quartz test tube using 16 RPR-3000 lamps in a merry-go-round apparatus. The solution was purged with prepurified nitrogen prior to irradiation. Measurement of the light intensity was made by simultaneously irradiating a 0.15 M solution of potassium ferrioxalate.[28] The irradiated solution was analyzed by vpc using 9-fluorenone or dimethyl diphenate as internal standards. Under conditions of the vpc analysis no decomposition of the azide was noted [Varian Aerograph Model 1200 flame ionization vpc, 5 ft $\times\ ^{1}/_{8}$ in. 5% SE-30 on 100-120 mesh Var-A-Port 30, injector 170°, column 160°] (see Table VI).

Table VI

2-Azidobiphenyl consumed, mmole	Mequiv absorbed	% conversion	Φ
2.05×10^{-2}	4.84×10^{-2}	11	0.49
3.45×10^{-2}	9.12×10^{-2}	19	0.44

In an analogous fashion 14 ml of a benzene solution of 2-azidobiphenyl (1.85×10^{-2} M) and acetophenone (2.02 M) was irradiated with a bank of 16 RPR-3000 lamps while simultaneously irradiating an actinometer solution. The quantum yield for azide disappearance (8% conversion) was found to be 0.30 ± 0.07 (0.0686 mequiv absorbed).

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The Heats of Combustion and Strain Energies of Bicyclo[*n.m.*0]alkanes

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Abstract: The heats of combustion, vapor pressures, and liquid heat capacities of a number of bicyclic alkanes have been determined. The derived liquid and gas heats of formation in kilocalories mole^{-1} at 25° are as follows: *cis*-bicyclo[3.1.0]hexane, 1.3 ± 0.7, 9.3 ± 0.8; *cis*-bicyclo[4.1.0]heptane, −8.7 ± 0.8, 0.4 ± 1.0; *cis*-bicyclo[5.1.0]-octane, −14.2 ± 0.5, −3.8 ± 0.7; *cis*-bicyclo[6.1.0]nonane, −19.4 ± 0.8, −7.6 ± 1.0; *cis*-bicyclo[4.2.0]octane, −16.3 ± 0.8, −6.1 ± 1.1; *cis*-bicyclo[3.3.0]octane, −32.6 ± 0.3, −22.3 ± 0.5; *trans*-bicyclo[3.3.0]octane, −26.1 ± 0.4, −15.9 ± 0.6; *cis*-bicyclo[5.3.0]decane, −43.9 ± 0.9, −31.1 ± 1.2. Experimental strain energies are derived from group contributions. Strain energies and geometries are also calculated by energy minimization with a set of transferable valence force potential functions. The agreement of calculated and experimental strain energies is satisfactory. The gas phase thermodynamic functions (free energy and enthalpy functions, heat capacity, and entropy) are also calculated.

In view of the great interest in recent years in the chemistry of strained cyclic hydrocarbons, studies of molecular properties and structure of such compounds are greatly in need. Of particular importance is the desirability of obtaining heats of formation from which empirical strain energies may be derived. It is the purpose of the present work to study an important family of strained ring compounds, the [*n.m.*0] bicyclic alkanes. The heats of formation *via* oxygen combustion calorimetry of a number of such compounds have been measured in this work to arrive at strain energies.

The heats of formation of this family of hydrocarbons provide an important testing ground for calculation of molecular properties by energy minimization using transferable empirical valence force potential functions. In this work we have also made such calculations for the compounds measured and the other appropriate cycloalkanes for which data exist.

The compounds measured are *cis*-bicyclo[3.1.0]hexane, *cis*-bicyclo[4.1.0]heptane, *cis*-bicyclo[5.1.0]octane, *cis*-bicyclo[6.1.0]nonane, *cis*-bicyclo[4.2.0]octane, *cis*-bicyclo[3.3.0]octane, *trans*-bicyclo[3.3.0]octane, and *cis*-bicyclo[5.3.0]decane.

Experimental Section

Compounds Studied. The four cyclopropane ring containing compounds had been synthesized by the Simmons-Smith reaction[2] and were furnished to us by Dr. Simmons. Bicyclo[4.2.0]-octane was synthesized by us by photolysis of cycloocta-1,3-diene[3] in benzene followed by hydrogenation. *cis*- and *trans*-bicyclo-[3.3.0]octane were synthesized in Professor N. L. Allinger's laboratory at Wayne State University and the details are given in the M.S. Thesis of one of us (M. J. H.).[4] *cis*-Bicyclo[5.3.0]decane was made by hydrogenation (at 1 atm catalyzed by reduced platinum oxide) of a commercial sample of azulene (Aldrich Chemical Co.) that had been purified by sublimation by us. The compounds were either purified by gas-liquid chromatography (glc) or showed no extraneous peaks by glc after distillation.

Heats of Combustion. These were measured with a calorimeter and techniques previously described.[5,6] A G-2 Mueller bridge (Leeds and Northrup 8069-B) was used for the resistance ther-

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(2) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959).

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Table I. Energy of Combustion at 298 °K of Bicyclo[5.1.0]octane[a]

M_s	M_f	M_m	ΔR	Q_i	Q_c	Q_a	Q_{std}	$-\Delta E_c°$
0.134333	0.002105	0.049410	0.197217	0.39	0.56	0.47	0.77	11023.6
0.138163	0.002165	0.050281	0.202663	0.39	0.38	0.47	0.77	11032.3
0.137297	0.001928	0.049203	0.200758	0.39	0.57	0.63	0.77	11028.4
0.137757	0.002168	0.050264	0.202159	0.39	0.54	0.63	0.77	11032.8
0.135720	0.002121	0.048549	0.198522	0.39	0.62	0.48	0.77	11031.5
0.135954	0.002058	0.053100	0.201676	0.39	0.56	0.67	0.77	11036.5
0.149715	0.002379	0.028280	0.201183	0.68	0.00	0.00	0.68	11029.2
0.151845	0.002185	0.030385	0.204958	0.68	0.00	0.00	0.68	11028.7
0.150760	0.002356	0.029894	0.203318	0.68	0.00	0.00	0.68	11022.8
							mean =	11029.5 ± 2.91
							=	11018.0 ± 2.91[b]

[a] M_s = weight of sample (g in air *vs.* SS); M_f = weight of fuse (g in air *vs.* SS); M_m = weight of "Mylar" (g in air *vs.* SS); ΔR = corrected temperature rise (ohms); Q_i = energy of ignition (calories); Q_c = correction for soot traces (calories); Q_a = nitric acid correction (calories); Q_{std} = correction to standard states (Washburn); $-\Delta E_c° = (\epsilon\Delta R + Q_c - Q_f - Q_m - Q_i - Q_a - Q_{std})/M_s$ (cal g^{-1} in air *vs.* SS) where ϵ, the energy equivalent of the calorimeter, was 8929.0 ± 1.7 cal ohm^{-1} for the first six runs, and 9034.0 ± 1.59 cal ohm^{-1} for the final three runs which were carried out after equipment modifications; Q_m = energy of Mylar combustion was calculated using combustion energies of −5476.1 cal g^{-1} and −5483.14 cal g^{-1} for the first six and last three runs, respectively; Q_f = energy of combustion of fuse was calculated using a value of 4184 cal g^{-1} for the combustion energy of cotton thread. [b] When weights are corrected to vacuum.

mometry. The "Mylar" bag technique was used to confine the samples.[7] A set of typical results is shown in Table I.

