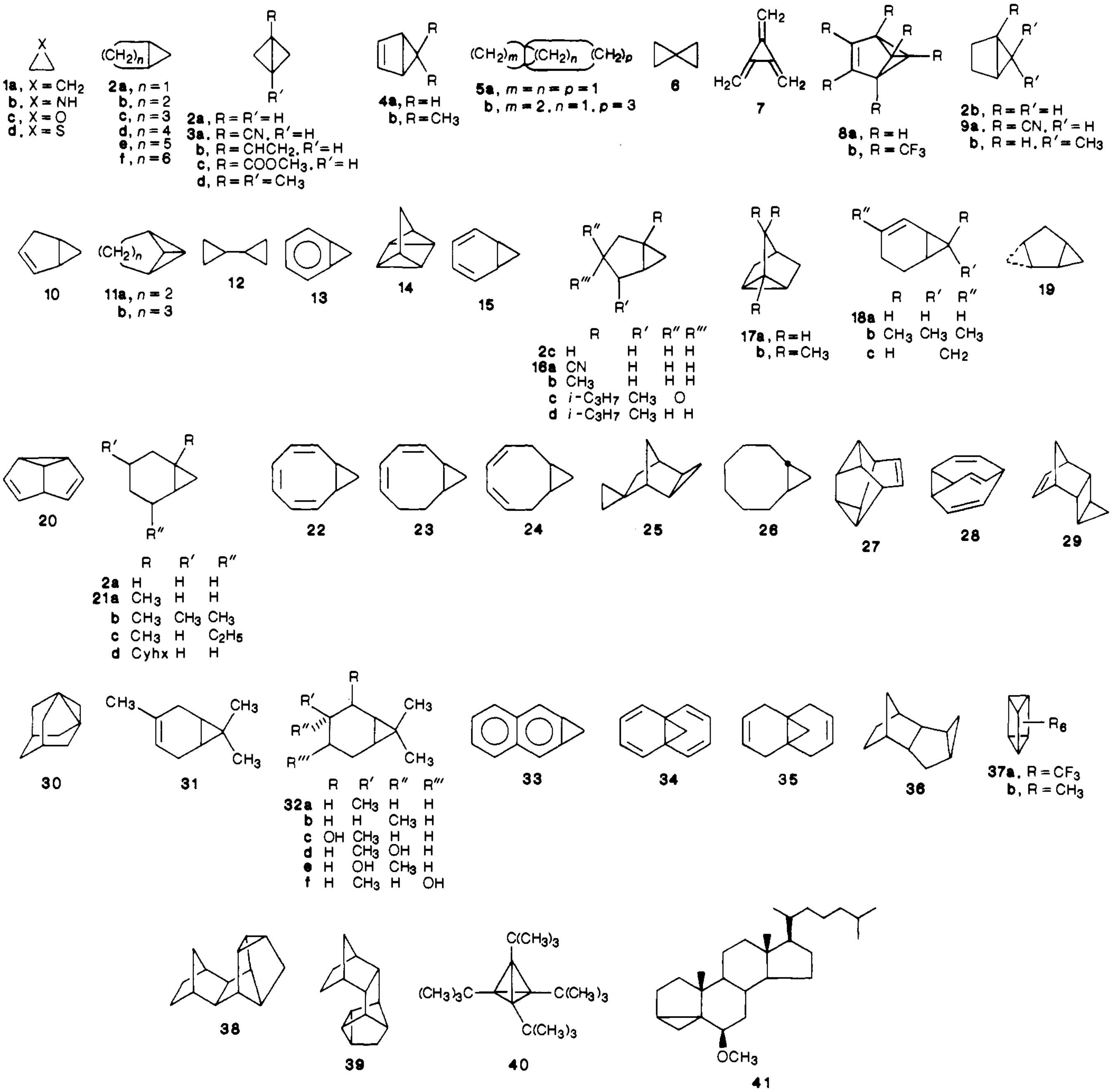
(1)

TABLE IV. Heats of Formation of Three-Membered Rings That Contain Sulfur[a]

		ΔH_f, kJ/mol			
formula	name	[ΔH_f(s)] or ΔH_f(l)	ref	ΔH_f(g)	ref
C_2H_4S	thiirane (**1d**) (ethylene sulfide)	51.6 (1.3)	7	83.0 (1.3)	7
C_3H_6S	methylthiirane (propylene sulfide)	11.3 (1.3)	7	45.8 (2.1)	7
C_4H_8S	2,2-dimethylthiirane	-24.5 (1.3)	7	11.3 (2.1)	7
C_4H_8S	*cis*-2,3-dimethylthiirane	-24.5 (1.3)	7	11.3 (2.1)	7
C_4H_8S	*trans*-2,3-dimethylthiirane	-29.7 (1.3)	7	3.6 (2.1)	7
$C_5H_{10}S$	trimethylthiirane	-60.8 (1.3)	7	-21.5 (1.8)	7
$C_6H_{12}S$	tetramethylthiirane	[-83.3 (1.6)]	7		

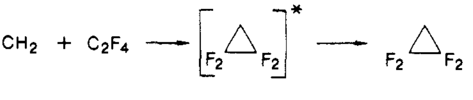
[a] The data in square brackets refers to the solid state. Literature citation numbers are given for all of the compounds.

CHART I



complications abound in this appearance potential measurement and its interpretation. First of all, the radical ion of hexafluorocyclopropane is Jahn–Teller distorted from the equilateral triangle geometry of the neutral. Thus, judging from the subtleties in obtaining the corresponding value for the parent hydrocarbon cyclopropane[9] (**1a**, Chart I) the adiabatic ionization potential of hexafluorocyclopropane may well have not yet been found. Second, there has been considerable disagreement in the literature as to the heat of formation of the difluoromethylene fragment: see the discussion in ref 10 wherein normally trusted methodologies are shown to result in values that disagree by some 10 kcal/mol. Finally, the suggested heat of formation of gaseous hexafluoropropene has been revised downward from the 1962 value[11a] of −268.9 kcal/mol used in ref 8 to −275.3 kcal/mol reported[11b] in 1987. It is well established that conventional calorimetric techniques are fraught with difficulty when applied to highly fluorinated species,[12] and no such measurement is available for hexafluorocyclopropane. It is with regret that we do not attempt to reevaluate the heat of formation of hexafluorocyclopropane. Instead, we present the original authors' value for the heat of formation of hexafluorocyclopropane.

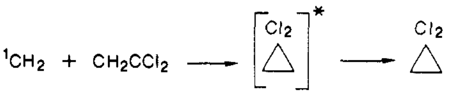
The value for the heat of formation of gaseous 1,1,2,2-tetrafluorocyclopropane was derived from the gas-phase reaction of methylene and tetrafluoroethylene and Rice–Ramsperger–Kassel–Marcus (RRKM) treatment of the subsequent cooling-down process (eq 2).



(2)

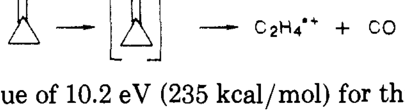
Making use of the experimental measurements and analysis of ref 13, a subsequent study[14] related insights derived from comparing the energetics of the thermal difluoromethylene extrusion reactions to the strain energies of a collection of highly fluorinated cyclopropanes. The value of −141 (±10) kcal/mol presented in our Table I is from the latter study,[14] but it must be admitted that these comparisons are clouded by the cited uncertainties of the hexafluorocyclopropane measurements.

The value for the heat of formation of 1,1-dichlorocyclopropane is for the liquid and is from a direct measurement reported in ref 15. No experimental heat of vaporization has been reported. Instead, the data for gaseous 1,1-dichlorocyclopropane were derived[16] from the energetics of the gas-phase reaction of methylene and 1,1-dichloroethylene (eq 3). As with the related halogenated species, 1,1,2,2-tetrafluorocyclopropane, RRKM analysis was used for the energetics of the subsequent cooling-down reactions of the dichlorocyclopropane. Note that the nearly 17 kcal/mol difference determined above for the heats of formation of liquid and gaseous 1,1-dichlorocyclopropane is some 8 kcal/mol larger than would have been anticipated on the basis of our earlier experience on heats of vaporization.[17] Something is clearly wrong here. Would the study of the analogous addition of CCl_2 to C_2H_4 provide a more compatible set of answers? We eagerly await the answer.



(3)

Consider now cyclopropanone. Two measurements have been reported on the appearance potential of ethylene radical cation (+ CO) arising from cyclopropanone fragmentation (eq 4). Electron impact[18] gave a value of 10.2 eV (235 kcal/mol) for this process, while the generally more reliable photoionization[19] gave a value of 9.7 eV (224 kcal/mol). The heat of formation value we give for cyclopropanone is derived from the latter with an additional ca. 2 kcal/mol correction caused by our use of a new value[20] for the heat of formation of ethylene radical cation. Given the existence of some cyclopropanones that can be "conveniently" handled, we welcome determination of their heat of formation by direct combustion calorimetry and by these ion fragmentation processes. Such experiments would provide useful information about cyclopropanones. In addition, these experiments would, because combustion measurements on compounds containing only carbon, hydrogen, and oxygen are relatively straightforward, help us disentangle the above-discussed energetics for the fluorinated cyclopropanes as well.



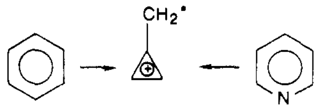
(4)

The value given above for the heat of formation of liquid bromocyclopropane, 6.6 kcal/mol, is from the reaction calorimetry studies reported in ref 21. Reaction of liquid organic bromides with elemental magnesium followed by reaction of the resulting Grignard reagent with hydrogen bromide (cf. eq 5) was shown

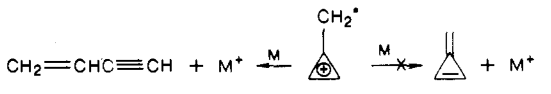
$$RBr(soln) + Mg(s) \rightarrow RMgBr(soln) + HBr(l) \rightarrow RH(soln) + MgBr_2(s) \quad (5)$$

generally to agree to within 0.5 kcal/mol with the heat of formation values obtained by conventional calorimetric methods. PNK give the heat of formation of the liquid isomeric allyl bromide as but 2.9 (±0.9) kcal/mol. As such, it is very likely that the reported value for bromocyclopropane is not likely to be for its isomer formed by ring opening. We would thus like to suggest that this measurement method will prove useful for variously strained species containing the heavier halogens bromine and iodine.

