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Enthalpies of Formation of Globular Molecules. II. Three Bicyclooctanes and Two Bicyclononanes[1]

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Abstract: The enthalpies of combustion (ΔH_c) of plastically crystalline substances bicyclo[2.2.2]octane, bicyclo-[2.2.2]oct-2-ene, 1-azabicyclo[2.2.2]octane, and 3-oxabicyclo[3.2.2]nonane were measured in a rotating bomb calorimeter at 298.15°K as -1195.49 ± 0.21, -1156.72 ± 0.19, -1089.25 ± 0.22, and -1164.74 ± 0.21 kcal/mol, respectively. To avoid the transition region present near 298°K, 3-azabicyclo[3.2.2]nonane was measured as -1240.51 ± 0.19 kcal mol^{-1} at 300.95°K. Direct comparison in the gas phase, various schemes, and/or liquid-phase hydrogenation reactions were used whenever possible to evaluate the strain energies of these substances. The enthalpy of combustion of succinic acid was also determined as -3019.8 ± 0.2 cal/g. It is considered suitable as a secondary combustion standard.

The strain energies involved in bicyclic compounds are of considerable interest and have aroused much discussion.[3,4] In bicyclo[2.2.1]heptane, the solitary methylene brings carbon atoms 1 and 4 into closer approach than in an isolated boat-type ring and consequently considerable angular strain would be expected. Measurements of enthalpies of formation (ΔH_f)[5] and of sublimation (ΔH_s) lead to the conclusion that the total strain energy in this molecule is 17.55 kcal/mol.[4] Replacement of the methylene group by an oxygen atom gives 7-oxabicyclo[2.2.1]heptane and is said to reduce the total strain of the molecule.[5] Bicyclo[2.2.2]octane (**1**) is claimed to be virtually free from angular strain, but the nontwisted (D_{3h}) form is said to possess maximum hydrogen–hydrogen nonbonded interaction energy and torsional strain in three pairs of C–C bonds. Although conformational analysis,[6,7] X-ray diffraction,[8] nmr,[9] determination of quadrupole moments,[10] and spectroscopic studies[11] have not resolved the issue of whether the bicyclo[2.2.2]octanes are twisted (D_3) or nontwisted (D_{3h}), Ermer and Dunitz[6] have calculated for bicyclo[2.2.2]octane-1,4-dicarboxylic acid (on the assumption that the bond lengths remain effectively constant during a torsional vibration) that the energy minimum may be slightly displaced from D_{3h} symmetry. The barrier between the minima, however, is only about 100 cal/mol, so the molecule has effectively this symmetry at all temperatures.

This paper reports enthalpy of combustion (ΔH_c) studies on five symmetrical-top or almost-symmetrical-top, globular molecules: **1**, bicyclo[2.2.2]octene-2 (**2**), 3-azabicyclo[2.2.2]octane (or quinuclidine) (**3**), 3-oxabicyclo[3.2.2]nonane (**4**), and 1-azabicyclo[3.2.2]nonane (**5**). The structures of these molecules are schematically indicated below. Such data are useful for many purposes, including the testing of quantitative conforma-

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(1) This research was supported by the Division of Research of the U. S. Atomic Energy Commission.

(2) To whom communications concerning this paper should be addressed.

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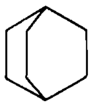
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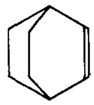
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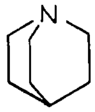
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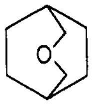
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tional analysis schemes which are being developed, particularly for those involving bridged structures.

Experimental Section

(1) Preparation and Purification of Substances. The five globular substances studied all form the plastically crystalline phase prior to fusion. Each sample had been purified for heat capacity measurements in this laboratory by preliminary recrystallization from organic solvents, vacuum distillation, and/or gradient sublimation, and was finally zone melted. The sample source, purification, and characterization of compounds **1**, **2**, and **4** are detailed[12] and summarized elsewhere.[13-16] The solid-insoluble, liquid-soluble impurities in most of the samples determined by fractional fusion in the course of the heat capacity measurements[12] are summarized in Table I. That of **3** is not given because its reaction with the silver calorimeter during fusion precluded a purity determination. Owing to the plastic nature of the globular molecules and their sensitivity to oxygen, water, and carbon dioxide, the pelleted samples were prepared between Teflon disks in a Teflon-sleeved stainless-steel pellet press[16] operated within the nitrogen atmosphere of a drybox. Only in this manner was the production of good, transparent pellets possible on several of these tenaciously adhering, tacky substances. The pellets were sealed in Mylar bags before being removed from the anhydrous atmosphere for weighing.