Vapor-Pressure Measurements. In order to correct heats of combustion to the vapor phase, heats of vaporization were determined from vapor pressures. A "boiling-point" method employing a semimicro ebulliometer was used.[8] The liquid was boiled at a fixed pressure and the temperature of the boiling liquid measured. The results of fitting eq 1 to the data are presented in Table II. In

$$\log P = A/T + B + C \log T \qquad (1)$$

a number of cases the temperature range measured was small enough that the $C \log T$ term was not used. Heats of vaporization were determined from eq 1 without correction for vapor imperfection or liquid volume and thus are given by

$$\Delta H_{\text{vap}} = R(-2.303A + CT) \qquad (2)$$

Where liquid heat capacity data were available it was combined with the calculated gas phase heat capacities and correction of the heat of vaporization was made from the temperature range of the vapor pressure measurements to 25°.

Table II. Values of Constants *A*, *B*, and *C* from the Vapor Pressure Curves of the Compounds[a]

Compound	*A*	*B*	*C*
cis-Bicyclo[3.1.0]hexane	−1861.1	10.242	−0.817
cis-Bicyclo[4.1.0]heptane	−1987.0	8.021	
cis-Bicyclo[5.1.0]octane	−2277.9	8.539	
cis-Bicyclo[6.1.0]nonane	−2631.1	9.165	
cis-Bicyclo[4.2.0]octane	−2671.3	19.851	−4.011
cis-Bicyclo[3.3.0]octane	−2867.6	23.262	−5.116
trans-Bicyclo[3.3.0]octane	−2593.0	17.583	−3.198
cis-Bicyclo[5.3.0]decane	−3801.1	33.065	−8.260

[a] $\log P$ (mm) = A/T (°K) + B + $C \log T$ (°K).

Heat Capacities. A Perkin-Elmer differential scanning calorimeter (DSC-1B) became available during the course of the work and was used to determine heat capacities of some of the liquids. These are shown in Table III.

Table III. Heat Capacities of Some Liquid Bicycloalkanes

Compound	C_p (cal mol^{-1} °K^{-1})	(°K)
cis-Bicyclo[4.1.0]heptane	44.9 ± 0.5	(315)
cis-Bicyclo[6.1.0]nonane	56.2 ± 0.8	(315)
cis-Bicyclo[4.2.0]octane	61.8 ± 1.1	(345)
cis-Bicyclo[3.3.0]octane	51.0 ± 1.0	(308)
	54.4 ± 1.0	(334)
trans-Bicyclo[3.3.0]octane	43.1 ± 1.0	(308)
	49.0 ± 1.0	(334)
cis-Bicyclo[5.3.0]decane	74.4 ± 0.8	(377)

Summary of Results. Our thermochemical results are summarized in Table IV. The heats of combustion of *cis*- and *trans*-bicyclo[3.3.0]octane have been measured before but the values are not very recent.[9] Barrett and Linstead reported values of −30.9 and −24.8 kcal mol^{-1} for the heats of formation of the liquid *cis* and *trans* compounds, respectively. Their values are about 1.5 kilocalories more negative than ours, but the heat of isomerization from *cis* to *trans* is in good agreement.

Discussion

In pursuit of our goals of measuring and interpreting the strain energies of bicycloalkanes, we first present for the bicycloalkanes studied here and those in the literature a table (Table V) of experimental strain energies defined in the conventional manner. That is, they are defined as the difference between the experimental heat of formation and a predicted one based on group contributions for heats of formation of unstrained alkanes. Thus, the experimental strain energy is defined as

$$SE\,(\text{exptl, } 298\,°\text{K}) = \Delta H_f°\,(\text{exptl, } 298\,°\text{K}) - \sum \Delta H_f°\,(\text{group}) \qquad (3)$$

For the right-hand terms we have used a scheme worked out here (see below) that is similar to and inspired by that of Schleyer, *et al.*[10] Also included in Table V is a simple but naive approach to the interpretation of strain. The sum of the experimental strain energies of component monocyclic rings is compared with the experimental strain energy of the bicyclic hydrocarbon. This approach will be more or less in error since the conformations of the fused rings will, in general, be different from the separate rings and a torsional interaction will be missing from the fused system. Since the former will increase the strain energy and the latter lower it, they will be somewhat compensatory. It is seen in Table V that fairly substantial deviations from

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(9) J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 611 (1936).

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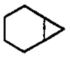
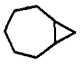
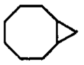
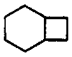
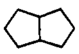
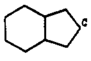
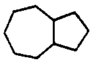
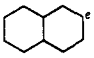
Table IV. Summary of Thermochemical Data for Bicyclooalkanes (kcal mol^{-1}, 25°)

Compound		$-\Delta H_c$°	ΔH_{vap} (at T °K)	ΔH_f°
cis-Bicyclo[3.1.0]hexane	(l)	907.1 ± 0.5		1.3 ± 0.7
			8.00 ± 0.1 (298)	
	(g)			9.3 ± 0.8
cis-Bicyclo[4.1.0]heptane	(l)	1059.5 ± 0.6		−8.7 ± 0.8
			9.10 ± 0.2 (298–330)	
	(g)			0.4 ± 1.0
cis-Bicyclo[5.1.0]octane	(l)	1216.2 ± 0.3		−14.2 ± 0.5
			10.4 ± 0.2 (297–332)	
	(g)			−3.8 ± 0.7
cis-Bicyclo[6.1.0]nonane	(l)	1373.6 ± 0.6		−19.4 ± 0.8
			11.8 ± 0.2 (297–332)	
	(g)			−7.6 ± 1.0
cis-Bicyclo[4.2.0]octane	(l)	1214.3 ± 0.6		−16.3 ± 0.7
			9.45 ± 0.10 (347)	
	(g)		10.2 ± 0.3 (298)	−6.1 ± 1.0
cis-Bicyclo[3.3.0]octane	(l)	1198.1 ± 0.3		−32.6 ± 0.3
			9.91 ± 0.1 (318)	
	(g)		10.3 ± 0.2 (298)	−22.3 ± 0.5
trans-Bicyclo[3.3.0]octane	(l)	1204.5 ± 0.4		−26.1 ± 0.4
			9.86 ± 0.1 (320)	
	(g)		10.2 ± 0.2 (298)	−15.9 ± 0.6
cis-Bicyclo[5.3.0]decane	(l)	1511.4 ± 0.8		−43.9 ± 0.9
			11.20 ± 0.10 (377)	
	(g)		12.80 ± 0.30 (298)	−31.1 ± 1.2

Table V. Strain Energies in Bicyclo[*n*.*m*.0]hydrocarbons

n	*m*			ΔH_f°(g), kcal mol^{-1}	Strain energy, kcal mol^{-1}	Sum of two rings	Δ
1	1	[a]	*cis*	51.9	65.9	56	10
2	1	[b]	*cis*	37.0	56.1	55	1
3	1		*cis*	9.3	33.5	35	−2
4	1		*cis*	0.4	29.6	29	1
5	1		*cis*	−3.8	30.5	35	−5
6	1		*cis*	−7.6	31.8	39	−7
4	2		*cis*	−6.1	28.2	28	0
3	3		*cis*	−22.3	12.0	14	−2
			trans	−15.9	18.4	14	4
4	3	[c]	*cis*	−30.4	8.9	8	1
			trans	−31.4	7.9	8	0
5	3		*cis*	−31.1	13.4	14	−1
			trans	−31.4[d]	13.1	14	−1
4	4	[e]	*cis*	−40.4	4.1	2	2
			trans	−43.5	1.0	2	−1

