V vs. NHE (turnover frequency $\sim 10^3$ mol of CO produced per mol of nickel complex, in 1 h) and selective, even in a purely aqueous medium. The stability of the complex used makes it a promising electrocatalyst (10^4 electrocatalytic cycles on Ni cyclam^{2+} without degradation). In the present study, we have detected a nickel(I) carbonyl complex which may participate in the catalytic cycle. Other important reaction parameters have been investigated. The efficiency of Ni cyclam^{2+} in the electroreduction of CO_2 may be due to the size of the cyclam ring (14 atoms), which greatly stabilizes nickel complexes. A reason for the selectivity of the electrocatalyst may be difunctional activation of CO_2. The acidic character of the N–H protons of cyclam could favor CO_2 fixation by hydrogen bonding (N–H···O) in addition to the carbon to nickel(I) link.

Theoretical Determination of Molecular Structure and Conformation. 20. Reevaluation of the Strain Energies of Cyclopropane and Cyclobutane—CC and CH Bond Energies, 1,3 Interactions, and σ-Aromaticity

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Abstract: In order to rationalize the striking similarity of the strain energies (SE) of cyclopropane (**1**, 28 kcal/mol) and cyclobutane (**2**, 27 kcal/mol), the energetic consequences of Pitzer strain, Baeyer strain, hybridization effects (CH bond strengthening), Dunitz–Schomaker strain (1,3 CC interactions), and bond stretching effects have been quantitatively assessed at the HF/6-31G** level of theory. Calculations have been based on chemically meaningful definitions of bond length, bond angle, bond energy, and bending force constant in strained molecules. Results reveal that Pitzer strain in both **1** and **2** is just 4 kcal/mol and that CH bond strengthening stabilizes **1** by 6 kcal/mol (**2** by 3 kcal/mol), far less than has been assumed previously. The calculated Baeyer strain of **1** and **2** is 41 and 13 kcal/mol, respectively. SE(**1**) and SE(**2**) can only be compared if a correction term of 9 kcal/mol due to Dunitz–Schomaker strain (present in **2**, but absent in **1**) is taken into account. The analysis of the various energy contributions to the SEs of **1** and **2** reveals that **1** is stabilized by at least 17 kcal/mol. Both MO and electron density analysis suggest that **1** is totally different from the other cycloalkanes in being stabilized by 3-center 2-electron delocalization. σ-Electrons are delocalized in the surface of the three-membered ring, a phenomenon which may be described by the term σ-aromaticity. The concept of σ-aromaticity helps to rationalize the unusual properties of **1**, the changes in the stability of **1** upon substitution, the stability of sila and germa analogues of **1** and **2**, as well as the properties of bi- and tricyclic compounds containing **1** and **2** as subunits.

(I) Introduction

It is a puzzling observation that the conventional ring strain energies (CRSE) of cyclopropane (**1**, 27.5 kcal/mol) and cyclobutane (**2**, 26.5 kcal/mol) are almost the same.[1,2] According to the classical definition of strain introduced by Baeyer more than a century ago,[3] the three-membered ring should be clearly more strained than the four-membered ring. Its bond angles deviate from the standard, strain-free CCC angle (109.5°) by $\Delta\alpha = 49.5°$ while those of a planar four-membered ring deviate just by 19.5°. Assuming that bond angle strain $\Delta E(B)$ (Baeyer strain) increases with the square of $\Delta\alpha$ according to

$$\Delta E(B) = n\frac{k_\alpha}{2}(\Delta\alpha)^2 \qquad (I)$$

(n, size of ring; k_α, CCC bending force constant), Baeyer strain of **1** should be 5 times as high as that of **2**. Utilizing k_α of propane

(1) (a) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: London, 1970. (b) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

(2) (a) Ferguson, L. N. *Highlights of Alicyclic Chemistry*; Franklin: Palisades, NJ, 1973; Part 1, Chapter 3. (b) Greenberg, A.; Liebman, J. *Strained Organic Molecules*; Academic: New York, 1978 and references cited. See also: (c) Charton, M. In *The Chemistry of Alkenes*; Zabicky, J., Ed.; Wiley-Interscience: New York, 1970; Vol. 2. (d) Wendisch, D. In *Methoden der Organischen Chemie*; Houben-Weyl-Müller; Thieme Verlag: Stuttgart, 1971; Vol. IV, p 3. (e) Schleyer, P. v. R.; Williams, J. E., Blanchard, K. R. *J. Am. Chem. Soc.* 1970, *92*, 2377–2386. (f) Wiberg, K. *Angew. Chem., Int. Ed. Engl.* 1986, *25*, 312–322.