Table I. Physical Constants of Globular Compounds at 298.15°K

Compd	Mol wt,[a] g/mol^{-1}	Impurity,[b] mol %	Density,[c] g/cm^3	$(\partial V/\partial T) \times 10^6$, l./(g °K)	C_p,[d] cal/(mol °K)
1	110.2008	0.0014	0.964[e]	0.72[g]	0.342
2	108.1848	0.0018	0.952	0.72[g]	0.346
3	111.1884		1.014[f]	0.72[g]	0.367
4	126.2002	0.0034	1.035	1.04[h]	0.350
5	125.2155	0.0021	0.99	1.04[h]	0.414

[a] *Cf.* S.-w. Wong, Ph.D. Dissertation, submitted to the Horace H. Rackham School of Graduate Studies, University of Michigan; *Diss. Abstr. B*, **28**, 2383 (1967). [b] Liquid soluble, solid insoluble by fractional fusion; ref 12–14. [c] Densities of **2**, **4**, and **5** are determined from Debye–Scherrer X-ray diffraction patterns. [d] References 12 and 13. [e] A. E. Cameron and E. Wichers, *J. Amer. Chem. Soc.*, **84**, 4175 (1962). [f] J. Bauer, *Sb. Vysok. Skoly Chem.-Technol. v Praze, Oddil, Fak. Anorg. Org. Technol.*, 145 (1957). [g] The expansion coefficient of 1,3,3-trimethylbicyclo[2.2.2]-Δ^5-octen-2-one is used for **1**, **2**, and **3**: E. Josephy and F. Radt, Ed., "Elsevier's Encyclopedia of Organic Chemistry," Vol. 12A, Elsevier, New York, N. Y., 1948, p 1071. [h] Estimated by analogy with other material. *Cf.* W. Nowacki, *Helv. Chim. Acta*, **29**, 1798 (1946).

(2) Calorimetric Apparatus. Combustions were made in a rotating-bomb calorimeter which, together with the adjuvant apparatus and Bomb Pt-MM-1 (which were used for measurements on **2** and **5**), has been described previously.[17] Bomb Pt-NR-2 (which was used for the measurements on the other three compounds) is similar to Pt-MM-1 except that the internal volume is 0.3520 l.

A platinum baffle partially covered the deep crucible in which the sample pellets were burned. To Bomb Pt-MM-1 was added 1.040 ml of water; 1.06 ml of water was added to Bomb Pt-NR-2. The bomb was charged with oxygen at an initial pressure of 30.00 atm at 25°C. All combustions were initiated by a platinum wire and cotton fuse. After each combustion the bomb was examined carefully for soot, and the reaction was rejected if any was found.

(3) Primary Calibration Experiments with Benzoic Acid. The energy equivalent of the calorimeter [$\mathcal{E}$°(calor)] was determined by combustion of a NBS 39i benzoic acid standard sample having $-\Delta U_b$ = 26,434.0 ± 3.3 J/g (*in vacuo*)[18] at 25°C with estimated uncertainties of ±0.01%. The temperature (T_h) to which the idealized combustion reaction is referred was 24.95°C for all the compounds except **5**. Because this substance undergoes a transition to the plastic crystalline state at 297.78°K,[15] a temperature falling within the normal range of operation of the calorimeter, it was found necessary to raise the temperature of the entire calorimeter system to 27.80°C in order to obtain reproducible results for this substance. The values of $\mathcal{E}$°(calor) are for Pt-MM-1 at T_h = 24.95°C, 3976.13 ± 0.16; for Pt-MM-1 at T_h = 27.80°C, 3978.55 ± 0.22; and for Pt-NR-2 at T_h = 24.95°C, 3992.76 ± 0.11 cal/°K.