[a] K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968). [b] R. B. Turner, *Theor. Org. Chem., Pop. Kekule Symp.*, 81 (1959). [c] C. C. Browne and F. D. Rossini, *J. Phys. Chem.*, **64**, 927 (1960). [d] N. L. Allinger and V. Zalkow, *J. Amer. Chem. Soc.*, **83**, 1144 (1961), from Δ*H* (isomerization) reported there. [e] D. M. Speros and F. D. Rossini, *J. Phys. Chem.*, **64**, 1723 (1960).

additivity can be present and that they are often in the direction of the strain being less than the sum of two rings.

We now proceed to the more sophisticated method of using transferable potential functions and energy minimization to predict the heats of formation and other properties.[11] A number of authors have developed potential functions for such calculations. Some of these have been designed for special purposes, such as prediction of simple alkane or polymer conformations.[12-14] Others have been used for the study of conformation and strain in cyclic hydrocarbons.[15-17] We have found these functions to be inadequate in application to the more complicated multicyclic hydrocarbons. Allinger[18,19] has made comprehensive calcu-

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(17) M. Bixson and S. Lifson, *Tetrahedron*, 23, 769 (1967).

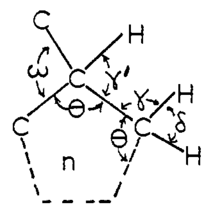

Figure 1. Notation for angles used in Table VI.

Table VI. Potential Functions Used for Calculations on Alkanes[a]

Valence Force Potential (VF)

Bond Stretching (harmonic function)

	k_r	R_0
C-H		
($-CH_3$)	4.70	1.09
($-CH_2-$ and $-CH$)	4.55	1.09
(Cyclopropane)	5.00	1.08
(Cyclobutane)	4.68	1.09
C-C	4.40	1.53
(Cyclobutane)	4.20	1.53

Bond Bending (harmonic function)[b]

Ring size n	k_θ	θ_0, deg	k_ω	ω_0, deg	k_γ	γ_0, deg	γ_0', deg	k_δ	δ_0, deg
3			0.80	117	0.608	117	116	0.508	116
4	2.20	90	0.80	114	0.500	114	110	0.500	110
5	0.80	109.5	0.80	109.5	0.608	109.5	109.5	0.508	109.5
≥ 6	0.80	111.0	0.80	111.0	0.608	109.5	109.5	0.508	107.9

Bond Torsion

$U = U_0/_2\,[1 + \cos 3\phi]$

$U_0 = 0.0146$

$= 0.013$ (cyclobutane)

$= 0.010$ (bond adjacent to cyclopropane ring)[c]

Nonbonded and Torsional Barrier[d]

	A	B	C
C···C	104.0	3.09	4.45
C···H	30.0	3.415	0.96
H···H	18.4	3.74	0.19

$U = A \exp(-BR) - C/R^6$

Urey–Bradley Potential (UB)[e]

$k_\theta,k_\omega = 0.55$; $k_r(C,C) = 0.25$; $R_0(C,C) = 2.50$

$k_\gamma = 0.39$; $k_r(C,H) = 0.50$; $R_0(C,H) = 2.155$

$k_\delta = 0.52$; $k_r(H,H) = 0.040$; $R_0(H,H) = 1.78$

$k_r(C{-}H) = 4.425(-CH_3)$

$= 4.023\ (-CH_2-, \geqslant CH)$

$k_r(C{-}C) = 2.40$

$U_0 = 0.0153$

[a] All units are such that energies are in units of 10^{-11} ergs, angles in radians, and distances in Ångströms. Bond stretching and bending potentials are harmonic with the force constants and natural lengths and angles given. To convert 10^{-11} ergs molecule^{-1} to kcal mol^{-1}, multiply by 144.0. [b] Angles to be reduced to radians for use. [c] This value is reduced from 0.0146 to account for orbital distortion and leads to better agreement with experiment. [d] All pairs not in same bond angle interaction. [e] Same natural angles and nonbonded potentials as VF.

lations on strained hydrocarbons with considerable success but has used a C–C–C bending function that corresponds to the force constant becoming smaller with decreasing bond angle. The senior author (R. H. B.) feels that the lack of definite spectroscopic evidence for this in cyclopentane and the fact that the force constant in cyclobutane is much higher than in cyclopentane or cyclohexane mitigates strongly against this approach. We have kept this force constant independent of angle and consider the cyclobutane and cyclopropane rings to be special electronic systems (with their own force constants) which can be incorporated into more complicated ring systems (see below).

We have taken the view that the valence functions used should lead to results that are simultaneously consistent insofar as possible with the three general properties of heats of formation, molecular geometry, and vibrational frequencies. It is our belief that this overall view is vital even at the sacrifice of some detailed agreement in any one of these areas alone. One of us has developed[20] an energy minimization procedure that appears to be efficient in terms of computation time and performs a vibrational analysis on the final geometry. Thus the potential functions may be adjusted to fit experimental results of all of the three kinds. Lifson and Warshel[21] have used a similar approach in calculations on the C_5–C_{10} cycloalkanes and obtained good results. However, no other strained molecules were included. We have developed a model and set of parameters that appear to be reasonably successful in calculations on a variety of unstrained and strained hydrocarbons and have reported them in part.[22] A somewhat more elaborate version is presented here in Table VI. Figure 1 shows the notation used for the angles in Table VI.

The model used is elaborated upon below.

(a) It is assumed that the molecular energy can be empirically described as a sum of equilibrium intrinsic bond energies (or group contributions) and energies of bond stretching, bending, and twisting plus nonbonded interaction energies.

(b) As with a number of other workers, the torsional barrier is assumed to be an inherent barrier in a carbon–carbon single bond, described by a cosine potential plus nonbonded interactions between the substituents on each carbon.

(c) The same nonbonded interactions as in b are used between all atoms not involved in bond bending, stretching, or twisting. The nonbonded potentials used are slight modifications of those developed for C···C, C···H, and H···H by Williams[23,24] to represent *inter*molecular interactions. The modification was to use parameter set IV of ref 24 but to make the C···C repulsive interaction slightly less steep. When cast in the form

$$V(r) = \frac{\epsilon}{1 - 6/\alpha}\left[\frac{6}{\alpha}e^{-\alpha(1 - r/r_m)} - (r_m/r)^6\right] \qquad (4)$$

where ϵ is the well depth and r_m the distance of the minimum, the steepness parameter, α, was changed from 14 to 12, keeping ϵ and r_m the same. The C···H potential was altered to keep α the arithmetic mean of α for C···C and H···H with ϵ and r_m unchanged. The H···H potential was unaltered. The inherent barrier was fixed by the torsional frequency of ethane with this choice of H···H potentials.