(3) Baeyer, A. *Chem. Ber.* 1885, *18*, 2269–2281. See also: Huisgen, R. *Angew. Chem., Int. Ed. Engl.* 1986, *25*, 297–311.

(3) (1.071 mdyn·Å/rad^2)[4] the Baeyer strain of **1** and **2** is calculated to be 173 (!) and 36 kcal/mol, respectively. These values suggest (a) that the difference in the CRSE values of **1** and **2** should be larger than observed and (b) that it may be too simple-minded to use geometrical angles α and k_α of **3** to evaluate $\Delta E(B)$: The CRSE of **2** is just 26.5 kcal/mol[1] and a difference of more than 130 kcal/mol between the $\Delta E(B)$ values of **1** and **2** is certainly too large. Nevertheless, Baeyer strain of **1** should be considerably larger than that of **2** and, therefore, the similarity of the CRSE values is unexpected, a fact which for a long time has been disguised by discussing strain energies per CH_2 group (9.2 kcal/mol for **1** and 6.6 kcal/mol for **2**) rather than total CRSE values.

In principle, there are two different explanations possible for the striking anomaly in the CRSE of **1** and **2**. On the one hand, the experimentally found CRSE of **1** could signal a stabilizing effect which reduces the actual Baeyer strain of **1**. This would mean that the CRSE of **2** is normal. On the other hand, the CRSE of **2** could be abnormally high while that of **1** is normal.

Both explanations have been aired, and a number of electronic effects adding to the Baeyer strain of **1** and **2** have been invoked[5–9] to rationalize the magnitudes of CRSE (**1**) and CRSE (**2**). These are torsional strain (Pitzer strain),[2] rehybridization effects (CH bond strenghtening),[5] nonbonded interactions (Dunitz–Schomaker strain),[6,7] and effects arising from σ-electron delocalization.[8–10]

(4) (a) Snyder, R. G.; Schachtschneider, J. M. *Spectrochim. Acta* 1965, *21*, 169–195. (b) Snyder, R. G.; Zerbi, G. *Spectrochim. Acta* 1967, *23A*, 391–437.

(5) Coulson, C. A.; Moffitt, W. E. *Phil. Mag.* 1949, *40*, 1–35.

Some years ago, Dewar[9] suggested that cyclopropane and benzene are isoconjugate since both molecules possess a sextet of strongly delocalized electrons. In this way, benzene presents a π-aromatic system and **1** can be considered to be σ-aromatic. Delocalization of σ-electrons adds to the stability of **1**, thus compensating part of its Baeyer strain. σ-Aromaticity could explain the rather unusual properties of **1** most of which have largely been ignored for lack of explanation.[11]

Cremer and Kraka[10] added support to the idea of σ-delocalization by analyzing the properties of the electron density distribution $\rho(r)$ of **1**. Contrary to **2** and other cycloalkanes, electron density is smeared out in the ring surface of **1**, a phenomenon that has been termed surface delocalization. Independently, Dewar[9] and Cremer and Kraka[10] have estimated the extra-stabilization of **1** due to σ-delocalization to be of the order of 50 kcal/mol. These estimates, however, were based on rather coarse approximations of the Baeyer strain of **1** and, therefore, represent the most upper bounds to the extra-stabilization of **1**.

Recently, Schleyer[12] has reviewed the problem of the strain energies of **1** and **2**. After discussing the various effects possible in the case of **1** and **2** he comes to the conclusion that the similarity in the CRSEs of **1** and **2** is mainly due to the opposing effects of CH bond strengthening in the case of **1** and destabilizing Dunitz–Schomaker strain in the case of **2**, thus cancelling the differences in Baeyer strain energies. Following the line of argument first presented by Bauld and co-workers,[7] Schleyer considers **2** to be abnormally strained, while **1** should be normal. Accordingly, σ-electron delocalization as revealed by the properties of $\rho(r)$ of **1**[10] should entail no important energetic consequences, let alone a σ-aromatic stabilization of 50 kcal/mol.