(4) Secondary Calibration Experiments with Succinic Acid. In order to assure the accuracy of the determination of ΔH_c by the calorimeter used in this work, a secondary calibration was considered desirable. Succinic acid was chosen as the material since a well-established value for $\Delta E_c°/M$ may be obtained by a careful compilation and correction of literature values. The sample used in this work was prepared by recrystallization of USP grade material four times from distilled water, oven drying between 110 and 114°C for 80 hr, then grinding into powder and drying in the oven for another 16 hr. The melting point, measured in a sealed tube, ranged from 187.5 to 188.0°C. Titration of this material with dilute sodium hydroxide gave the neutralization equivalent as 99.87% of the theoretical value. Values for a typical combustion experiment are included in Table II. The mean value at 298.15°K of $-\Delta E_c°/M$, 3019.8$_0$ ± 0.2, is the average of four of the six experimental determinations (3019.44*, 3019.95, 3019.86, 3019.24*, 3019.68, and 3019.72). The two determinations marked with asterisks were rejected from the average because of traces of soot detected after the combustion. This value is in good accord with four earlier literature values[19-22] which when adjusted to current constants and standard states,[23] average together to 3020.2 ± 1.0. It is in good accord with the values of Huffman (3020.2 ± 0.6),[24] of Good, *et al.* (3019.8 ± 0.4),[25] and of Pilcher and Sutton (3020.6 ± 0.4)[26] (who did not use standard benzoic acid) as well as with the less precise results of Keith and Mackle (3019.9 ± 1.0),[27] of Wilhoit and Shiao (3019.6 ± 1.0),[28] and of Adams, *et al.* (3020.4 ± 1.2).[29,30] Recent thermal data[31] indicate the efficacy of a drying procedure utilizing pelleting to break up the vacuoles containing aqueous solution. Hence succinic acid appears to be an excellent choice for a secondary combustion standard. The overall standard

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Table II. Summary of Typical Combustion Experiments[a]

Quantity	Succinic acid	1	2	3	4	5
m'(compd), g, *in vacuo*	2.164024	0.578545	0.583391	0.639021	0.683027	0.629855
$\Delta t = t_f - t_i + \Delta t_{corr}$ °K	1.65841	1.66245	1.65881	1.65703	1.66636	1.65620
$\mathcal{E}$(calor)($-\Delta t$), cal	−6543.84	−6551.75	−6536.16	−6530.33	−6567.02	−6504.02
$\mathcal{E}$(cont)($-\Delta t$), cal	−7.28	−8.16	−7.21	−8.20	−8.25	−8.19
ΔE_{ign}, cal	0.41	0.40	0.41	0.45	0.38	0.44
$\Delta E_{dec}{}^f(HNO_3 + HNO_2)$, cal	0.48	0.12	1.15	2.94	0.21	3.70
ΔE_Σ corr to std states, cal	7.02	1.69	1.99	1.75	1.93	1.64
$-m''\Delta E_c°/M$(Mylar), cal		285.08	304.38	274.62	270.74	268.75
$-m'''\Delta E_c°/M$(fuse), cal	6.92	6.67	7.38	7.09	6.26	7.34
$m'\Delta E_c°/M$(compd), cal	−6535.06	−6265.31	−6227.42	−6251.06	−6295.08	−6229.77
$\Delta E_c°/M$(compd), cal/g	−3019.86	−10829.43	−10674.52	−9782.22	−9216.45	−9890.80

[a] The temperature for compound **5** is 300.95°K (27.80°C); that of all the others is 298.15°K.

Table III. Summary Combustion Energies for Individual Determinations[a]

	1	2	3	4	5
$-\Delta E_c°/M$, cal/g	10827.40	10674.57	9778.59	9214.25	9890.62
	10829.43	10677.06	9782.22	9212.94	9890.80
	10829.41	10677.57	9785.13	9216.45	9891.53
	10828.51	10675.10	9779.68	9217.09	9892.69
	10832.63	10674.52	9783.71	9215.61	9892.19
		10675.26			9890.88
Mean[b]	10829.5 ± 1.8	10675.7 ± 1.4	9781.9 ± 2.5	9215.3 ± 1.6	9891.4 ± 1.3

[a] The temperature for compound **5** is 300.95°K (27.80°C); that of all the others is 298.15°K. [b] Mean values and standard deviation of the mean.