The energetics of methylenecyclopropene were determined indirectly. We made use of the standard assumptions[22] that the most stable $C_4H_4^+$ ion is cyclopropeniomethyl radical, i.e., the radical cation of methylenecyclopropene, and that its heat of formation is well established from numerous appearance potential measurements (eq 6). Can one neutralize this $C_4H_4^+$ ion and form neutral methylenecyclopropene? Seemingly not. "Dumping" an electron into this ion, however gently, apparently results[23] in vinylacetylene, an isomeric C_4H_4 (eq 7). As such, these charge-exchange measurements, designed to "bracket" the adiabatic ionization potential of methylenecyclopropene (e.g., see ref 9 for such a study for cyclopropane), are without use here. However, the recent direct measurement[24] of the desired adiabatic ionization potential of methylenecyclopropene allows us to derive the heat of formation of the neutral by use of the near equality $\Delta H_f(M) \simeq \Delta H_f(M^+) - IP_a(M)$. The thermochemical result for methylenecyclopropene reported in our table is directly from this analysis.

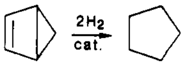


(6)



(7)

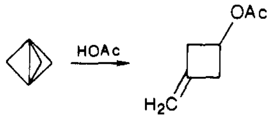
The value for the heat of formation of bicyclo[2.1.0]pentene (4a) was derived by combining the directly measured hydrogenation enthalpy[26] with the heat of formation of the product cyclopentane (eq 8). Since



(8)

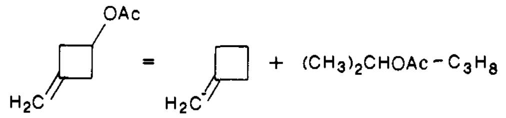
this hydrogenation was done in isooctane, we assumed it to correspond to that involving gaseous species based on the now-standard assumption[27] that reduction in the equally nonpolar solvent hexane mimics that in the gas phase. Analysis of hydrogenation enthalpies of acyclic species[27] and of compounds with five-membered rings[28] convinced us that the error should be under 1 kcal/mol.

The value for the heat of formation of [1.1.1]propellane (**5a**) was obtained[29] by reaction calorimetry using solution-phase acetolysis to give 3-methylenecyclobutyl acetate by ring opening (eq 9). That the



(9)

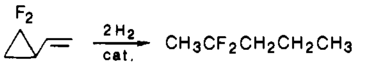
heat of formation of this ester is, in fact, unmeasured does not impede the thermochemical analysis. After all, this quantity may be simply and reliably estimated from arithmetically combining the known heats of formation of methylenecyclobutane, isopropyl acetate, and propane as in eq 10. The heat of vaporization of



(10)

the propellane was estimated by making almost a kcal/mol correction to the corresponding value for bicyclo[1.1.1]pentane, its formal hydrogenation product.

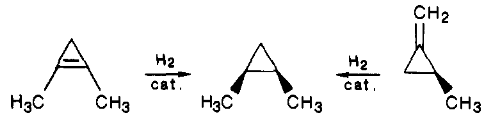
The next entry in Table I needing discussion is 1,1-difluoro-2-vinylcyclopropane, another fluorinated species. The heat of hydrogenation of this compound was measured[30] (eq 11), and since the solvent was isooctane, again this process was assumed to correspond to that in the gas phase (vide supra). No experimental thermochemical data are available on the resulting 2,2-difluoropentane. This is not a problem. If we assume that thermochemical effects of *gem*-difluoro groups and keto groups are parallel,[32] then the heat of formation of 2,2-difluoropentane may immediately be estimated from arithmetically combining those of 2,2-difluoropropane,[33] 2-pentanone, and acetone as in eq 12. A simple test of the effects of *gem*-difluorination on cyclopropanes is the hydrogenation experiments[30] on vinylcyclopropane and its derivatives. The underivatized vinylcyclopropane had a heat of hydrogenation some 12 kcal/mol less than its *gem*-difluoro derivative. This is intuitively satisfying given the general assumption that *gem*-difluoro groups destablize cyclopropanes; e.g., see ref 14 and 34. Indeed, the parallel of *gem*-difluoro groups and keto groups can be documented by these numbers as well. From the experimental heats of formation of cyclopropanone (vide supra), acetone,[7] cyclopropane,[7] and propane,[7] we find that the heat of hydrogenation of cyclopropanone to form acetone is some 15 kcal/mol less than cyclopropane to form propane.



(11)

$$CH_3CH_2CH_2CF_2CH_3 = CH_3CF_2CH_3 + CH_3COCH_2CH_2CH_3 - CH_3COCH_3 \quad (12)$$

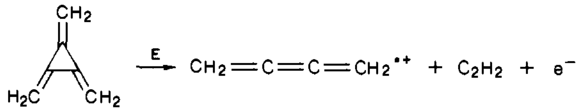
We now turn to a discussion of three C_5H_8 isomers, ethylidenecyclopropane, 1,2-dimethylcyclopropene, and 2-methyl-1-methylenecyclopropane. All three heats of formation were obtained by arithmetically combining the heats of hydrogenation found in Jensen's review[35] with the directly measured heats of formation of the product (vide infra). We assumed that the products were formed by cis hydrogenation of the least hindered side of the parent olefins (cf. eq 13). Finally, we added a constant 0.7 kcal/mol correction to these results to derive gas-phase heats of formation (cf. ref 27 and 28) because the hydrogenation was done in acetic acid and not in a nonpolar solvent. Jensen[35] expressed some doubts about the heat of hydrogenation numbers because the reactions of the various C_5H_8 species with H_2 were incomplete. Given this and our list of assumptions, it is legitimate to ask if the derived heats of formation are reliable. We must admit our pessimism. That ethylidenecyclopropane and 2-methyl-1-methylenecyclopropane are more stable than 1,2-dimethylcyclopropene is reasonable: the presence of a second sp^2 carbon in the three-membered ring of the last compound increases strain, much as 1-methylcyclopropene is less stable than methylenecyclopropane. However, the difference of heats of formation in the methylcyclopropene/methylenecyclopropane case is 10.5 kcal/mol, meaningfully greater than the ca. 7 kcal/mol here for the dimethylcyclopropene/2-methyl-1-methylenecyclopropene case. In addition, the first methylation of cyclopropene on an olefinic carbon decreases the heat of formation by some 7 kcal/mol. We cannot explain how introducing a second methyl after the first to form 1,2-dimethylcyclopropene decreases it by an additional 14 kcal/mol. Most assuredly, our understanding of substituent effects and strain and/or the numerical accuracy in some key thermochemical measurements is wanting.



(13)

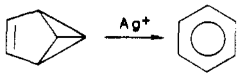
Recall our distrust of the apparent heat of vaporization of 1,1-dichlorocyclopropane. Can one use the seemingly reliable data on *cis*- and *trans*-1,1-dichloro-2,3-dimethylcyclopropane to disentangle whether to trust more the heat of formation of liquid or gaseous 1,1-dichlorocyclopropane? Let us assume that *gem*-dichlorination effects produce the same change in heats of formation in cyclopropane and *cis*- and *trans*-1,2-dimethylcyclopropane. From the numbers in Table I, we find for the gaseous species that the decrease of the heat of formation upon *gem*-dichlorination is ca. −11.5 kcal/mol for the dimethyl case but only −2.5 kcal/mol for the parent hydrocarbon. The corresponding value for the liquids requires knowledge of the heat of vaporization (condensation) of cyclopropane. Estimating this last quantity from a simple literature approach[36] to be 4.1 kcal/mol, we find the decreases still differ by ca. 9 kcal/mol. It appears safe to say that the heat of formation of 1,1-dichlorocyclopropane is suspect in both the liquid and gaseous phases.

The value presented earlier for [3]-radialene (**7**), the first of two interesting C_6H_6 isomers to be discussed here, is that in ref 37, a value accepted by KK. We now recall a quandary expressed in the major review of the energetics of the isomeric neutral C_6H_6 species and their ions.[22] The heat of formation of [3]-radialene was derived from an appearance potential measurement (eq 14). Given the nearly ubiquitous formation of cyclopropeniomethyl from most neutral C_6H_6 species, including benzene (recall our discussion on methylenecyclopropene), it is surprising to see the 4-carbon fragment from [3]-radialene asserted in ref 37 to be the radical cation of butatriene. That the accompanying neutral was asserted to be acetylene is not surprising, but it does reconfirm the propensity of species to rearrange during fragmentation. Finally, the derived heat of formation of [3]-radialene is in considerable disagreement with that predicted by both simple and complicated approaches by the original authors in ref 37 and the later study, ref 22.



(14)

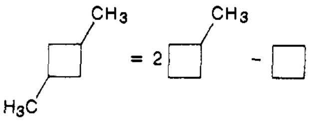
By contrast to the case for [3]-radialene, our understanding of benzvalene (**8a**) seems not to be a problem. The neutral heat of formation of the liquid given here was directly determined[38] from the heat of reaction of the direct Ag^+-catalyzed isomerization of a benzene solution of benzvalene to liquid benzene (eq 15). The derived value for the gaseous heat of formation obtained by adding the above value for the liquid to the estimated heat of vaporization[36] is nearly identical with that suggested in ref 22. This vindicates our trust of the value for benzvalene and our skepticism about the value for [3]-radialene.



(15)

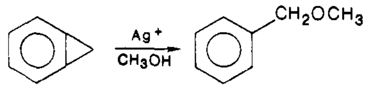
The values for the heats of formation of the isomeric fluorinated species 1,1-difluoro-2-[(*E*)-1-propenyl]cyclopropane and *cis*-1,1-difluoro-2-methyl-3-vinylcyclopropane were ascertained by using the same approach as that found for 1,1-difluoro-2-vinylcyclopropane. More precisely, we used the experimentally determined heat of hydrogenation[30] and the same solvation assumptions[27,28] and estimated the heats of formation of the products 2,2- and 3,3-difluorohexane as we had for the difluoropentane. Likewise, the values for the heats of formation of the isomeric 2-[(*E*)-1-propenyl]cyclopropane and *cis*-1-methyl-2-vinylcyclopropane were obtained by use of their experimental heats of hydrogenation[30] and the same solvation assumptions.[27,28] At least for the nonfluorinated hydrocarbons, we are confident that the values of heats of formation are presented to ca. 1 kcal/mol, based on the experimental uncertainties given in ref 30 and the validity of the additional solvation assumptions.