In this paper the question of σ-aromaticity of **1** is reconsidered by properly evaluating the various effects contributing to the stability of **1** and **2**. In section II we discuss the problem of choosing an appropriate reference molecule or reference group needed for a definition of strain. In section III we compare Pitzer strain in **1** and **2**. Then, in section IV, accurate ab initio CH and CC bond energies are presented and the energetic consequences of hybridization effects in **1** and **2** are evaluated. Section V contains a reevaluation of 1,3 CC interaction energies. In section VI we develop a way of calculating Baeyer strain for **1** and **2**. In section VII, we conclude the comparison of the SEs of **1** and **2** by showing that **1** is stabilized by 3-center 2-electron delocalization. Finally, in section IX, both justification and chemical relevance of the description of **1** as a σ-aromatic compound are given.

(II) Determination of Theoretical Strain Energies (TSE)

Following a suggestion of George and co-workers[13] we define the theoretical strain energies (TSE) of **1** and **2** at 0 K by $-\Delta E_R$ of the homodesmotic reactions 1 and 2

$$1 + 3CH_3CH_3 \rightarrow 3CH_3CH_2CH_3 \qquad (1)$$

$$2 + 4CH_3CH_3 \rightarrow 4CH_3CH_2CH_3 \qquad (2)$$

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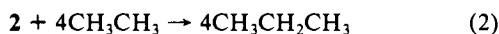
(6) Dunitz, J. D.; Schomaker, V. *J. Chem. Phys.* **1952**, *20*, 1703–1707.

(7) Bauld, N. L.; Cessak, J.; Holloway, R. L. *J. Am. Chem. Soc.* **1977**, *99*, 8140–8144.

(8) Delocalization of σ-electrons leading to σ-aromaticity has been invoked to explain the conformational behavior of dimethylcarbene. Cremer, D.; Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1974**, *96*, 6900–6903.

(9) (a) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669–682. (b) Dewar, M. J. S. *Bull. Soc. Chim. Belg.* **1979**, *88*, 957–967. (c) Dewar, M. J. S.; McKee, M. L. *Pure Appl. Chem.* **1980**, *52*, 1431–1441.

(10) (a) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800–3810. (b) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1989**, *107*, 3811–3819.

(11) For example, the ^{1}H NMR signals are shifted upfield by 1 ppm. Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon: Oxford, 1966, p 690. Zilm, K. W.; Beeler, A. J.; Grant, D. M.; Michl, J.; Chou, T.; Allred, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 2119–2120. These authors note that "circulation of electrons in the cyclopropane molecular plane" leads to a most unusual upfield shift (~20 ppm) of the ^{13}C NMR signal of **1**.

(12) Schleyer, P. v. R. *Proceedings of the NATO Advanced Research Workshop on "Substituent Effects in Radical Chemistry"*, Louvain-la-Neuve, 1986, in press.

(13) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317–323.

Table I. HF/6-31G** Geometries and Energies of Cyclopropane (**1**), Planar (**2a**) and Puckered Cyclobutane (**2b**), and Propane (**3**)[a]

molecule	geometry	energy
1	$R(CC)$ 1.497; $R(CH)$ 1.076; $\alpha(CCH)$ 118.1; $\alpha(HCH)$ 114.1	−117.06906
2a	$R(CC)$ 1.548; $R(CH)$ 1.084; $\alpha(CCH)$ 114.6; $\alpha(HCH)$ 107.9	−156.10818
2b	$R(CC)$ 1.544; $R(CH_{ax})$ 1.085; $R(CH_{eq})$ 1.084; q 0.239; $\alpha(CCC)$ 88.6; $\alpha(CCH_{ax})$ 117.7; $\alpha(CCH_{eq})$ 111.7; $\alpha(HCH)$ 108.3; $\tau(CCCC)$ 17.6; $\tau(H_{ax}CCH_{eq})$ 25.5; $\tau(H_{ax}CCH_{ax})$ 151.7; $\tau(H_{eq}CCH_{eq})$ 100.7	−156.10971
3	$R(CC)$ 1.528; $R(sec\text{-}CH)$ 1.088; $R(CH_i)$ 1.086; $R(CH_o)$ 1.087; $\alpha(CCC)$ 112.9; $\alpha(CCH_i)$ 111.3; $\alpha(CCH_o)$ 111.1; $\alpha(CCH_s)$ 109.4; $\alpha(H_iCH_o)$ 107.8; $\alpha(H_oCH_o)$ 107.6; $\alpha(H_sCH_s)$ 106.3	−118.27616

[a] Bond distances and puckering amplitude q^{17} in Å, geometrical angles α and dihedral angles τ in deg, energies in hartree. Subscripts ax, eq, s, i, and o denote axial and equatorial H atoms in the case of **2b**, secondary, in-plane, and out-of-plane H atoms in the case of **3**. All geometrical parameters but τ values of **3** are given to facilitate the calculation of the various energetic contributions to molecular strain.