Table IV. Derived Chemical Thermodynamic Data (kcal/mol) at 298.15°K

	1	2	3	4	5[a]
$\Delta E_c°$	−1193.42 ± 0.20	−1154.95 ± 0.16	−1087.63 ± 0.28	−1162.97 ± 0.20	−1238.56 ± 0.16[a]
$\Delta H_c°$	−1195.49 ± 0.20	−1156.72 ± 0.16	−1089.25 ± 0.28	−1164.74 ± 0.20	−1240.51 ± 0.16[a]
$\Delta H_f°$(c)[b]	−35.15 ± 0.20	−5.60 ± 0.16	−13.17 ± 0.28	−65.89 ± 0.20	−24.29 ± 0.16
$\Delta G_f°$(c)	18.27 ± 0.22	38.48 ± 0.18	42.23 ± 0.30	−7.04 ± 0.23	38.87 ± 0.18
$\Delta H_f°$(g)	−23.67 ± 0.23	4.88 ± 0.19	−1.03 ± 0.31	−53.20 ± 0.24	−10.44 ± 0.19
$\Delta G_f°$(g)	21.62 ± 0.25	41.33 ± 0.19	46.20 ± 0.31	−2.63 ± 0.24	43.58 ± 0.20

[a] The combustion values for **5** are at 300.95°K. [b] The symbols (c) and (g) refer to the crystalline and gaseous phases.

deviations from the mean can be expressed as $\pm\sigma(\Delta E_c°/M) = \pm(\sigma_1^2 + \sigma_2^2)^{1/2}(\Delta E_c°/M)$, in which σ_1 and σ_2 are relative standard deviations[32] of calibration runs and combustion experiments, respectively. The precision indices indicated in this paper are twice the overall standard deviation unless otherwise indicated.

(5) Units of Measurement and Auxiliary Quantities. The results of the combustion experiments are expressed in terms of the defined calorie equal to 4.1840 J and refer to the isothermal process at 25°C and to the true mass. The molecular weights were computed from the 1961 (^{12}C = 12.0000 g/mol) table of international atomic weights.[33] For use in reducing the weight of the sample in air to *in vacuo* conditions and in correcting the energy of the actual bomb process to the isothermal process at standard states, the values of density (ρ), specific heat (C_p), and $(\partial V_s/\partial T)_p$ used are listed in Table I. The corrections, which included those for the formation of nitric acid, were made as described elsewhere.[34] Enthalpies of formation, $\Delta H_f°$, of water and carbon dioxide were taken to be 68317.4[35a] and 94051.8[35b] cal/mol; values of the energy of the idealized combustion reaction, $-\Delta E_c°/M$, for the cotton fuse and Mylar (at the ambient relative humidity) were 4108 and 5467.48 cal/g.

Results

Table II details a typical combustion for each globular compound and Table III summarizes the results of all the determinations. The thermodynamic increments for the idealized combustion reaction and formation are compiled in Table IV for both the crystalline (c) and the gaseous (g) phase at 298.15°K for the five plastically crystalline substances by use of entropies of the elements[36] and the entropies, vapor pressures, and enthalpies of sublimation of the compounds.[14] Since **5** has a solid–solid phase transition at 297.78°K[15] the combustion values shown in Tables II and III correspond to the values for crystal I at 27.80°C. Values for this compound at 25°C in Table IV lie within the transition region and, though not uniquely definable, have been predicated upon a 3°K extrapolation of the heat capacity for the crystal I phase.

Discussion

Evaluation of Strain Energy by Direct Comparison. Estimation of molecular strain may be achieved by comparison of the standard enthalpies of formation for appropriate pairs of compounds. The quantities cited in the subsequent portion of this paper are all referred to 298.15°K. For example, the total strain in **1** is estimated as the difference between the liquid-phase enthalpies of (hypothetical) hydrogenation of **1** to

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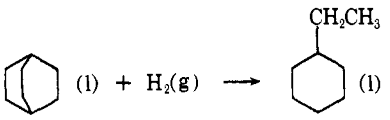
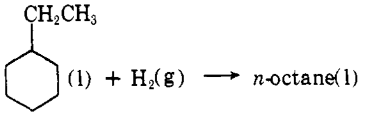
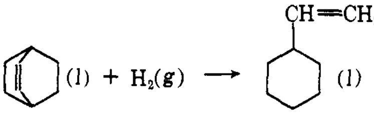
ethylcyclohexane



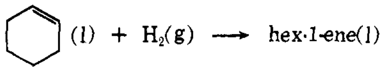
$\Delta H_h(l) = -17.56$, $\Delta H_h(g) = -17.38$ kcal/mol, and of ethylcyclohexane to *n*-octane