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(18) N. L. Allinger, M. A. Miller, F. A. Van Catledge, and J. A. Hirsch, *J. Amer. Chem. Soc.*, **89**, 4345 (1967).

(19) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. Tyminski, and F. A. Van Catledge, *ibid.*, **90**, 1199 (1968).

(20) R. H. Boyd, *J. Chem. Phys.*, **49**, 2574 (1968).

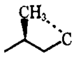
(21) S. Lifson and A. Warshel, *ibid.*, **49**, 5116 (1968).

(22) C. F. Shieh, D. McNally, and R. H. Boyd, *Tetrahedron*, **25**, 3653 (1969).

(23) D. E. Williams, *J. Chem. Phys.*, **45**, 3770 (1966).

(24) D. E. Williams, *ibid.*, **47**, 4680 (1967).

Table VII. Group Contributions to the Heat of Formation, the Intrinsic Bond Energies in the Hypothetical Motionless State (E_I^*), Deformation and Nonbonded Energies ($DE + NB$), Enthalpies ($H_{298K}^\circ - H_0^\circ$), and Zero-Point Energies (ZPE)[a]

	ΔH_f^6 (25°)$_{group}$	E_I^* (group)	$(DE + NB)_{group}$	$(H^\circ_{298K} - H_0^\circ)_{group}$	ZPE_{graup}
$-CH_3$	−10.12	355.74	0.39	1.41	22.58
$-CH_2-$	−5.08	294.13	0.32	0.80	17.30
$-\overset{\vert}{\underset{\vert}{C}}H-$	−1.92	234.29	0.53	0.02	11.80
$-\overset{\vert}{\underset{\vert}{C}}-$	0.67	174.73	0.35	−0.35	5.99
 (Skew methyl group interaction)	0.60		0.60		

[a] Kilocalories mol^{-1}; Δ, correction = 29.52; □, correction = 22.99.

Table VIII. Comparison of Various Quantities from Group Contributions with Experimental and Calculated Values

Compd (1)	ΔH_f° [a] (exptl) (2)	($H_{298K}^\circ - H_0^\circ$)[a] (exptl) (3)	ZPE[b] (exptl) (3)	E_a^* [c] (exptl) (5)	E_a^* [d] (calcd) (6)	($H_{298K}^\circ - H_0^\circ$)[e] (calcd) (7)	($H_{298K}^\circ - H_0^\circ$)[f] (group) (8)	ZPE[e] (calcd) (9)	ZPE[f] (group) (10)	($DE + NB$)[e] (calcd) (11)	($DE + NB$)[f] (group) (12)
Ethane	−20.23	2.856	45.17	710.73	710.73	2.812	2.82	44.91	45.16	0.75	0.78
Propane	−24.82	3.512	62.44	1003.87	1004.47	3.488	3.62	62.40	62.46	1.14	1.10
n-Butane	−30.15	4.645	79.73	1298.25	1298.28	4.280	4.42	79.72	79.76	1.46	1.42
n-Pentane	−35.00	5.629	97.23	1592.21	1592.13	5.119	5.22	97.01	97.06	1.74	1.74
n-Hexane	−39.96	6.622	114.35	1885.91	1885.99	5.965	6.02	114.37	114.36	2.01	2.06
Isobutane	−32.15	4.276	79.61	1299.76	1300.10	4.292	4.25	79.69	79.54	1.41	1.70
Isopentane	−36.73[g]	5.295	96.84	1593.22	1593.11	5.043	5.05	97.10	96.84	2.53	2.62
2-Methylpentane	−41.66	6.097	(114.1) est	1886.84	1887.01	5.891	5.85	114.44	114.14	2.76	2.94
3-Methylpentane	−41.02	6.148	(114.1) est	1886.30	1885.97	5.743	5.85	114.57	114.14	3.80	3.54
2,3-Dimethylbutane	−42.49	5.916	113.73	1887.11	1887.46	5.847	5.68	114.57	113.92	4.08	3.84
Neopentane	−39.67[g]	5.030	96.28	1595.80	1596.00	5.074	5.29	96.79	96.31	1.69	1.91
2,2-Dimethylbutane	−44.35	5.912	113.60	1888.84	1888.16	5.841	6.09	114.30	113.61	3.66	3.42

[a] From F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953. [b] From calculated frequencies of ref 25. [c] Computed using values of first three columns and eq 6 of text. [d] Calculated using values of Table VII for E_I^*, the values of column 11 for $DE + NB$ and eq 7 of text. [e] Calculated in this work using parameter set VF of Table VI. [f] From the values of Table VII. [g] W. D. Good, *J. Chem. Thermodyn.*, **2**, 237 (1970).

(d) The force constants for stretching and bending are taken from the work of Snyder and Schachtschneider[25] but adjusted iteratively by sucessive linear interpolation to fit the frequencies of cyclohexane. This was necessary to take into account the effects of including nonbonded interactions and the torsional barrier representation used here. The C–C–C bending constant was chosen to fit the E_g and E_u frequencies of cyclohexane but was biased to some extent by the heat of formation of cyclopentane.

(e) It is desirable to retain the concept of strain energy in discussions of molecular stability. However, energy minimization calculations do not give strain energies directly but rather the sum of bond deformation (stretching, bending, and twisting) energies plus the nonbonded interaction energies. Unstrained molecules will have appreciable deformation and nonbonded energies. We have worked out (Table VII) a set of group contributions to these for unstrained alkanes. We have followed Schleyer, *et al.*, in including a skew methyl interaction as an additional group. This results in more consistent group representation of the deformation and nonbonded energies. Table VIII compares the deformation and nonbonded energies for a variety of alkanes calculated by energy minimization using the parameters of Table VI with the group contributions. These group contributions are to be subtracted from calculated deformation and nonbonded energies in strained molecules to arrive at strain energies. We further assume that the strain energy calculated in this way is appropriate to the molecule in a hypothetical motionless (with respect to translation, rotation, and vibration) state, or

$$SE^*(\text{calcd}) = DE + NB - \sum(DE + NB)_{\text{group}} \quad (5)$$

where the asterisk refers to the hypothetical motionless state, DE refers to the deformation energy of a molecule (due to bond stretching, bending, and twisting from "natural values"), and NB refers to the sum of nonbonded energies of a molecule.