The value given in Table I for 1,3-dimethylbicyclobutane (**3d**) was obtained by using an experimental heat of hydrogenation,[35] the earlier assumptions for solvent effects,[27,28] and an estimated heat of formation of 1,3-dimethylcyclobutane. Surprisingly, it is this last quantity that is in doubt. While we have estimated this heat of formation as the difference of twice the heat of formation of methylcyclobutane and the heat of formation of the unsubstituted cyclobutane (cf. eq 16), doubts have been expressed about both the former[5] and latter[40] quantities. Perhaps a review of the thermochemistry of four-membered rings paralleling this on three-membered rings should be written. But, for now, we opt not to.



(16)

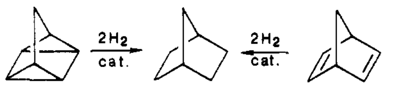
The heat of formation of benzocyclopropene (**13**) was deduced[42] by using solution-phase Ag^+-catalyzed methanolysis to form benzyl methyl ether (eq 17). These authors[42] readily and reliably estimated the heat of formation of the product ether and the heat of vaporization of benzocyclopropene. We recognize that benzocyclopropene is the smallest benzoannelated polycycle. In accord with the ever-large increase of heats of formation upon benzoannelation that occurs as the annelated ring becomes more strained,[43] the 9 kcal/mol increase found for cyclohexene is meaningfully less than the nearly 11 kcal/mol increase for cyclobutene. The 21.5 kcal/mol increase on benzoannelation of cyclopropene follows this trend but is much larger than we would have thought.



(17)

B. Some Special C_7H_8 Species: The Quadricyclane–Norbornadiene and Norcaradiene–Tropylidene Comparisons

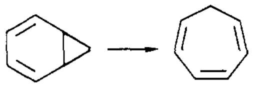
The heat of formation of quadricyclane (**14**), both absolutely and relative to that of its isomer norbornadiene, has been measured numerous times. The most logical measurements—combustion calorimetry, hydrogenation calorimetry of both isomers to form the common product norbornane (eq 18), and the direct (catalyzed) heat of isomerization of quadricyclane into norbornadiene—have all been reported by more than one research group. Some of the best examples of each type of study were consolidated in 1987 in a primary research paper.[44] The values are splattered across a nearly 14 kcal/mol spread ranging from 10 to some 24 kcal/mol, with disparities in the individual heats of formation of norbornadiene and quadricyclane being even worse. The authors of ref 44 did not explain most of the observed discrepancies among the results. Rather they presented their own photocalorimetric result from a sensitized isomerization and briefly discussed the possibility of addition reactions as a reason for the discrepancy of their value from the ca. 22 kcal/mol generally accepted. We, too, will not attempt now to explain all of the discrepancies. Rather, we will accept the general consensus and adopt the heat of formation of quadricyclane given by KK for our choice. In section VIII we will discuss the thermochemistry of the inter-



(18)

conversion of substituted norbornadiene and quadricyclane derivatives.

Norcaradiene (**15**), the second C_7H_8 isomer we present in this review, is also an object of considerable interest and dissension. In the current case, the thermochemical problem is exacerbated over that of quadricyclane because norcaradiene immediately isomerizes to tropylidene (eq 19). Were only the parent hydrocarbons involved, the precise energy difference might be irrelevant. However, as with the norbornadiene–quadricyclane case, there is a wide range of energy differences of substituted norcaradienes and tropylidenes. The value we present in Table I for liquid norcaradiene was obtained by a composite[45] of ab initio calculations; Gibbs energy, enthalpy, and entropy corrections of experimental results; and intuition about substituent effects of "normal" (non-cyclopropane) species. We assumed that the difference in heats of formation of norcaradiene and tropylidene was independent of phase or solvation effects to derive the value for the heat of formation of gaseous tropylidene. The interesting question of the thermochemistry of substituted norcaradienes will be avoided for now and deferred to section VIII.

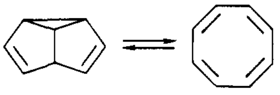


(19)

C. C_7H_{10} through $C_{14}H_{18}$

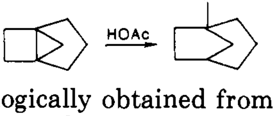
The heats of formation of the 5,5-dimethyl derivatives of bicyclo[2.1.0]pentene and bicyclo[2.1.0]pentane, **4b** and **9b**, respectively, were determined by using the same logic as that used earlier for the unsubstituted bicyclo[2.1.0]pentene. Encouragingly, there are no surprises: the changes in heats of formation upon *gem*-dimethylation are nearly identical for bicyclo[2.1.0]pentene (**4a**), bicyclo[2.1.0]pentane (**2b**), and cyclopropane (**1a**).

The value for the heat of formation of semibullvalene (**20**) was obtained from studies of the thermal equilibration of this C_8H_8 isomer with cyclooctatetraene[47] (eq 20). We defer to H.-D. Martin, the senior strained-ring chemist of ref 47, a discussion of the details of this species. (See Martin's article with Walsh and Hassenrück in this issue of *Chemical Reviews*.)



(20)

The heat of formation of [3.2.1]propellane (**5b**) was derived analogously to that ot its smallest congener, [1.1.1]propellane, namely, measurement of the heat of acetolysis[48] to form the 1-bicyclo[3.2.1]octyl acetate (eq 21). Experimentally unavailable, the heat of formation of this ester is logically obtained from those of bicyclo[3.2.1]octane, *tert*-butyl acetate, and isobutane (eq 22). Surprisingly, PNK fail to report heats of formation for both bicyclo[3.2.1]octane and *tert*-butyl acetate. Thermochemical analysis of the equilibration of bicyclo[3.2.1]octane with its isomers bicyclo[2.2.2]octane and *cis*-bicyclo[3.3.0]octane (eq 23) shows[49] the [3.2.1] species to be ca. 0.2 kcal/mol less stable than its [2.2.2] isomer and nearly 2 kcal/mol more stable than the [3.3.0] isomer. A heat of formation of liquid bicyclo[3.2.1]octane of ca. −31 kcal/mol is immediately deduced. In turn, using heat of formation data from PNK, we estimate the heat of formation of liquid *tert*-butyl acetate as ca. −133 kcal/mol by noting that the difference in heats of formation of *tert*-butyl-O–X and isopropyl-O–X derivatives is nearly identical for X = H, methyl, and isopropyl.



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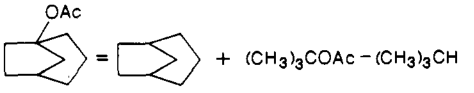
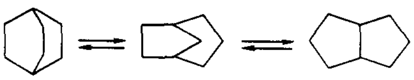
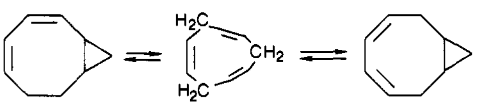


(22)



(23)

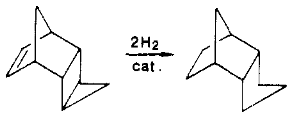
The value of the heat of formation of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**22**) was obtained[50] by assuming that its heat of hydrogenation to *cis*-bicyclo[6.1.0]nonane (**2f**) is the same as that shown[50] for other medium-sized (seven-, eight-, and nine-membered) rings. The heats of formation of the isomeric bicyclo[6.1.0]nona-2,4-diene (**23**) and bicyclo[6.1.0]nona-3,5-diene (**24**) were obtained from the enthalpies of activation of interconversion[51] (both directions) of these two bicyclononadienes with each other and of the 2,4-diene with cyclonona-1,4,7-triene (eq 24). The required heat of formation of the triene was obtained in turn from its trice-corrected[27,28] heat of hydrogenation in acetic acid.[35] The heat of vaporization was taken to be the same as that of cyclononane. The results for the bicyclo[6.1.0]nonadienes and -nonatriene, species **23**, **24**, and **22**, taken together provide a surprise. The difference of the totally conjugated 2,4-diene and triene is 5.3 kcal/mol. The corresponding difference for 1,3-cycloheptadiene and cycloheptatriene is 5.0 kcal/mol, while the difference for norcaradiene (**15**) and bicyclo[4.1.0]hept-2-ene (**18a**) is 4.8 kcal/mol (thereby vindicating the value for norcaradiene used earlier). The difference for 1,3-cyclohexadiene and benzene (cyclohexatriene) is −5.5 kcal/mol. This would suggest that bicyclo[6.1.0]nonatriene is about half as aromatic as benzene. This is quite inexplicable and suggests further study is desirable.



(24)

The value for cyclohexylcyclopropane is interesting. KK cite a value for hexylcyclopropane and express doubts about its accuracy. KK also cited the first edition of Pedley's compendium[52] as an ancillary source of information about this compound. Interestingly, the second edition (PNK, ref 7) of this compendium ascribes the numerical value to cyclohexylcyclopropane. This, too, seems to be in error in that hydrogenation to form propylcyclohexane appears to be almost 20 kcal/mol endothermic using the heat of formation of the latter from PNK as well.

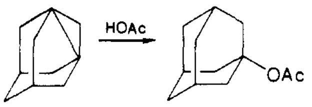
The heat of formation of (1*rH*,2*tH*,3*cH*,5*cH*,6*tH*,7*cH*)-tetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-ene (**29**) was derived from its heat of hydrogenation[30] to the exo isomer of tricyclo[5.2.1.0^{2,6}]decane (eq 25), where we made the same ancillary corrections[27,28] as for other bicyclo-



(25)

pentane derivatives. It was additionally necessary to correct the heat of formation of the product *endo*-tricyclodecane[5] by the endo–exo enthalpy difference. Molecular mechanical calculations using either Allinger's MM1 or Schleyer's EAS force fields[54] give enthalpy differences respectively of ca. 6.5 kcal/mol, in acceptable agreement with the directly measured[55] Gibbs energy difference of 4.8 kcal/mol.