$\Delta H_h(l) = -9.02$, $\Delta H_h(g) = -8.77$ kcal mol^{-1}, if a small correction is made for the strain in ethylcyclohexane. The values for these hypothetical reactions are calculated from the $\Delta H_f°$'s of the compounds, *i.e.*, those of ethylcyclohexane, $\Delta H_f°(l) = -50.72$,[37] $\Delta H_f°(g) = -41.05$ kcal/mol;[38] and those of *n*-octane, $\Delta H_f°(l) = -59.7$,[37] $\Delta H_f°(g) = -49.8$ kcal/mol.[39] ΔH_m of **1** (1.99 kcal/mol) was determined by heat capacity measurements[12] on the same sample. The strain energy in ethylcyclohexane, estimated by the Allen–Skinner scheme,[40] is 0.3 kcal/mol; thus, the strain energy in **1** will be approximately 9.2 kcal/mol. The strain energy in **2** may likewise be obtained by taking the differences between the $\Delta H_h°(l)$ of **2** to vinylcyclohexane



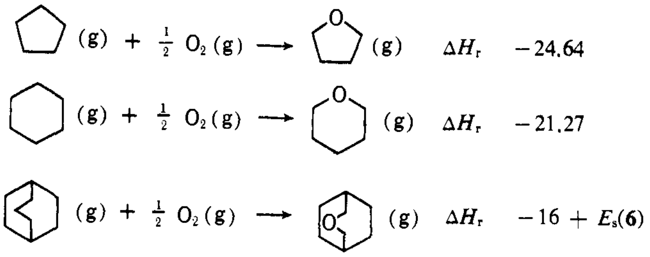
$\Delta H_h = -16.91$ kcal/mol, and that of cyclohexene to hex-1-ene



$\Delta H_h = -8.02$ kcal/mol, plus a small adjustment for the strain in cyclohexene. Enthalpy increments for these hypothetical reactions are calculated from the $\Delta H_f°(l)$'s of the compounds (kcal/mol) vinylcyclohexane, -21.2,[41] cyclohexene, -9.3,[41] and hex-1-ene, -17.3.[42] The ΔH_m of **2** (1.29 kcal/mol) is also employed.[12] The strain energy of **2** (9.69 kcal/mol) is ascribed to the difference in the enthalpy increments of these two hypothetical reactions plus the strain energy in cyclohexene (0.8 kcal/mol).

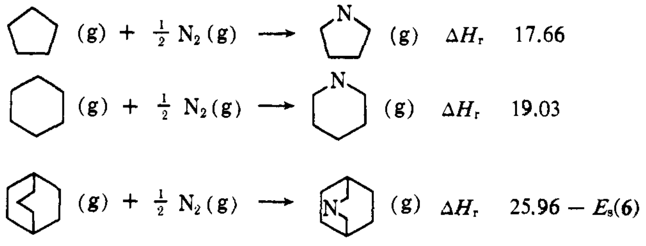
Since the usual ΔH_h's are a measure of the difference between the $\Delta H_f°$'s of the saturated and unsaturated compounds, it will reflect the strain energies in both the saturated and unsaturated compounds. Comparison of ΔH_h for **2**(l) (-28.85 kcal/mol evaluated from the present ΔH_c and the ΔH_m[12]) with the ΔH_h value for cyclohexene(l) (-28.06 kcal/mol calculated from the measured ΔH_c[41]) indicates that the ΔH_h of **2** is 0.8 kcal/mol higher. Insofar as this is significant, it could be attributed to a higher strain energy. The difference, 1.2 kcal/mol, in the ΔH_h's of **2** and of cyclohexene in aqueous acetic acid solutions (28.25 and 27.10 kcal/mol, respectively)[43] is comparable.

The molar strain energy (E_s) of **4** can be obtained by comparing the ΔH_r's (kcal/mol) of the following three hypothetical reactions.



The ΔH_r values are obtained from $\Delta H_f°(g)$'s: cyclopentane, -18.46;[37] tetrahydrofuran, -43.1;[44] cyclohexane, -29.43;[37] tetrahydropyran, -50.7;[44] bicyclo[3.2.2]nonane (**6**), $-37.78 + E_s$; and **4**, -53.82 kcal/mol, respectively. The $\Delta H_f°(g)$ of **6** is calculated by Allen's scheme[45] as modified by Skinner,[40] and the parameters used are those of Skinner and Pilcher.[46] For **6**, $\Delta H_f(g) = 9\Delta H_f°(C,g) + 16\Delta H_f°(H,g) - 10B_{CC} - 16B_{CH} - 13\Gamma_{CCC} - 2\Delta_{CCC} + (E_s) = -37.78 + E_s(\mathbf{6})$ kcal/mol. The ΔH_v of **6** is assumed to be 12 kcal/mol; cyclohexane and tetrahydropyran are assumed to have no strain. Replacement of the bridging methylene group in **6** by an oxygen atom to give **4** reduces the strain in the system to the extent of $(-5 + E_s)$ kcal/mol. Since E_s here refers to **6**, the strain energy involved in **4** will be the difference between E_s and $[-5 + E_s(\mathbf{6})]$, *i.e.*, 5 kcal/mol.