(f) The calculated strain energy in eq 5 in the hypothetical motionless state is not, in general, appropriate for comparison with the experimental strain energy of eq 3 at 298°K. It is known that experimental strain energies are significantly dependent on temperature

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[25] R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **21**, 169 (1965).

and on zero-point energy effects.[26,27] Taking advantage of the fact that the energy minimization procedure provides calculated thermodynamic functions and zero-point energies, a calculated strain energy at 298°K may be arrived at. The experimental molecular *energy* (energy of atomization, $E_a{}^*$) in the hypothetical motionless state of a C_aH_b hydrocarbon (where a = number of carbons in a C_aH_b alkane and b = number of hydrogens in a C_aH_b alkane) may be expressed as

$$E_a{}^*(\text{exptl}) = -\Delta H_f{}^\circ(\text{exptl, } 298\,^\circ\text{K}) + (H_{298\,^\circ\text{K}} - H_0{}^\circ) + ZPE + 170.890a + 52.090b - {}^5\!/_2(a + b)RT_{298\,^\circ\text{K}} \quad (6)$$

where the heats of atomization of C (graphite) and H_2 (g) at 298°K have been taken from Stull and Sinke[28] and $H_{298\,^\circ\text{K}} - H_0{}^\circ$ and ZPE are the enthalpy and zero-point energies of the compound. From section a above it follows that

$$E_a{}^*(\text{calcd}) = \sum E_I{}^*(\text{group}) - (DE + NB) \quad (7)$$

where the $E_I{}^*$ are a set of intrinsic bond energies or group contributions. Comparison of eq 6 and 7 for unstrained alkanes allows a set $E_I{}^*$(group) to be worked out (Table VII). We then define

$$-SE^*(\text{exptl}) = E_a{}^*(\text{exptl}) - \sum E_I{}^*(\text{group}) + \sum(DE + NB)_{\text{group}} \quad (8)$$

Using the analogy of eq 6 for calculated values we can arrive at an expression for the calculated heat of formation at 298°K as

$$\Delta H_f{}^\circ(\text{calcd, } 298\,^\circ\text{K}) = -\sum E_I{}^*(\text{group}) + (DE + NB) + (H_{298\,^\circ\text{K}}{}^\circ - H_0{}^\circ) + ZPE + 170.890a + 52.090b - {}^5\!/_2(a + b)RT_{298\,^\circ\text{K}} \quad (9)$$

Thus we may define

$$SE(\text{calcd, } 298\,^\circ\text{K}) = \Delta H_f{}^\circ(\text{calcd, } 298\,^\circ\text{K}) - \sum \Delta H_f{}^\circ(\text{group}) \quad (10)$$

We are then in a position to compare calculated and experimental strain energies both at room temperature (SE) and in the hypothetical motionless state (SE^*) if a set of $\Delta H_f{}^\circ$(group) is determined. First, however, we note that in arriving at $E_a{}^*$ (exptl) (eq 6) for computation of SE^* (exptl) (eq 8) it will usually be necessary, as in the work reported here on bicyclo compounds, to use calculated values of $H_{298\text{K}}{}^\circ - H_0{}^\circ$ and ZPE. Since these will be the same calculated values as in eq 9 we may write in this case

$$SE^*(\text{exptl}) = SE^*(\text{calcd}) + \Delta H_f{}^\circ(\text{exptl}) - \Delta H_f{}^\circ(\text{calcd}) \quad (11)$$

A set of group contributions to $\Delta H_f{}^\circ$ has been arrived at by determining group contributions to each of the appropriate terms in eq 9. $E_I{}^*$(group) and $(DE + NB)_{\text{group}}$ have already been discussed under (e) above and are listed in Table VII. Enthalpy groups were deduced from the enthalpies calculated for unstrained alkanes by energy minimization using the parameters of Table VI. The experimental values were not used since, as stressed by Schleyer, *et al.*,[10] these reflect a mixture of conformations in a number of cases. The calculated values represent the single most stable conformation. It is to be observed in Table VIII that where *gauche* isomers can exist the calculated enthalpies are lower than the experimental. The zero-point energy groups were determined from the zero-point energies derived from the frequencies of Snyder and Schachtschneider[25] which we regard as "experimental." Comparison of the zero-point energies from experiment, calculated from energy minimization and from groups, are compared in Table VIII. Combining the group contributions of $E_I{}^*$, $(DE + NB)$, $(H_{298\text{K}}{}^\circ - H_0{}^\circ)$, and ZPE through eq 9 results in the group contributions to $\Delta H_f{}^\circ$ listed in Table VII. In defining the strain energies of cyclic compounds we have not included any *gauche* interaction group in either $\Delta H_f{}^\circ$(group) or $(DE + NB)_{\text{group}}$. Thus, such interactions appear as strain. It is a matter of taste then to say that noncyclic alkanes containing similar skew methyl interactions are not strained but cyclic compounds containing *gauche* conformations are. Of course, any definition of strain is arbitrary in that the strain depends on the reference structures used in the definition. The important requirement of conformational calculations is the ability to calculate the actual heat of formation or binding energy.

Table IX. Comparison of Vibrational Frequencies of Cyclohexane Calculated with Valence Force and Urey–Bradley Potentials with Experimental

Symmetry species	VF, cm^{-1}	UB, cm^{-1}	Exptl,[a] cm^{-1}
A_{1g}	2930	2896	2939
	2869	2857	2855
	1463	1448	
	1179	1222	1158
	768	793	802
	350	351	386
A_{2g}	1335	1383	
	1056	1085	
E_g	2923	2908	2926
	2867	2873	2855
	1541	1445	1444
	1406	1302	1348
	1197	1239	1267
	1009	1111	1029
	755	767	
	429	421	427
A_{1u}	1416	1266	
	1178	1246	
	1007	1081	
A_{2u}	2924	2918	2931
	2852	2875	2855
	1550	1449	1451
	862	869	1018
	565	556	527
E_u	2925	2897	2931
	2865	2864	2855
	1483	1442	1441
	1375	1367	1350
	1218	1272	1259
	905	926	905
	848	882	864
	221	223	239[b]

[a] Experimental values are those tabulated in ref 25. [b] Experimental value from R. M. Brugger, K. A. Strong, R. J. Pugmire, and D. M. Grant, *J. Chem. Phys.*, **50**, 1029 (1969).

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(26) T. L. Allen, *J. Chem. Phys.*, **31**, 1048 (1959).

(27) B. Nelander and S. Sunner, *ibid.*, **44**, 2476 (1966).

(28) D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," Advances in Chemistry Series, No. 18, American Chemical Society, Washington, D. C., 1956.

Table X. Some Miscellaneous Alkane Properties Calculated from VF Parameters of Table VI Compared with Experimental

Compd	Property	Calcd	Exptl
Ethane	HCC angle	110.5°	111.5 ± 0.3°[a]
	Torsional freq	270.5	268 cm^{-1}[b]
n-Butane	*gauche–trans* energy difference at	0.72	0.70 ± 0.10 kcal mol^{-1}[c]
	298°K and motionless state	0.66	298°K and motionless state
	CCC bond angles (*trans*)	111.9°	112.6 ± 0.3°[c]
n-Pentane	*gauche–trans* energy difference at	0.72	0.45 ± 0.06 kcal mol^{-1}[c]
	298°K and motionless state	(0.66)	
	CCC bond angles (*trans*)	111.9°	112.6 ± 0.3°[c]
Cyclobutane	Dihedral angle	30°	~33°[d]
	Inversion barrier	1.17	1.28 kcal mol^{-1}[d]
Cyclohexane	Torsional angle	55.6°	
	CCC angle	111.2°	111.5°[e]
Methylcyclohexane	Axial–equatorial free-energy difference	1.23	1.8 ± 0.3[f] kcal mol^{-1}
	at 298°K and motionless state	(1.00)	

[a] K. Kuchitsu, *J. Chem. Phys.*, **49**, 4456 (1968). [b] K. A. Strong and R. M. Brugger, *ibid.*, **47**, 421 (1967). [c] See ref 12 for references. [d] T. Ueda and T. Shimanouchi, *J. Chem. Phys.*, **49**, 470 (1968). [e] M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963). [f] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, p 44.