We now turn to 1,3-dehydroadamantane (**30**). Accompanying the study of [3.2.1]propellane (**5b**), Wiberg and co-workers[48] reported the liquid-phase acetolysis of this [3.3.1]propellane analogue to form 1-adamantyl acetate (eq 26). Because the reaction started with solid dehydroadamantane and resulted in the solid acetate, the authors argued that the acetolysis heat was essentially the same whether the reactants and product be liquids or solids. We know of no thermochemical data for 1-adamantyl acetate in any phase. Heat of formation estimates are most valid when made for gas-phase species. The heat of formation of gaseous 1-adamantyl acetate is easily arithmetically estimated by using literature values for 1-adamantanol[5] and *tert*-butyl alcohol, and our earlier (derived) value of *tert*-butyl acetate; cf. eq 27. The value for the heat of formation of liquid 1-adamantyl acetate takes the just-derived value for the gas and substracts the heat of vaporization of our ester as suggested by the CHLP procedure in ref 17.



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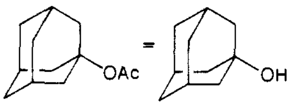
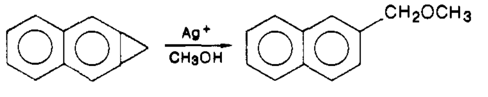


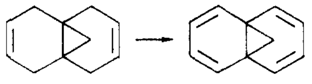
+ $(CH_3)_3COAc$ − $(CH_3)_3COH$ (27)

The heat of formation of naphtho[*b*]cyclopropene (**33**) was found by two different methods.[42] The first method was direct measurement of the heat of combustion of the solid. An estimate was then made of its heat of sublimation, a procedure shown to be generally[56] less reliable than the corresponding estimate of the heat of vaporization. The original authors equated the value with naphthalene; we would have cautiously chosen 2-methylnaphthalene. In fact, the preferred value for the heat of sublimation of naphthalene is 17.4 kcal/mol (PNK), some 2 kcal/mol higher than for its 2-methyl derivative.[57] In this case, the 2 kcal/mol discrepancy is small enough not to affect any conclusion about this molecule. The second method made use of eq 28, the solution-phase Ag^+-catalyzed methanolysis, wherein the heat of formation of the product 2-methoxymethylnaphthalene was simply and reliably obtained. Using this derived heat of formation of the "normal" ether and the experimentally measured reaction enthalpy gave another estimate for the heat of formation of gaseous naphtho[*b*]cyclopropene. Encouragingly, the two results were nearly identical. From the heats of formation of gaseous naphtho[*b*]cyclopropene and benzocyclopropene, the strain energies of these two hydrocarbons were shown to be nearly identical. Whether benzo-, naphtho[*a*]-, or naphtho[*b*]annelation on another ring results in nearly identical changes in strain energy remains unknown—we know of no thermochemical study on naphthoannelated species, save this cyclopropene derivative.

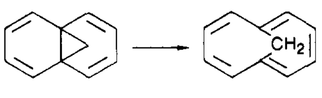


(28)

We now turn to derivatives of tricyclo[4.4.1.0^{1,6}]undecane ([4.4.1]propellane, i.e., species **5** with $m = 4$, $n = 4$, $p = 1$). The heat of combustion of the liquid 3,8-diene (**35**) has been reported,[58] from which one can immediately obtain the heat of formation. In principle, one can "unsaturate" both cyclohexene rings to form cyclohexadienes. While this reaction may be difficult to do experimentally, the desired dehydrogenation reaction (eq 29) is conceptually straightforward from both structural and thermochemical considerations. This was done by the authors of ref 58, and the heat of formation of the resulting readily derived species, tricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene (**34**), is given here. In addition, this species is related to 1,6-methanoannulene much as norcaradiene is related to tropylidene. The difference of heats of formation of norcaradiene and tropylidene is 39.0 − 33.9 = 5.1 kcal/mol for the liquids and 48.3 − 43.3 = 5.0 kcal/mol for the gases. Tetraene[34] is likewise unstable relative to 1,6-methano[10]annulene; cf. eq 30. The corresponding differences in heats of formation are 66.7 − 60.7 = 6.0 and 80.8 − 75.3 = 5.5 kcal/mol for the liquids and gases, respectively. That the differences in the seven- and eleven-carbon cases are within a kcal/mol is no doubt fortuitous—the bicyclo[4.1.0]heptane (**2d**) and tricyclo[4.4.1.0^{1,6}]undecane polycycles have different strain energies, and the tropylidene and the bridged [10]annulene have different degrees of delocalization—conjugation, homoconjugation, and aromaticity. Substituent effects on molecular structure are rampant in the current propellane case. For example, the 11,11-difluoro derivative is best described as a methano[10]annulene, while the 11,11-dichloro and 11,11-dibromo derivatives are norcaradienes.[59] Perhaps this case could be clarified if we knew enough about simple *gem*-dihalocyclopropanes. Though polyfluorinated cyclopropanes remain enigmatic, we are quite confident of our understanding of 1,1-difluorocyclopropane derivatives. However, recall the stated ambiguities discussed earlier with regard to the corresponding dichlorocyclopropanes. Dibromocyclopropanes are worse: 1,1-dibromoethane is seemingly the sole *gem*-dibrominated species for which thermochemical data exist.



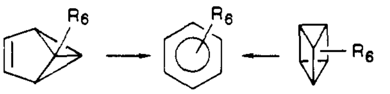
+ $2H_2$ (29)



(30)

D. Thermochemistry of Hexasubstituted Benzvalene and Prismanes

We now turn to the hexakis(trifluoromethyl) derivatives of benzvalene and prismane, **8b** and **37a**. It is well established that trifluoromethyl groups confer stabilization on strained rings, a phenomenon generally known as the "perfluoroalkyl (R_f) effect".[60,61] This has two manifestations. The first is the lessened energy difference between the "normal" and strained species that results from this substitution. For example, hexamethylprismane (**37b**) is some 91 kcal/mol higher in energy than hexamethylbenzene,[62] while only 59 kcal/mol separates the corresponding hexakis(trifluoromethyl) species.[60] The second is the increased "robustness" of the strained perfluoroalkylated species; cf. eq 31. It appears that this effect is kinetic in origin.[63] In this review we are interested only in thermochemical considerations. The energy differences between the benzenoid and valence isomers allow us to derive now the heats of formation of the latter, here identified as cyclopropane derivatives as well. In order to consider hexakis(trifluoromethyl) derivatives of benzvalene and prismane, **8b** and **37a**, respectively, it is necessary to have the heat of formation of the corresponding derivative of benzene. To a first approximation, one can assume the heat of formation of hexakis(trifluoromethyl)benzene to be the difference of 6 times the heat of formation of (trifluoromethyl)benzene and 5 times that of benzene. This ignores the likely repulsion of the trifluoromethyl groups. We do not know the heat of formation of any benzene derivative with two trifluoromethyl groups. We use cyano as a mimic for the trifluoromethyl group. This replacement is known to be quite reliable[32] when comparing the proton affinities of cyano- and trifluoromethyl-substituted bases of diverse structure. From the heats of formation of *o*-, *m*-, and *p*-dicyanobenzene,[7] we derive corrections for two cyano groups ortho, meta, and para to each other of 4.5, 3.3, and 2.2 kcal/mol, respectively. In our hexakis(trifluoromethyl) compounds, there are 6 ortho, 6 meta, and 3 para interactions to be accounted for.[64] This results in a predicted heat of formation of hexakis(trifluoromethyl)benzene of −905 kcal/mol, and with the experimental benzene/valence isomer enthalpy differences, predicted heats of formation of −871 and −846 kcal/mol for the corresponding benzvalene and prismane derivatives.



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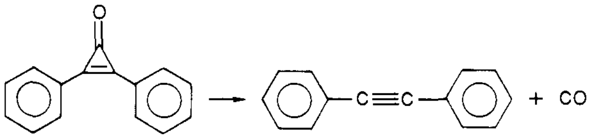
Obtaining the heat of formation of hexamethylprismane (**37b**) is also derived through multiple steps and assumptions as well. At the temperature of the valence isomerization of hexamethylprismane to hexamethylbenzene, both species are liquids. PNK lack data on liquid hexamethylbenzene. Another recent compendium[65] provides us with phase transition enthalpies and so we can proceed from data on the "normal" crystal II phase to the crystal I phase to the desired liquid. Neglecting heat capacity effects since they are presumed to be small, the heat of isomerization of liquid hexamethylbenzene to liquid hexamethylprismane[62] gives the heat of formation of the latter substance that appears in Table I.

E. Thermochemistry of Cyclopropenones

The next compound we discuss is diphenylcyclopropenone. This species is an archetypical example[67] of "difficulties in apportioning 'destabilization', 'strain', and 'delocalization energy' in a complex molecule". Reference 68 represents a heroic attempt at disentangling the conflicting influences on the stability of a molecule. The exocyclic carbonyl and the endocyclic olefinic bond can delocalize, resulting in a 2π-electron aromatic system. By contrast, it is well established[1] that both endo- and exocyclic double bonds destabilize three-membered rings. What is the case here? The earliest calorimetric studies[68] suggested cyclopropenones are not particularly stabilized thermodynamically, despite ample literature references documenting kinetic stability. The differences of thermodynamic and kinetic stability are well documented: the earlier-mentioned "perfluoroalkyl (R_f) effect" is but one example. Making use of the *gem*-difluoro-keto equivalence (cf. our cyclopropanone discussion) reinforced the traditional assumption that cyclopropenones should be aromatic, and new heat of combustion measurements confirmed it.[69] The authors admitted that their calorimetric results needed refinement, a situation remedied soon thereafter with more accurate combustion measurements.[70] Photoacoustic calorimetry[71] of the decarbonylation reaction (eq 32) derived a related value to that of ref 70, although the ca. 5 kcal/mol discrepancy was larger than anyone expected. Of course, it is necessary to know the energetics of the products in any form of reaction calorimetry, and photoacoustic calorimetry is no exception. Both qualitative reasoning and quantitative hydrogenation enthalpy measurements[72,73] showed that the heat of formation of the "normal" species diphenylacetylene was in error: correcting it provided the authors with a new heat of formation of diphenylcyclopropenone that is in almost perfect agreement with that of the heat of combustion study.[70] It would thus appear that the diphenyl derivative of cyclopropenone is now rather well understood, although the effects of the phenyl groups are still moot in the absence of any thermochemical data on dialkylcyclopropenones. We note that comparison between cyclopropanones and cyclopropenones is also moot in the absence of thermochemical data on any substituted cyclopropanone.