Table II. Atomic and Fragment Energies (Charges) as Calculated by the Virial Partitioning Method[a]

molecule	$E(H)$ ($Q(H)$)	$E(C)$ ($Q(C)$)	$E(CH_2)$ abs	$E(CH_2)$ rel
1	−0.6552 (−52.8)	−37.7126 (105.6)	−39.0230 (0)	−23.6
2b	−0.6687[b] (−87.0) −0.6691 (−84.9)	−37.6896 (171.9)	−39.0274 (0)	−26.3
3, sec-CH$_2$	−0.6738 (−92.2)	−37.6378 (222.9)	−38.9854 (38.5)	0
3-4, −CH$_2$−			−39.0379 (0)	−32.9

[a] Energies E in hartree, charges Q in me. HF/6-31G** calculations. [b] Equatorially positioned H.

i.e., we determine ring strain of **1** and **2** relative to propane (**3**) as the "strain-free" alicyclic reference molecule.

Since correlation effects play a minor role when calculating ΔE_R of homodesmotic reactions,[13] it is sufficient to evaluate the energies of **1, 2, 3**, and ethane (**4**) at the Hartree–Fock (HF) level of theory. On the other hand, the inclusion of polarization functions for both the C *and* the H basis set[14] as well as complete optimization of the geometries of **1–4** is essential for evaluating reliable TSE values of **1** and **2** and for a consistent description of CC and CH bonds needed for the determination of bond energies from ab initio wave functions (see below). For this reason we carried out HF/6-31G**//HF/6-31G**[15,16] calculations for **1–4**, results of which are summarized in Table I.

In the case of **2**, we calculated both the planar (**2a**) and the puckered form (**2b**). The inversion barrier thus obtained (1.0 kcal/mol) is only slightly larger than the one reported previously (0.9 kcal/mol; HF/6-31G*//HF/6-31G*),[17] while the experimentally determined barrier is 1.3 kcal/mol.[18] Accordingly, the

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(14) In a previous investigation of bonding in **1** and **3**[10] no definite conclusions with regard to the CH bond strengths could be drawn from the analysis of $\rho(r)$. This was mainly due to the use of an insufficient basis set augmented by polarization functions only in the C basis.

(15) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222. Following the usual notation, the acronym *behind* the double slash denotes the level of theory at which geometry optimization has been carried out.

(16) All calculations have been carried out with the computer program COLOGNE85: Gauss, J.; Kraka, E.; Cremer, D. Universität Köln, 1985. COLOGNE85 comprises parts of GAUSSIAN82: Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A., Carnegie-Mellon University, Pittsburgh, 1982.

(17) Cremer, D. *J. Am. Chem. Soc.* **1977**, *99*, 1307–1309 and references cited therein.

(18) Egawa, T.; Yamamoto, S.; Kuchitsu, K., *Proceedings of the Eleventh Austin Symposium on Molecular Structure*, Austin, 1986, p 40.

Table III. Heats-of-Formation ($\Delta H_f°$), Zero-Point Energies (ZPE), Energies at 0 K for Fixed Nuclei (E(THEO)), and Strain Energies (SE) for Some n-Membered Cycloalkanes, Propane, and Ethane[a]

molecule	n	$\Delta H_f°$(298)	$\Delta H_f°$(0)	ZPE	E(THEO) total	E(THEO) CH$_2$	SE
cyclopropane (1)	3	12.7	16.8	49.6	-117.9291	-39.3097	28.9
cyclobutane (2b)	4	6.8	12.8	67.1	-157.2564	-39.3141	27.3
cyclopentane (5)	5	-18.4	-10.2	85.5	-196.6141	-39.3228	6.9
cyclohexane (6)	6	-29.5	-19.8	103.6	-235.9502	-39.3250	0
propane (3)		-24.8	-19.4	62.9	-119.1727 }	-39.3250[b]	0[b]
ethane (4)		-20.2	-16.5	45.3	-79.8477 }		

[a] $\Delta H_f°$, ZPE, and SE in kcal/mol, E(THEO) in hartree. Experimental values of $\Delta H_f°$ from ref 1; vibrational frequencies from ref 25. The symbol E(THEO) is used for consistency with ref 20 where its derivation is presented. [b] Obtained by the difference E(THEO,3) - E(THEO,4).

calculated puckering amplitude ($q = 0.24$ Å, Table I) and the HCCH dihedral angles of **2b** are slightly underestimated by theory.