If it is felt that ($H_{298\mathrm{K}}{}^\circ - H_0{}^\circ$) and *ZPE* are adequately represented by group contributions; the distinction between SE^* and $SE(298°\mathrm{K})$ is dropped and eq 5 used for strain energy in general. Also, a simpler representation for the heat of formation predicted by energy minimization results

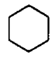
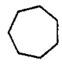
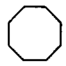
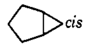
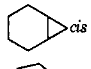
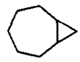
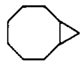
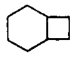
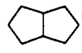
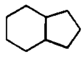
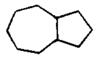
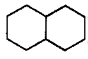
$$\Delta H_f{}^\circ(\text{calcd}) = \Delta H_f{}^\circ(\text{group}) + (DE + NB)_{\text{calcd}} - (DE + NB)_{\text{group}} \quad (12)$$

However, in this work, since we are interested in investigating the adequacy of this approach for *cyclic* compounds, we have retained the distinction and eq 9 is used to arrive at $\Delta H_f{}^\circ$ (calcd) and to define *SE* (calcd, 298°K), through eq 10. Equations 5 and 11 are used for SE^*(calcd) and SE^*(exptl), respectively.

Several comments on the results in Table VIII are in order. First, $H_{298\mathrm{K}}{}^\circ - H_0{}^\circ$ and *ZPE* for *noncyclic* alkanes are adequately represented by groups. Thus, in agreement with other workers we find no necessity for making such corrections and room-temperature bond energy schemes are adequate. Second, the agreement between $E_a{}^*$(exptl) and $E_a{}^*$(calcd) is satisfactory and is a noticeable improvement over schemes based on only the first four groups of Table VII (Franklin's method[29] for heats of formation). This is significant since this improvement is the result of superimposing the nonbonded interaction energies used here on intrinsic group or bond energies and does not depend on *ad hoc* conformational corrections such as the skew methyl correction we have used for the group contributions to the nonbonded interactions.

(g) The equilibrium bond angle for C–C–C was taken to be 111.0° which leads to calculated values in linear alkanes of about 112.0°. The smaller rings (n = 3,4) have to be considered as electronic systems different from the other alkanes and special parameters assigned to them. These are then used with these parameters to build multicyclic rings. The same group contributions to the intrinsic bond energies were used and a correction factor for the ring added. In cyclopropane the correction represents SE^* but in cyclobutane due to the choice of equilibrium angles it does not. In cyclobutane, the equilibrium C–C–C angle was taken to be 90°. There is no special significance to this angle except that particularly simple analytical formulas result that connect the dihedral angles, the C–C–C force constant, the torsional force constant, effective out-of-plane deformation force constant, and the barrier to inversion. In building multicyclic rings using n = 3,4 rings an ambiguity results in selecting equilibrium angles at the juncture points. The arbitrary rule was followed that the equilibrium angles at the juncture points that are exterior to the rings are considered to be that of the smaller ring involved.

Table XI. Comparison of Calculated and Experimental Strain Energies in the Hypothetical Motionless State and at 298°K of Cyclo- and Bicycloalkanes[a,b]

		SE^*		$SE_{298°\mathrm{K}}$		$\Delta H_f{}^\circ$, 298°K	
		Calcd	Exptl	Calcd	Exptl	Calcd	Exptl
		8.6	8.5	7.1 (7.1)	7.0	−18.4	−18.46
		1.9	2.2	0.7 (0.7)	1.0	−29.7	−29.43
		7.8	8.1	6.9 (7.4)	7.2	−28.7	−28.41
		12.0	11.4	11.3 (12.2)	10.7	−29.3	−29.90
	*cis*	37.0	36.0	34.5 (33.8)	33.5	10.3	9.3
	*cis*	33.7	31.9	31.4 (31.1)	29.6	2.2	0.4
	*cis*	31.5	31.5	30.5 (30.5)	30.5	−3.8	−3.8
	*cis*	36.3	33.7	34.4	31.8	−5.0	−7.6
	*cis*	31.6	30.6	29.2	28.2	−5.1	−6.1
	*cis*	14.5	14.3	[c](12.2)	12.0	−22.1	−22.3
	trans	27.6	20.8	25.2 (24.6)	18.4	−9.1	−15.9
	*cis*	9.8	10.4	8.3 (8.3)	8.9	−31.0	−30.4
	trans	10.3	9.3	8.9 (8.6)	7.9	−30.5	−31.4
	*cis*	14.2	15.1	12.5 (13.2)	13.4	−32.0	−31.1
	trans	4.7	15.1	12.7	13.1	−31.8	−31.4
	*cis*	5.8	5.1	4.8 (4.4)	4.1	−39.7	−40.4
	trans	1.9	2.1	0.8 (0.5)	1.0	−43.8	−43.5

[a] Values in parentheses are from UB parameters of Table VI. [b] Experimental heats of formation are from this work, references of Table V and footnote *a*, Table VIII. [c] VF calculation failed to converge.

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(29) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

Table XII. Calculated Thermodynamic Functions of Cyclo- and Bicycloalkanes[a]