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V. Commentary on the Derived Thermochemistry of Three-Membered-Ring Compounds Containing Nitrogen

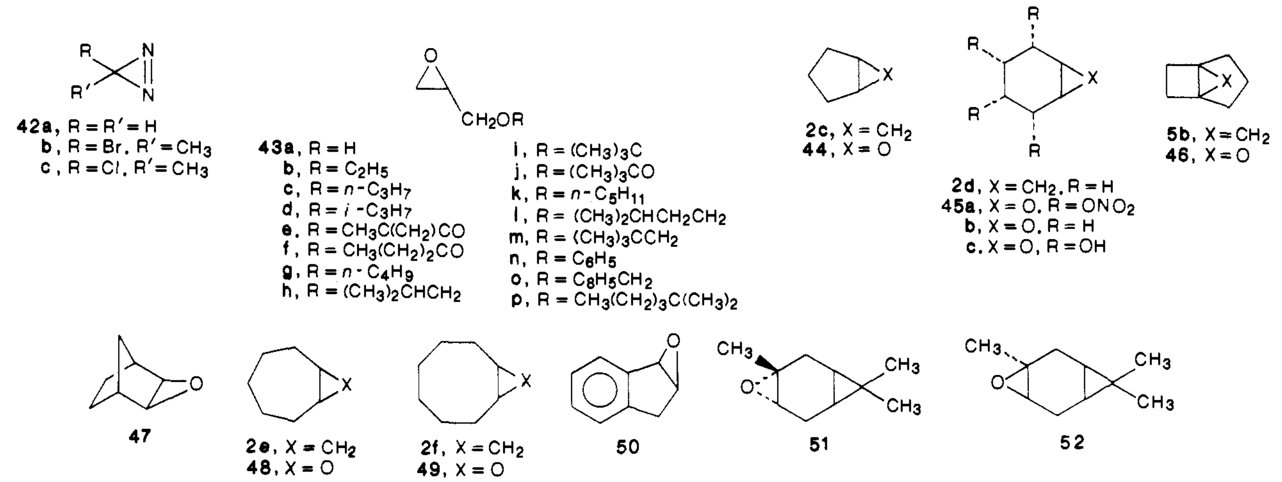
A. Aziridines

The heats of formation of four three-membered-ring species that contain nitrogen were chronicled in Table II. Given the general importance of aziridines, it is surprising that data for only one such compound, the parent heterocycle, have been reported.[7]

B. Diazirines

In contrast to the single aziridine studied, there are data for three diazirines, which will now be discussed. The heat of formation of the parent diazirine (**42a**, Chart II) was determined[77] indirectly by measuring the

CHART II



42a, R = R' = H
b, R = Br, R' = CH_3
c, R = Cl, R' = CH_3

43a, R = H
b, R = C_2H_5
c, R = n-C_3H_7
d, R = i-C_3H_7
e, R = $CH_3C(CH_2)CO$
f, R = $CH_3(CH_2)_2CO$
g, R = n-C_4H_9
h, R = $(CH_3)_2CHCH_2$
i, R = $(CH_3)_3C$
j, R = $(CH_3)_3CO$
k, R = n-C_5H_{11}
l, R = $(CH_3)_2CHCH_2CH_2$
m, R = $(CH_3)_3CCH_2$
n, R = C_6H_5
o, R = $C_6H_5CH_2$
p, R = $CH_3(CH_2)_3C(CH_3)_2$

2c, X = CH_2
44, X = O

2d, X = CH_2, R = H
45a, X = O, R = ONO_2
b, X = O, R = H
c, X = O, R = OH

5b, X = CH_2
46, X = O

47

2e, X = CH_2
48, X = O

2f, X = CH_2
49, X = O

50

51

52

energy threshold of three gas-phase photochemical reactions and combining the results to derive the earlier-stated results for the heat of formation. In particular, these authors described the UV photodecomposition of gaseous diazirine (eq 33) and the UV-promoted photoionization and fragmentation of diazirine (eq 34).

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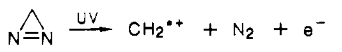

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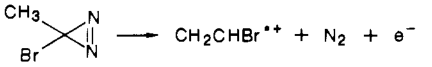
From the well-established heats of formation of all of the fragment species and their excitation energies, the value of 63.3 kcal/mol for the heat of formation of diazirine was deduced with what we consider encouragingly narrow error bars of under 3 kcal/mol.

The heat of formation of 3-bromo-3-methyldiazirine (**42b**) was also found[78] by photoionization and accompanying fragmentation into the molecular ion of vinyl bromide and neutral N_2 (eq 35). Vinyl bromide is



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thermochemically well characterized,[7] and its ionization potential is also accurately known. In principle, the resulting heat of formation of gaseous 3-bromo-3-methyldiazirine of ca. 70 ± 4 kcal/mol is thus also established. However, this photofragmentation process is not a simple one. More precisely, not only are two bonds broken in the diazirine, a complication shared by the parent heterocycle and by cyclopropanone described above, but the resulting bromomethylcarbene must also rearrange. It cannot be taken as a given that the reaction energy threshold was in fact reached, and so the cited value is somewhat suspect.

Nonetheless, we believe that the value is probably reliable because in the same paper, these authors reported the ion fragmentation study of the analogous chlorinated species, 3-chloro-3-methyldiazirine (**42c**). From their measurements, they derived a heat of formation of 58 ± 6 kcal/mol. Another study[79] (one adopted by the PNK archive) used the corresponding energetics of the thermally induced decomposition of the neutral diazirine to form neutral vinyl chloride and N_2. This resulted in a heat of formation of 60 ± 10 kcal/mol. This latter fragmentation and rearrangement is also not a simple process but the results (including error bars) encompass those of the other study. It would be surprising if the heats of formation derived from the neutral and cation decomposition processes were nearly equal should the two reactions not be proceeding close to the reaction threshold. We thus trust these results and cite those with the smaller error bars. In addition, we may make the simple comparison of a pair of other organic halides, ethyl chloride and ethyl bromide, for which the difference in their gas-phase heats of formation is 12.0 kcal/mol. This difference is nearly identical with the 11.5 kcal/mol obtained by directly taking the difference of the heats of formation of the two halodiazirines. It appears that chlorine and bromine have comparable effects on three-membered rings, but our analysis ignored the large error bars.

VI. Commentary on the Thermochemistry of Three-Membered-Ring Compounds Containing Oxygen: A Comparison of Oxiranes and Their Cyclopropane Analogues

Table III provides considerable data on the energetics of three-membered rings that contain oxygen. Surprisingly, there are few cases where there are data on corresponding oxiranes and cyclopropanes, that is, species that may be conceptually interconverted by interchanging O and CH_2 (see ref 80 and Table V). It is disappointing that there is no apparent pattern to incorporate all the chronicled differences in the heats of formation of oxiranes and the corresponding cyclopropanes.

VII. Commentary on the Thermochemistry of Three-Membered-Ring Compounds Containing Sulfur: A Comparison of Methylthiiranes and Their Cyclopropane Analogues

The thermochemical literature on three-membered rings containing sulfur is limited to direct measurements of the heat of formation of the parent thiirane (**1d**) and all of its methyl derivatives. Moreover, the data for the tetramethyl compound are limited to that of the solid, while for the other species there are data for both the liquid and gas. As such, comparison between tetramethylthiirane and the other thiiranes is less reliable. The electronegativities of carbon and sulfur are rather close. This suggests that substituent effects

TABLE V. Differences of the Heats of Formation of Compounds with Three-Membered Rings That Contain Oxygen and Their Corresponding Carbocyclic Analogues (i.e., X = O and CH_2, Respectively)[a]

formula	name	$[\Delta H_f(s)]$ or $\Delta H_f(l)$	$\Delta H_f(g)$
C_2H_4X	oxirane (**1c**)	104[b]	106
C_3H_6X	methyloxirane	124	119
C_4H_8X	ethyloxirane	144	145[c]
C_5H_8X	6-oxabicyclo[3.1.0]hexane (**44**)	136	136
$C_5H_{10}X$	2,2,3-trimethyloxirane	161	163[c]
$C_6H_{10}X$	*cis*-7-oxabicyclo[4.1.0]heptane (**45b**)	139	138
$C_7H_{10}X$	8-oxatricyclo[3.2.1.0^{1,5}]octane (**46**)	209	211
$C_7H_{12}X$	*cis*-8-oxabicyclo[5.1.0]octane (**48**)	137	136
$C_8H_{14}X$	*cis*-9-oxabicyclo[6.1.0]nonane (**49**)	141[d]	143

[a] All names are for the oxygen-containing species, the primary data are in kJ/mol, and the requisite references are found in Tables I and III. [b] The heat of formation of the necessary liquid cyclopropane was obtained by subtracting a calculated heat of vaporization (cf. ref 36) from the heat of formation of the gaseous species. [c] The heats of formation of the necessary gaseous oxiranes were obtained by adding a calculated heat of vaporization via the CHLP procedure (cf. ref 17) to the heat of formation of the gaseous species. [d] The heat of formation of the liquid necessary oxirane was obtained by subtracting a calculated heat of vaporization via the CHLP procedure (cf. ref 17) from the heat of formation of the gaseous species.

TABLE VI. Differences of the Heats of Formation of Identically Substituted Cyclopropanes and Thiiranes[a]

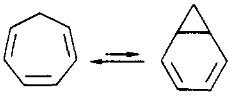
methylation pattern	$[\Delta H_f(s)]$ or $\Delta H_f(l)$	$\Delta H_f(g)$
unsubstituted	16[b]	29.7
monomethylated	9.6	21.5[c]
gem-dimethylated	8.8	19.5
cis-dimethylated	1.8	9.6
trans-dimethylated	1.0	7.4
trimethylated	35.4	44.2
tetramethylated	37[d]	41[d]

[a] All data are in kJ/mol, and the requisite references are found in Tables I and IV for cyclopropanes and thiiranes, respectively. [b] The heat of formation of liquid cyclopropane was obtained by subtracting a calculated heat of vaporization (cf. ref 36) from the heat of formation of the gaseous species. [c] The heat of formation of gaseous tetramethylthiirane is an estimated lower bound following a procedure discussed in ref 56. It was obtained by taking the heat of formation of the solid, neglecting the heat of fusion, and estimating the heat of vaporization of the resulting liquid. [d] This difference is for the liquid species. As such, the number cited is an upper bound since it ignores the heat of fusion of tetramethylthiirane.