The strain energy in **5** can be similarly estimated. In the following three hypothetical reactions



the values of ΔH_r (kcal/mol) are calculated from the previously cited $\Delta H_f°(g)$'s plus those for pyrolidine, -0.8;[47] piperidine, -10.4;[48] and **5**, -11.82[49] kcal/mol. If cyclohexane and piperidine are assumed to have no strain, then $E_s(\mathbf{5})$ will be 7 kcal/mol smaller than that in **6**.

Evaluation by Various Schemes. The strain energy of all five compounds may also be evaluated by the Allen–Skinner scheme,[40] the Benson, *et al.*, scheme,[50] and two by the Schleyer, *et al.*, scheme,[4] as shown in Table V. Available enthalpies of vaporization (ΔH_v)

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Table V. Comparison of Strain Energies Estimated by Various Schemes (kcal/mol at 298.15 °K)

Compd	Direct comparison[a]	Allen–Skinner[b]	Benson[c]	Schleyer's[d] "strain-free" increments
1	9.2(l), 9.3(g)	9.2	9.8	11.0,[d] 11.4[i]
2	9.7(l)	10.5	11.3	12.2[i]
3		9.4	11.1	
4	$\sim$7(g), $\sim$11(g)[e]	9.5	10.5[h]	
5	$\sim$5(g), $\sim$10(g)[f]	9.1[g]	11.0	

[a] Phase as indicated applies to calculational route employed. [b] Reference 40. [c] Reference 50. [d] Reference 4. [e] If strains of 6.7 and 2.2 kcal/mol are ascribed (by the Benson scheme[50]) to tetrahydrofuran and tetrahydropyran, respectively. [f] By analogy with *e*. [g] ΔH_v is taken to be 12 kcal/mol. [h] Using −8.2 kcal/mol for C–(O)(C)(H)$_2$. [i] Based on $\Delta H_f°$ from this research.

have been taken from the determinations reported by Westrum, *et al.*[13]

Conclusions

As previously noted, the strain of **1** appears to come mainly from three pairs of eclipsed hydrogens which can be approximated roughly from the internal rotation energy barrier of ethane,[51] 3(2.9) = 8.7 kcal/mol. 1-Azabicyclo[2.2.2]octane (**3**) and 1,4-diazabicyclo[2.2.2]octane (triethylenediamine, **7**) have the same structure as **1**. Their strain energies also may be attributed mainly to the three pairs of eclipsed groups. Indeed, values obtained from the Allen–Skinner scheme (9.5 kcal/mol) for both **3** and **7**[52] are comparable with the strain of **1**. Substitution of a nitrogen atom for the carbon atom at the bridgehead may cause some distortion in bond angle which will increase the strain energy of these two compounds. However, compensation for part of this strain may come from the diminution of hydrogen upon each substitution of carbon by nitrogen. Hence the hydrogen–hydrogen nonbonded interactions in the molecule will be less in a nitrogen-substituted one.

Comparison of the ΔH_c's per methylene group in cyclopentane (158.7 kcal/mol) and cycloheptane (158.3 kcal/mol) with the value for cyclohexane (157.4 kcal/mol) suggests that the first two compounds have strain energies of 6 kcal/mol. Since both molecules adopt a puckered formation, the interactions between eclipsed hydrogen atoms lead to this strain. In the five- and six-membered ring systems, the difference between the $\Delta H_f°$'s of these two compounds will decrease when a CH$_2$ is replaced by an NH or an oxygen.[53] Such replacement will not markedly affect the structure of the ring. Cycloheptane has the same amount of strain energy due to interactions of nonbonded atoms. A similar reduction of strain energy will be expected when a CH$_2$ group is replaced. The strain energy of oxabicyclo[2.2.1]heptane has been estimated as 6.5 kcal/mol, so the strain energies calculated in this work for **4** (5 kcal/mol) and for **5** (7 kcal/mol) are consistent with this view.

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