T	$(G° - G_0°)/T$	$(H° - H_0°)/T$	$S°$	$C_p°$	ZPE
Cyclopropane, D_{3h}, $\sigma = 6$					
298.16	47.74	9.36	57.10	13.72	50.23
400.00	50.72	11.05	61.77	18.21	(49.04)[b]
500.00	53.38	12.89	66.28	22.15	
Cyclobutane,[c] D_{4h}, $\sigma = 8$					
285.67			62.43 (62.7)[d]		
298.16	52.36	10.77	63.13	16.98	66.99
400.00	55.90	13.19	69.09	23.79	(67.02)[e]
500.00	59.08	15.90	74.98	29.82	
Cyclopentane,[f] pseudorotator, D_{5h}, $\sigma = 10$					
298.16	57.81 (57.93)	12.41 (12.07)	70.22 (70.00)	20.11 (19.82)	85.22
400.00	61.87 (61.88)	15.41 (15.12)	77.24 (77.00)	28.25 (28.24)	(86.15$_7$ 85.26)[f]
500.00	65.67 (65.62)	18.76 (18.52)	84.43 (84.14)	35.78 (35.86)	
Cyclohexane,[g] D_{3d}, $\sigma = 6$					
298.16	57.24 (57.07)	14.36 (14.21)	71.60 (71.28)	25.67 (25.40)	103.28
400.00	62.03 (61.80)	18.52 (18.38)	80.55 (80.18)	35.64 (35.82)	(103.31)[h]
500.00	66.63 (66.39)	22.89 (22.85)	89.52 (89.24)	44.72 (45.47)	
Cycloheptane, C_2, $\sigma = 2$, d, 1 pair					
298.16	64.91	17.07	81.99	30.70	120.76
400.00	70.61	22.02	92.63	42.24	
500.00	76.08	27.16	103.23	52.76	
Cyclooctane, D_2, $\sigma = 4$					
298.16	65.04	19.33	84.37	35.50	138.42
400.00	71.52	25.14	95.65	48.69	
500.00	77.76	31.10	108.86	60.72	
cis-Bicyclo[3.1.0]hexane, C_s					
298.16	60.64	13.89	74.54	24.02	89.36
400.00	65.23	17.63	82.86	32.98	
500.00	69.59	21.52	91.11	40.92	
cis-Bicyclo[4.1.0]heptane, d, 1 pair					
298.16	64.76	15.85	80.60	28.67	107.15
400.00	70.05	20.49	90.54	39.37	
500.00	75.14	25.25	100.39	48.85	
cis-Bicyclo[5.1.0]octane, C_s					
298.16	65.47	17.76	83.23	33.33	124.95
400.00	71.45	23.32	94.78	45.73	
500.00	77.27	28.95	106.21	56.74	
cis-Bicyclo[6.1.0]nonane, d, 1 pair					
298.16	69.60	20.06	89.67	38.13	142.51
400.00	76.38	26.48	102.86	52.20	
500.00	82.99	32.92	115.91	64.74	
cis-Bicyclo[4.2.0]octane, d, 1 pair					
298.16	66.46	17.06	83.52	32.06	124.55
400.00	72.22	22.55	94.77	45.02	
500.00	77.87	28.24	106.10	56.52	
(UB) *cis*-Bicyclo[3.3.0]octane, C_{2v}, $\sigma = 2$					
298.16	65.15	17.05	82.20	31.05	124.92
400.00	70.87	22.28	93.14	44.01	
500.00	76.44	27.84	104.28	55.73	
(UB) *trans*Bicyclo[3.3.0]octane, C_s					
298.16	67.96	17.81	85.78	31.59	124.46
400.00	73.90	22.95	96.85	44.36	
500.00	79.61	28.44	108.05	55.98	
(UB) *cis*-Bicyclo[4.3.0]nonane, d, 1 pair					
298.16	69.79	19.19	88.99	35.75	142.77
400.00	76.26	25.26	101.53	50.24	
500.00	82.58	31.62	114.21	63.45	
(UB) *trans*-Bicyclo[4.3.0]nonane, C_2, $\sigma = 2$, d, 1 pair					
298.16	67.88	19.14	87.03	35.85	142.80
400.00	74.34	25.24	99.58	50.27	
500.00	80.66	31.61	112.27	63.46	
cis-Bicyclo[5.3.0]decane[i]					
298.16		21.62		40.41	160.33
400.00		28.44		56.24	
500.00		35.49		70.64	
trans-Bicyclo[5.3.0]decane[j]					
298.16		21.22		39.56	160.12
400.00		27.90		55.32	
500.00		34.88		69.69	
cis-Bicyclo[4.4.0]decane,[k] C_2, $\sigma = 2$, d, 1 pair					
298.16	69.23 (69.73)	20.72 (20.55)	89.95 (90.28)	40.48 (39.84)	161.26
400.00	76.30 (76.68)	27.82 (27.64)	104.12 (104.32)	56.64 (57.64)	
500.00	83.29 (83.70)	35.10 (35.02)	118.39 (118.71)	71.21 (71.64)	

Table XII (*Continued*)

T	$(G° - G_0°)/T$	$(H° - H°)/T$	$S°$	$C°_p$	
trans-Bicyclo[4.4.0]decane,[k] C_{2h} $\sigma = 2$					
298.16	68.75 (68.77)	21.26 (20.75)	90.01 (89.52)	40.91 (40.04)	160.92
400.00	75.96 (75.78)	28.31 (27.84)	104.28 (103.62)	56.90 (56.78)	(160.61)[h]
500.00	83.06 (82.83)	35.54 (35.17)	118.60 (118.01)	71.40 (71.14)	

[a] Units are calories and °K. Values in parentheses are experimental or calculated from spectra from indicated references. Calculated values use valence force set of Table VI, unless indicated otherwise as UB (Urey–Bradley). [b] H. H. Gunthard, R. C. Lord, and T. K. McCubbin, Jr., *J. Chem. Phys.*, **25**, 768 (1956). [c] The ring puckering energy levels of T. Ueda and T. Shimanouchi, *ibid.*, **49**, 470 (1968), were used with our other calculated frequencies and geometry. [d] Experimental value of G. W. Rathjens and W. D. Gwinn, *J. Amer. Chem. Soc.*, **75**, 5629 (1953). [e] R. C. Lord and I. Nakagawa, *J. Chem. Phys.*, **39**, 2951 (1963). [f] Values in parentheses are those tabulated by J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, **69**, 2483 (1947). A q_0 value of 0.38 Å from our calculated structure was used (*cf.* $q_0 = 0.47$ Å); K. S. Pitzer and W. E. Donath, *ibid.*, **81**, 3213 (1959). The second value of the zero-point energy is that reported in ref 26. [g] Values in parentheses are those tabulated by C. W. Beckett, K. S. Pitzer, and R. Spitzer, *ibid.*, **69**, 2488 (1947). [h] From ref 25. [i] This molecule has one calculated frequency that is nearly zero. The pseudorotator value of $1/2R$ was given to $(H° - H_0°)/T$ and $C_p°$ but no speculation regarding the entropy was made. [j] This molecule has two nearly zero frequencies that were assigned pseudorotation values. See *i* above. [k] Values in parentheses are from T. Miyazawa and K. S. Pitzer, *J. Amer. Chem. Soc.*, **80**, 60 (1958).

It was hoped that no special assumptions concerning the $n = 5$ ring need be made but it turned out to be necessary to assign the value of the C–C–C angle as 109.5°. This change is not particularly critical for cyclopentane itself but is necessary to obtain agreement for the heat of formation of several compounds containing $n = 5$ rings.

(h) The valence force potentials used here led to good distributions of vibrational frequencies for calculation of the thermodynamic functions and zero-point energy. Since no interaction constants are used the detailed agreement with vibrational frequencies is not impressive. Snyder and Schachtschneider[25] used transferable interaction constants and obtained good agreement of calculated and experimental frequencies. However, they also obtained fairly good agreement[30] by superimposing a Urey–Bradley force field on the valence force. In order to obtain better detailed agreement with spectroscopic results we have derived an alternative set of parameters by using the partial Urey–Bradley field to introduce interactions between stretching and bending. The Urey–Bradley constants and the angle force constants of Snyder and Schachtschneider[30] were modified to take into account the nonbonded potentials used here. The calculated spectra are noticeably improved (see Table IX), particularly the E_g, A_{2u}, and E_u CH_2 deformation frequencies. Strain energy calculations were made (designated UB in the tables) for many of the compounds using this field and are very similar to results using the valence force field (VF). In summary, we might say that the VF field can be used with its fewer interactions for structural and thermodynamic calculations. However, if better spectral agreement is desired the UB field with more interactions is probably to be preferred.

A variety of miscellaneous properties calculated with the VF parameters of Table VI are summarized in Table X.

The heats of formation of the bicycloalkanes form a very critical testing ground for any set of parameters for the calculation of hydrocarbon properties. We are, therefore, especially interested in the comparison between calculated and experimental strain energies of these compounds. This comparison is made in Table XI. It is seen that the agreement is, in general, gratifying and the strain energies can be calculated with a typical deviation of about 1 kcal mol^{-1}. A notable exception is *trans*-bicyclo[3.3.0]octane, where the calculated strain energy is over 6 kcal mol^{-1} greater than the experimental. We do not know the reason for the failure with this compound but it is unusual in that there is a large positive calculated C–C–C angle strain at the fusion points (see Figure 2). It may be that the potential functions used do not adequately describe these large positive deformations. It is to be noticed in Table XI that the strain energies in the hypothetical motionless state are somewhat higher than at room temperature. It is evident that taking into account the effects of zero point and vibrational energies is important in predicting the strain energies of *cyclic* hydrocarbons at room temperature. The differences are not as great as previously found[26,27] for cycloalkanes where the strain energies were based on reference structures containing mixtures of conformational isomers. However, there remains a real effect that results from the tendency of the enthalpy and zero-point energy groups derived from noncyclic structures to overestimate the values for cyclic compounds. Part of past difficulties in finding potential functions that simultaneously reproduce vibrational spectra and strain energies is due to using experimental strain energies that are too low because of the single conformation and vibrational effects above.