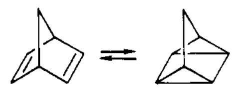
involving these elements should be comparable. In particular, one might expect that the difference of the heats of formation of identically substituted cyclopropanes and thiiranes are essentially constant. Table VI presents the requisite data. The conjecture is shown to be markedly in error: the differences of the heats of formation of the various methylcyclopropanes and the corresponding methylthiiranes vary wildly. This suggests that substituent effects on three-membered rings, even that of methylation, have considerable subtleties. Nonetheless, that the differences are so erratic also suggests that some of these measurements may be in error and that an experimental reinvestigation is in order.

VIII. Selected Derivatives of Polycyclic Compounds Having Cyclopropane Rings

In the following sections we describe the known thermochemistry of two selected classes of cyclopropane derivatives. Discussion focuses first on the 1,3,5-cycloheptatriene–bicyclo[4.1.0]hepta-2,4-diene (tropylidene–norcaradiene (**53**–**15**)) equilibrium and then on the equilibrium between bicyclo[2.2.1]hepta-2,5-diene and tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (norbornadiene–quadricyclane (**54**–**14**)). The propylidene–norcaradiene equilibrium has played an important role in the development of our understanding of substituent effects on the geometries of cyclopropane rings. The norbornadiene–quadricyclane equilibrium has been investigated over the past 20 years as a promising approach to solar energy storage. The values listed in the tables in these sections are experimental. In section C we briefly discuss related calculational issues. As in the earlier sections, not much experimental calorimetric data are available so that calculation is a tempting alternative.



53 **15**

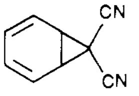


54 **14**

A. Tropylidene–Norcaradiene

Although tropylidene has been familiar to chemists for a long time, its valence isomer norcaradiene, accessible by a thermally allowed disrotatory ring closure, is not commonly observed. The equilibrium raises the issue of the relative stabilities of olefins and their cyclopropane isomers. If we employ Benson group increments for **15** ($\Delta H_f(g)$ = 55.2 kcal/mol) and compare it with the experimental value for **53** ($\Delta H_f(g)$ = 43.2 kcal/mol), it is clear that **53** is favored, especially since the entropy of bicyclic **15** is undoubtedly more negative than that of **53**.

The earliest observations of norcaradienes were made in the mid-1960s by Ciganek. The 7,7-dicyano derivative **55** was found to occur exclusively in the norcaradiene form.[82] A subsequent X-ray study of dimethyl derivative **56** indicated a short distal bond (C_1–C_6) relative to the substituted carbon and longer vicinal bonds (i.e., C_1–C_7, C_2–C_7).[83] It is noteworthy that the 7-cyano compound had earlier been shown to be a tropylidene (**57**).[84] The longer vicinal bond also appeared to rationalize the course of hydrogenation of **55** whereby cyclohexylmalononitrile is obtained in about 10% yield[82] (eq 36). If a trifluoromethyl group replaces one of the cyano groups in **55**, the resulting molecule **58** is now mainly in the tropylidene (**58a**) tautomeric form.[85] The CF_3 substituent enhances the relative stability of the tropylidene tautomer, and this is apparent for the 7,7-bis(trifluoromethyl) derivative **59**.[86]



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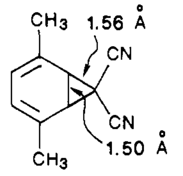

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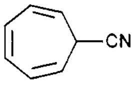

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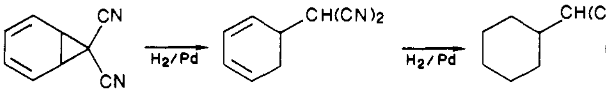

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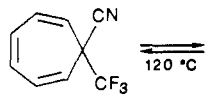
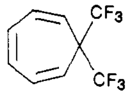


58a (80%) **58b** (20%)



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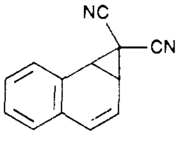
It is noteworthy that Ciganek also used dicyanocarbene to prepare the naphthalene adducts **60–62**,



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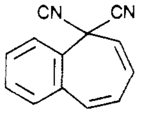

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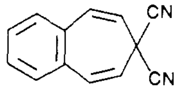
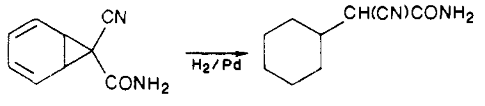


62

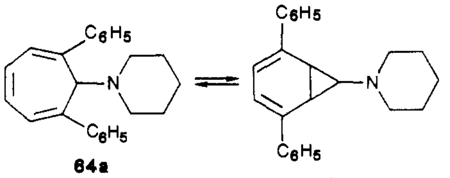
whose tautomeric structures were those which enhanced aromaticity.[82] In addition, amide **63** was formed via partial hydrogenolysis of **55**, and its ring-opening hydrogenation mimicked that of its immediate precursor (eq 37).[82]



63 (37)

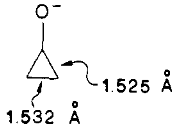
These observations led Hoffmann and Stohrer[87,88] to an explanation for the effects of substituents on cyclopropane-ring geometries and (implicitly) thermodynamic stabilities. Contrasting the effect of the cyano, a π-electron-withdrawing group, to CF_3, a σ-electron-withdrawing group, they emphasized the importance of the cyclopropane HOMO/substituent LUMO interaction, which removes antibonding character from the distal bond, shortening it, and removes bonding character from the vicinal bonds, lengthening them. These predictions are relevant to simpler cyclopropanes and have been shown to be correct for many molecules in which conjugation is conformationally feasible.[89,90]

Extension of this approach to π-donor substituents was not successful. For a π-donor substituent, the dominant interaction would be predicted to be of the type cyclopropane LUMO/substituent HOMO. The antibonding character around the three-membered ring should increase with donation of electron density, lengthening all three ring bonds. These predictions were not verified in general for cyclopropanes,[89,90] and the observation of the equilibrium **64a–64b**[91] was not in accord with the Hoffmann/Stohrer view.



64a **64b** (38)

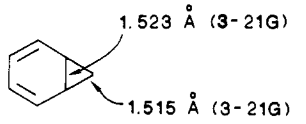
With the aid of hindsight based upon the subsequent research of numerous investigators, the origins of some of these inconsistencies become clearer. While the power and elegance of Hoffmann's predictions lie in their simplicity, i.e., examining π interactions only, there are certainly many substituents for which σ effects are more important. For example, an explanation of the presence of elongated bonds all around a substituted cyclopropane was based on the notion of electron withdrawal from bonding orbitals localized in the ring.[92,93] While this seemingly has nothing to do with the Hoffmann model, it is really not inconsistent. A powerful contribution was made by Durmaz and Kollmar,[94] who demonstrated via ab initio molecular orbital calculations that only exceedingly strong π donors such as X = O^- and CH_2^- (conjugated) should be capable of interacting strongly enough with the cyclopropane LUMO so as to lengthen all three ring bonds in the manner predicted for π donors. Structure **65** shows these predictions for the cyclopropoxide anion (X = O^-). For the sake of comparison, we note the corresponding calculated C–C bond length in cyclopropane: 1.513 Å.[94]



65

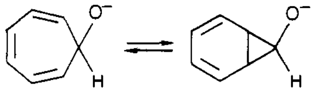
Cyclopropane is a weak π-electron acceptor and requires a strong π donor for significant conjugation. This is in contrast to cyclopropane's strong π-donor properties, which are clear from linear free energy relationships involving thermodynamic stabilization energies.[4a] Thus, π-donor substituents contribute much less to stabilization energies than π-acceptor substituents. This is also manifested in a small energy difference between the bisected (conjugated) and perpendicular (nonconjugated) conformers of the cyclopropylcarbinyl anion (X = CH_2^-), in striking contrast to the large energy difference for the cyclopropylcarbinyl cation (X = CH_2^+).[94] σ-Electron donation also has a stabilizing effect, while σ withdrawal is destabilizing. Thus, use of the value for $\Delta H_f(g)$ for 1,1-dichlorocyclopropane found earlier in this review (10 kcal/mol) along with the PNK[7] value for 2,2-dichloropropane yields a strain energy some 14 kcal/mol greater than that for the parent cyclopropane. Similar findings by Clark et al. for fluorocyclopropane indicate that the fluoro substituent is a σ withdrawer, not a π donor, and that lengthening of the distal bonds and shortening of vicinal bonds can be explained as a consequence of the dominant interaction of the substituent with the cyclopropane 1E″ orbital as well as substituent-induced hybridization effects.[95] This very valuable study strongly established the role of the electronegativity of substituents in affecting the geometries of cyclopropane rings, thus generally clearing up confusion on substituents like hydroxyl which, while π donors, exert their main effects inductively. The structure of 1,1-dichlorocyclopropane, although the subject of disparate research findings, appears to mimic the corresponding fluorinated compound.[96]

One interesting aspect of the Hoffmann/Stohrer arguments[87,88] is that they lack an explicit thermodynamic component. The argument is centered around the effect of a π-withdrawing substituent in shortening the distal bond in a cyclopropane ring, presumably reinforcing norcaradiene-like tendencies. The converse is that a substituent that would lengthen the distal bond would make the molecule more tropylidene-like. However, it is noteworthy that ab initio MO calculations (3-21G basis set) indicate[46] that the "natural tendency" for the norcaradiene structure is for the distal bond (relative to substitution at position 7) to be longer than the vicinal bonds (see structure **66**). Therefore, one might anticipate that the structural effects of geminal cyano groups (see **56**) may increase strain.



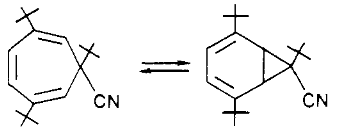
66

What would be the effect of the X = O$^-$ substituent on the tropylidene–norcaradiene equilibrium (**67a**–**67b**)?[47] The isopropyl stabilization energy for cyclopropoxide (**65**) is calculated to be 2.3 kcal/mol.[4a] This fairly small stabilization energy is consistent with cyclopropane's weak π-acceptor properties. (Our calculated "methyl stabilization energy" of 12 kcal/mol[4a] is very similar to the 11 kcal/mol value calculated by Durmaz and Kollmar,[94] lending credibility to our calculated "isopropyl stabilization energy".) Still, this 2.3 kcal/mol stabilization energy may be sufficient to allow experimental observation of the norcaradiene **67b**. The interesting point here is that one would expect all cyclopropane ring bonds in **67b** to be elongated, by analogy with **65**, yet the norcaradiene would be stabilized. Note that the elongation of the distal bond in **65** relative to the vicinal bond indicates a degree of congruence between the three-membered ring in norcaradiene itself (see **66**) and that in **67b**.

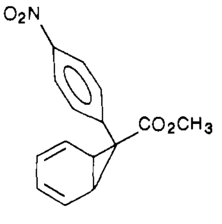


67a **67b**

Predictions of equilibria in the CHT–NCD series are not straightforward, and steric effects may play an important role. For example, paralleling effects on the benzene–Dewar benzene equilibrium,[98] it is known that appropriately positioned *tert*-butyl groups can favor the norcaradiene (**68a**–**68b**).[99] Furthermore, the unexpected finding that *p*-nitrophenyl was a weaker norcaradiene stabilizer in **69** than the corresponding phenyl substituent is now understood to be a consequence of the forced endo orientation of the phenyl substituent[100] in **69** forcing it into a conformation unsuitable for conjugation with the cyclopropane ring. (The better π acceptor, CO_2CH_3, is exo and does adopt a suitable conjugating conformation.[101])



68a **68b**



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In addition, substituents at the 1- and 6-positions of the tropylidene isomer introduce the need for assessing relative stabilities at the vinyl versus cyclopropyl positions. While exploration of the CHT–NCD equilibrium offers a sensitive probe for evaluating small energy differences, in contrast to taking a small difference between large numbers (e.g., the enthalpies of combustion of the isomers even were they to be separable), interpretations are often not straightforward.

Table VII lists thermodynamic data derived from studies of the equilibria of parent and substituted CHT/NCD tautomers. Schulman and co-workers[46] suggest that the apparent stabilization of 7,7-dicyanonorcaradiene (**55**) relative to its CHT tautomer is due only slightly (ca. 2.9 kcal/mol) to stabilization of the cyclopropane by geminal cyano groups. Most of the effect (7.9 kcal/mol) is attributed to destabilization of 7,7-dicyanotropylidene. Although these results are based upon ab initio MO calculations at the 6-31G* level, the prediction of such a large destabilization is unexpected.

Another interesting point is the use of ethene and cyclopropane stabilization energies and the use of the latter to predict the energetics of the CHT–NCD equilibria without explicit consideration of stabilization/destabilization energies in the tropylidene isomers. This approach, of course, would be contrary to that suggested by the finding of Schulman and co-workers noted above. How well do we fare with this approach? If we multiply the homodesmotic isopropyl stabilization of a cyclopropane substituted by a CO_2CH_3 group (2.2 kcal/mol[4a]) by 2, the predicted stabilization in the corresponding 7,7-disubstituted norcaradiene, assuming additivity, would be 4.4 kcal/mol. From Table VII, comparison of the first and third entries indicates a value of 5.5–5.7 kcal/mol, in fair agreement. However, the same approach applied to a CN substituent attached to cyclopropane (isopropyl stabilization, −0.1 kcal/mol) would predict relative destabilization of the norcaradiene, whereas Table VII indicates stabilization by 9.3–11.5 kcal/mol. If we ignore the presence of an unanticipated cyclopropyl vs isopropyl geminal effect (for just such an effect in *gem*-difluoro compounds, see ref 4a) as well as possible large $\Delta H_f(g)$ errors, this would support the view of dominant destabilization in this substituted tropylidene. A third interesting point is the strong correlation between ΔH and ΔS so apparent in Table VII. Linear regression provides a correlation coefficient r of 0.989 (n = 18).

The last point we make here is the interesting observation that the rate of solvolysis of the 7-cycloheptatrienylcarbinyl derivative is enhanced relative to its cycloheptyl analogue by a factor of 5.5 × 10^5.[108] This observation furnished the first example of a solvolysis preceded and initiated by a valence tautomerization. While it might be tempting to postulate solvolysis followed by tautomerization, the rate of formation of the primary carbonium would be too slow, even with anchimeric assistance, to account for the observed rate enhancement.[108]

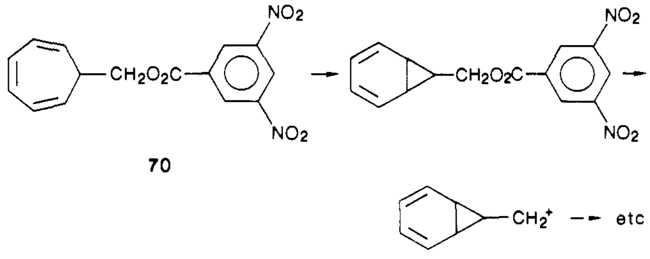

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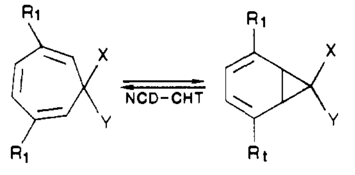
TABLE VII. Experimental (Unless Otherwise Noted) $\Delta G°$ and $\Delta H°$ of Isomerization (kJ/mol) for the Conversion of Tropylidenes (Cycloheptatrienes (CHT)) to Norcaradienes (NCD) (ΔS Values in J/(mol K))

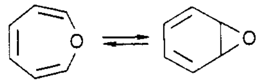


R_1	X	Y	ΔG_{298K}	ΔH	ΔS	ref
H	H	H	26	(23 (calcd))		97, 98
H	H	CN	8			97
H	CO_2CH_3	CO_2CH_3	3	-1	-13	102
H	CF_3	CN	4	-2	-21	103
H	H	CO_2H	4^a			104
H	p-$CH_3OC_6H_4$	CO_2CH_3	-0.4	-9.6	-31	100
H	p-$O_2NC_6H_4$	CO_2CH_3	-1	-15	-46	100
H	C_6H_5	CO_2CH_3	-2	-23	-7	100
H	CN	CO_2CH_3		<-16 (estd)		103
H	C_6H_5	CN		<-12 to -20 (estd)		103
H	CN	CN	-13	-25		97, *105*
C_6H_5	H	cyclohexyl	3			91
C_6H_5	H	1-piperidino	1			91
t-C_4H_9	H	p-$CH_3OC_6H_4$	2	1.3	0.3	106a
t-C_4H_9	H	p-$CH_3C_6H_4$	2	2.2	1.7	106a
t-C_4H_9	H	C_6H_5	2	1.8	0.4	106a
t-C_4H_9	H	p-ClC_6H_4	2	1.4	-1.1	106a
t-C_4H_9	H	p-BrC_6H_4	2	1.5	-0.4	106a
t-C_4H_9	H	m-ClC_6H_4	2	1.5	-5	106a
t-C_4H_9	H	p-$CF_3C_6H_4$	0.8	-0.2	-4	106a
t-C_4H_9	H	m,m′-$Cl_2C_6H_3$	1.2	-0.8	-7.5	106a
t-C_4H_9	H	CCH	2.0^b			106b
t-C_4H_9	H	CN	1.7^b			106b
t-C_4H_9	H	CCC_6H_5	1.3^b			106b

		Y = $(R_aO)(R_bR_cN)C^+Z^-$							
R_1	X	R_a	R_b	R_c	Z^-	ΔG_{298K}	ΔH	ΔS	ref
H	H	C_2H_5	CH_3	CH_3	BF_4	5.4	11.9	23	107
H	H	CH_3	CH_3	CH_3	FSO_3	4.2	8.4	15	107
H	H	CH_3	CH_3	CH_3	PF_6	4.6	7.5	10	107
H	H	CH_3	CH_3	CH_3	$SbCl_6$	5.4	6.3	5	107
H	H	CH_2CH_2		H	BF_4	1.7	-1.2	-10	107

[a] At 123 K. [b] At 153 K.

We conclude this section with brief mention of the oxepin–benzene oxide valence tautomerism (**71a**–**71b**).



71a **71b**

This system is a prototype of various oxides formed in the metabolism of carcinogenic polycyclic aromatic hydrocarbons. An experimental investigation found oxepin (**71a**) to be higher in enthalpy by 1.7 kcal/mol.[109] This solution-phase value has been equated to a gas-phase $\Delta E_T = +0.3$ kcal/mol.[110] Although ab initio HF STO-3G calculations favor the benzene oxide structure **71b**, higher levels of ab initio HF calculations (4-31G, 6-31G, 6-31G*) and some semiempirical techniques (MINDO/3, MNDO, AM1) favor oxepin (**71a**).[110] These conclusions are reversed when electron correlation is included, and MP2 6-31G* and MP3 6-31G* calculations favor the benzene oxide by 3.3 and 0.8 kcal/mol, respectively.[110]

B. Norbornadiene–Quadricyclane

This subject is a "glamour topic" in strained-ring research since it is relevant to the problem of photochemical energy storage. Data from no less than eight experimental determinations of the enthalpy of isomerization of the parent molecules are included in Table VIII. While there is reasonably good agreement between most of the data, clustering between 21.5 and 26.3 kcal/mol, there are certainly two data points well outside the experimental error limits. One set of combustion data provides results in considerable error for both isomers. While the enthalpy of isomerization provides some cancellation of errors, these large errors highlight the lesson that very few groups in the world are capable of obtaining accurate enthalpies of combustion—among the most demanding measurements in chemical science. In contrast, enthalpies of hydrogenation and isomerization involve a single measurement of a relatively small change. Here, a 1% error will yield an absolute error in the enthalpy of isomerization of ca. 0.2 kcal/mol instead of ca. 10 kcal/mol in an enthalpy of combustion. The photocalorimetric experiment cited in Table VIII gave a much lower value and here the authors attributed the discrepancy, perhaps with the aid of hindsight, to side reactions involving the photosensitizer required to make the reaction proceed.