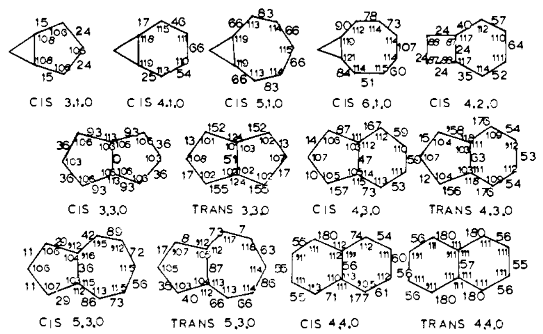

Figure 2. Calculated geometries of bicycloalkanes. Larger numbers aret orsional angles (based on eclipsed as 0); smaller numbers are CCC bond angles.

The calculated thermodynamic functions are given in Table XII and compared with experiment where possible. The thermodynamic functions are for the conformation calculated but in many cases there are, no doubt, several conformations of similar energy,

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(30) J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963); Table VI.

a situation that will have an appreciable effect on the entropy and free energy. The symmetry numbers and stereoisomeric pairs used in the entropy calculations are recorded in the table. The agreement with experimental values where the comparison can be made is excellent. We believe that the calculation of gas phase thermodynamic functions by a vibrational analysis using transferable potential functions with the minimum energy structure is now a very convenient and accurate way of predicting these quantities.

The calculated geometries are illustrated in Figure 2.

Acknowledgments. We are indebted to the U. S. Army Research Office (Durham) for financial support of this work. We are grateful to Dr. H. E. Simmons, Jr., Central Research Department, E. I. du Pont de Nemours Co. for furnishing the cyclopropanes, and to Professor N. L. Allinger of Wayne State University for his interest in the bicyclo[3.3.0]octanes and for providing the facilities for their synthesis. We express our appreciation to Professor P. v. R. Schleyer of Princeton University for communicating his work on goup contributions for strain energy definition to us.

Generation, Rearrangement, and Interconversion of Hydrocarbons Related to Bullvalene[1,2a–c]

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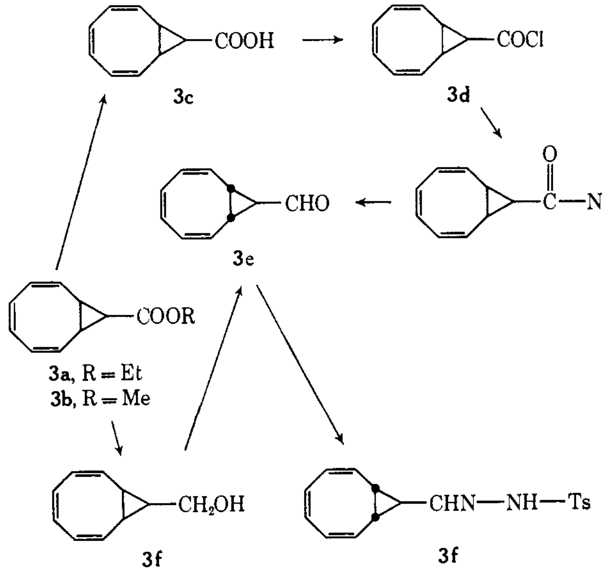
Abstract: Bicyclo[4.2.2]deca-2,4,7,9-tetraene (**8**), *cis*- and *trans*-9,10-dihydronaphthalene (**6** and **5**), and *cis*-1-phenylbutadiene (**7**) are formed on thermal decomposition of the salt of bicyclo[6.1.0]nona-2,4,6-triene-9-carboxaldehyde tosylhydrazone (**3f**). Similarly, *cis*-bicyclo[5.2.0]nona-2,4,8-triene (**20**), bicyclo[3.2.2]nonatriene (**21**), and bicyclo[4.2.1]nonatriene (**19**) are formed on thermal decomposition of the salt of bicyclo[5.1.0]octa-2,4-diene-8-carboxaldehyde tosylhydrazone (**18f**). The proofs of structure of several of these hydrocarbons are described and a mechanism involving cleavage of an initially formed carbene to a diradical proposed. The conversion of **8** to bullvalene (**1**) on photolysis is described, as is the further photolysis of **1**. The thermal conversions of several of these $(CH)_{10}$'s to **6** are described.

The discovery[4,5] that bullvalene (**1**) possessed the fully fluxional structure predicted[6,7] has been one of the most stimulating of recent years. More or less parallel to the emerging chemistry of bullvalene has been the examination of the properties of molecules closely related in either an isomeric or conceptual sense. The unravelling of the structures and interrelationships of the various $(CH)_{10}$'s has been a diverse and international effort and we describe here our part in it.

Our work began with the perhaps naive conception that the well known ring-expansion reaction of cyclopropylcarbenes[9] could be used to add a C_2H_2 unit to cyclooctatetraene[10] to produce the unknown (at that time) bicyclo[6.2.0]deca-2,4,6,9-tetraene (**2**).[11] The synthesis of the required carbene precursor proceeded through the ester **3a** or **3b**[12–14] in several ways. In practice, the route through the alcohol has been most convenient in our laboratories. In the initial addition to cyclooctatetraene, two stereoisomers are formed.



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(1) Support for this work through a grant from the Lilly Research Laboratories is gratefully acknowledged.

(2) This work is taken in part from the Theses of S. D. R. and L. T. S. submitted in partial fulfillment of the requirements for the A. B. degree at Princeton University. Preliminary communications have appeared. (a) M. Jones, Jr., and L. T. Scott, *J. Amer. Chem. Soc.*, **89**, 150 (1967); (b) M. Jones, Jr., and S. D. Reich, *ibid.*, **89**, 3935 (1967); (c) M. Jones, Jr., *ibid.*, **89**, 4236 (1967).

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(4) G. Schröder, *Chem. Ber.*, **97**, 3140 (1964).

(5) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).[8]

(6) W. von E. Doering, *Zh. Vses. Khim. Obshchest.*, **7**, 308 (1962).

(7) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(8) As one of those quoted (M. J., Jr.) in footnote 15 of ref 5, it is perhaps not out of order to suggest that the source of "this ignoble name" is neither lost nor contained in E. Partridge, "A Dictionary of Slang and Unconventional English," Macmillan and Co., New York, N. Y., 1961.

(9) W. Kirmse and K.-H. Pook, *Chem. Ber.*, **98**, 4022 (1965).

(10) We thank the Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene.

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(13) S. Akiyoshi and T. Matsuda, *ibid.*, **77**, 2476 (1955).

(14) D. D. Phillips, *ibid.*, **77**, 5179 (1955).