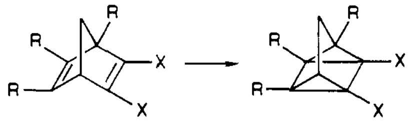
In Table IX are listed the enthalpies of isomerization for substituted norbornadienes/quadricyclanes. It does not appear that the values are very substituent dependent. While one might try to account for the numbers through comparison of corresponding cyclopropyl versus vinyl stabilizations[4a] (methyl, ethyl, and iso-

TABLE VIII. Experimental Values for ΔH_f(g) (kJ/mol) for 2,5-Norbornadiene and Quadricyclane and Related ΔH_{isom}[a]

	method							
	combust[a]	hydrog[b]	scanning calorim[c]	hydrog[d]	isom[e]	isom[f]	combust[g]	photocalorim[h]
2,5-norbornadiene	248 (3)	240		223			212 (1)	
quadricyclane	339 (2)	333	340 (4)	323	339	339	253 (1)	
diff	91 (4)	93 (1)	92 (4)	100 (4)	92	92	41 (2)	58.6 (4)

[a] The ΔH_f(g) value for norbornane is taken as −61.5 (3.3) kJ/mol. Steele, W. V. *J. Chem. Thermodyn.* **1978**, *10*, 919. [b] Rogers, D. W.; Choi, L. S.; Gerillini, R. S.; Holmes, T. J.; Allinger, N. L. *J. Phys. Chem.* **1980**, *84*, 1810. [c] Kabakoff, D. S.; Bünzli, J.-C. G.; Oth, J. F. M.; Hammond, W. B.; Berson, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1510. The ΔH_{isom} measured in toluene was 88.7 kJ/mol (in the gas phase, ΔE_{isom} = 80.3 (4) kJ/mol). The value of ΔH_{isom} = 92.0 kJ/mol was estimated by the authors for the gas phase. Their value for quadricyclane was based on the value for norbornadiene published in ref 11. The value employed in this table is based on the −61.5 kJ/mol value determined by Steele (see footnote *a*). [d] Turner, R. B.; Goebel, D.; Mallon, B. J.; Doering, W. E.; Coburn, J. F.; Pomerantz, M. *J. Am. Chem. Soc.* **1968**, *90*, 4315. We have combined their data with an assumed value of 248 kJ/mol for norbornadiene. [e] Yoshida, Z. *J. Photochem.* **1985**, *29*, 27. ΔH_{isom} was measured. The value for ΔH_f (quadricyclane) is based here on Steele's value for norbornadiene. [f] Wiberg, K. B.; Connon, H. A. *J. Am. Chem. Soc.* **1976**, *98*, 5411. ΔH_{isom} was measured. The value for ΔH_f(g) used in this table is based on Steele's value for norbornadiene. [g] Hall, H. K., Jr.; Smith, C. D.; Baldt, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 3197. [h] Harel, Y.; Adamson, A. W.; Kutal, C.; Grutsch, P. A.; Yasufuku, K. *J. Phys. Chem.* **1987**, *91*, 901. These authors employed a photosensitizer for the parent norbornadiene and feel their value for this compound is probably unreliable due to accompanying sensitizer-initiated reaction.

TABLE IX. Experimental Enthalpies of Isomerization of Substituted Norbornadienes



X	R	ΔH_i, kJ/mol	phase
H	H	96.2 (7.9)[a]	gas/soln
CN	H	92.0 (9.6)[b]	CH_3CN soln
CN	CH_3	87.9 (8.4)[b]	CH_3CN soln
CO_2CH_3	H	105.4 (14.6)[b]	CH_3CN soln
		77.4 (1.3)[c]	toluene soln
CO_2CH_3	CH_3	79[d]	neat
CN	CH_3	88[d]	CH_3CN soln; C_6H_5Cl soln

[a] This is the average of the first six values in Table VIII. All other values are different by more than twice the standard deviation (taken here as the square root of the sum of the squares of the errors of the six values) with the fifth error assumed to be ±4 kJ/mol. [b] Harel, Y.; Adamson, A. W.; Kutal, C.; Grutsch, P. A.; Yasufuku, K. *J. Phys. Chem.* **1987**, *91*, 901. [c] Kabakoff, D. S.; Bünzli, J. G.; Oth, J. F. M.; Hammond, W. B.; Berson, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1510. [d] Yoshida, Z. *J. Photochem.* **1985**, *29*, 27. See also: Yoshida, Y. *Chem. Abst.* **1983**, *98*, 53253*q*, 75439*g*.

propyl stabilization energy *differences* will be equal), it is not clear how much one will gain with this approach. First, one will have to know vicinal stabilization energies and their differences for parafinic and olefinic linkages. Second, the low IP of quadricyclane suggests larger stabilization energies for π-acceptor substituents than for cyclopropanes.[4a] Unfortunately, these values are not known.

C. The Role of Experiment, Estimate, and Calculation

The first sections of this review emphasized the general lack of thermochemical data on substituted cyclopropanes and provided examples of applications of suitable molecular orbital calculations as well as estimation techniques. It is important to realize that molecular mechanics techniques are not generally parameterized for differential effects of substituents on cyclopropane rings. The general agreement between theoretical calculation, using a good-sized basis set (e.g., 6-31G* or with inclusion of configuration interaction 6-31G* MP2), and heat of combustion experiments may be on the order of 2 kcal/mol. It can be cogently argued that this is the same level of error as combustion calorimetry presents for most substances that are not benzoic acid, the primary standard. However, the following points must also be made: first, ab initio calculations themselves need to be compared with experimental results for "tough cases" in order to truly inspire confidence in their use; second, for systems as large as substituted norbornadienes, quadricyclanes, etc., large basis sets in practice require the use of supercomputers. For example, one of the very few studies of substituted tropylidenes and norcaradienes explores the monocyano and dicyano derivatives at the 6-31G* level but does not include configuration interaction.[46] Finally, where equilibrium constants are measurable as in the difference in free energy between tropylidenes and norcaradienes, experimental values appear to be an order of magnitude more precise than values obtained from extensive calculation. Thus, the moral remains that additional accurate experimental calorimetric equilibrium data are still needed in this research area.

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(1) See, for example: (a) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978. (**b**) Kozina, M. P.; Mastryukov, V. S.; Mil'vitskaya, E. M. *Usp. Khim.* **1982**, *51*, 1337; *Russ. Chem. Rev.* (*Engl. Transl.*) **1982**, *51*, 765. (c) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 317. (d) The special topical issue of *Chemical Reviews* that the current article is part of.

(2) *The Chemistry of the Cyclopropyl Group* (2 Vols.); Rappoport, Z., Ed.; Wiley: Chichester, 1987.

(3) See, for example, the following chapters in Rappoport's volumes:[2] (a) Wiberg, K. B. "Structures, energies and spectra of cyclopropanes", p 1. (b) Schwarz, H. "The chemistry of ionized cyclopropanes in the gas phase", p 173. (c) Tidwell, T. T. "Conjugative and substituted properties of the cyclopropyl group", p 565. (d) Liebman, J. F.; Greenberg, A. "Cyclopropanes having extra strain", p 1083.

(4) See, for example: (a) Greenberg, A.; Stevenson, T. A. "Structure and Energies of Substituted Strained Molecules". In *Molecular Structure and Energetics: Studies of Organic Molecules*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, FL, 1986; p 193. (b) Dewar, M. J. S. "Localization and Delocalization". In *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1988; p 1. (c) Slee, T. S. "Structure and Bonding in Compounds Containing Three-Membered Rings". In *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1988; p 63. (d) Kafafi, S. F.; Martinez, R. I.; Herron, J. T. "Chemistry of Dioxymethylenes and Dioxiranes". In *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1988; p 203. (e) Politzer, P.; Murray, J. "Bond Deviation Indices and Electrostatic Potentials of Some

Strained Hydrocarbons and Their Derivatives". In *Structure and Reactivity*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1988; p 1. (f) Cremer, D.; Kraka, E. "The Concept of Molecular Strain—Basic Principles". In *Structure and Reactivity*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1988; p 65. (g) Mitsuhashi, T. "Polar Effects on the Lability of Carbon–Carbon Bonds". In *Structure and Reactivity*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1988; p 179.

(5) Kolesov, V. P.; Kozina, M. P. *Usp. Khim.* **1986**, *55*, 1603; *Russ. Chem. Rev.* (*Engl. Transl.*) **1986**, *56*, 912. We generally refer to this source as KK in the text.

(6) We thus intentionally ignore numerous species such as carboranes, olefin–metal complexes, and white phosphorus, all of which may formally be said to have three-membered rings. We likewise omit reactive intermediates such as bromonium ions, protonated alkanes, and the cyclopropyl radical, cation, and anion as well as charged counterparts of "conventional" cyclopropanes such as protonated cyclopropylamine and the radical cation and anion of cyclopropane itself. In this review, we also largely ignore the results of ab initio quantum chemical calculations. (For a simultaneously pedagogical and research introduction to this methodology, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.) This is not due to lack of faith, understanding, or even appreciation: computational theoretical chemistry offers considerable power in the qualitative understanding and quantitative predictions of classical and nonclassical species alike. Rather, to date, the degree of overlap between theory and experiment for the compounds encompassed by this review is astonishingly small. For example, consider the simple case of monosubstituted cyclopropanes. There are seemingly no experimental thermochemical data for cyclopropyl alcohol (nor even its ether or ester derivatives) and none for fluorocyclopropane itself despite considerable interest in polyfluorinated cyclopropanes. Conversely, bromocyclopropane remains unstudied by theory.

(7) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986. We generally refer to this source as PNK in the text.

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(17) To estimate the heat of vaporization of 1,1-dichlorocyclopropane, we opt to use a simple relationship admittedly designed for monosubstituted hydrocarbons (Chickos, J. S.; Hesse, D. E.; Liebman, J. F.; Panshin, S. Y. *J. Org. Chem.* **1988**, *53*, 3424). From immediate, if not simplistic, application of this paper's (CHLP) basic equation, we would predict a heat of vaporization of 8.4 kcal/mol (35 kJ/mol). Ongoing studies (e.g.: Chickos, J. S.; Hesse, D. E.; Liebman, J. F. *J. Org. Chem.*, in press) on multiply substituted hydrocarbons by Chickos, Hesse, and Liebman suggest that this value is an overestimate. The same value would have been predicted for the heat of vaporization of 2,2-dichloropropane. From ref 7, we find a value of 7.8 kcal/mol (33 kJ/mol), in good agreement with our "prediction" for this acyclic halogenated hydrocarbon.

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