By utilizing the ab initio energies given in Table I, the TSEs of **1** and **2** are calculated to be 28.0 and 27.3 kcal/mol, respectively. When correcting the theoretical values for zero-point energies and vibrational effects, we obtain theoretical strain enthalpies at 298 K (26.0 (**1**) and 25.0 kcal/mol (**2**)) that are almost identical with experimental SE values at 298 K (26.5 (**1**) and 25.1 kcal/mol (**2**))[1,13].

Choice of a Strain-Free CH$_2$ Reference Group. The assumption that **3** is the appropriate "strain-free" reference molecule is only valid if one corrects E(**3**) with the energy of **4** in order to yield the energy of a "strain-free" CH$_2$ group, with which the energies of the CH$_2$ groups in cycloalkanes can be compared. The CH$_2$ group in **3**, CH$_2$(**3**), itself is definitly not a valid reference group since it is positively charged while the CH$_2$ groups of **1** and **2** are electroneutral. Accordingly, its energy is higher than that of an ideal CH$_2$ group with zero charge. To illustrate this point, we have calculated atomic and CH$_2$ fragment energies for **1-3** using the virial partitioning method (see Appendix and ref 19). The data thus obtained (Table II) confirm that CH$_2$(**3**) is positively charged (38.5 me, Table II) and *destabilized* by more than 30 kcal/mol with regard to the CH$_2$ groups of the strained systems **1** and **2**. On the other hand, CH$_3$(**3**) is negatively charged (-19.2 me) and stabilized by 16.5 kcal/mol relative to CH$_3$(**4**). Correction of E(CH$_2$,**3**) with twice the energy difference E(CH$_3$,**3**) - E(CH$_3$,**4**) leads to a new CH$_2$ reference energy (Table II), which is lower by 32.9 kcal/mol than E(CH$_2$,**3**). This energy belongs to an hypothetical CH$_2$ group that has obtained 19.2 me negative charge from each CH$_3$ group in **3** in order to become electroneutral. In other words, the CH$_2$ reference group derived in this way comprises the total subspace of CH$_2$(**3**) and a considerable part of the subspaces of the two adjacent carbon atoms, which may be indicated by the notation -CH$_2$-.

While it is possible to exactly describe the properties of CH$_2$(**3**) by the virial partitioning method, those of -CH$_2$- cannot be described since there is no unique way of defining which part of the CH$_3$ groups has to be added to CH$_2$ to get -CH$_2$-. This is important as it immediately shows that care has to be taken if the properties of CH$_2$(**3**) are used to describe strain in cycloalkanes. This applies to energy, charge, (as discussed) and in particular the CCC bending force constant (section VI).

As for the hypothetical fragment -CH$_2$- it can be shown that its energy represents a reasonable reference energy. For this purpose, we define a new "strain-free" CH$_2$ reference group by assuming that cyclohexane (**6**) in the chair form is unstrained. This assumption is reasonable since valence and dihedral angles of **6** deviate only slightly from idealized values. For example, Schleyer and co-workers have estimated the strain of **6** to be just 1 kcal/mol[2e] while other estimates suggest a zero value.[1,2b,f] The energy E(THEO) of one of the CH$_2$ groups of **6** at 0 K for fixed nuclei can be derived from the experimental $\Delta H_f°$ value of **6** as described by Cremer.[20] In Table III, E(THEO,CH$_2$(**6**)) is com-

Table IV. Pitzer Strain of Cyclopropane (1) and Cyclobutane (2) as Determined from Ethane (4) with Appropriate Model Geometries[a]

molecule	conf[b]	geometry	energy	barrier V_3	Pitzer strain[c]
4	stag	R(CC) 1.527; R(CH) 1.086 α(CCH) 111.2	-79.23824	3.0	3.0
	ecl	R(CC) 1.540; R(CH) 1.085 α(CCH) 111.7			
1	stag	R(CC), R(CH) and α(CCH) from 1	-79.22290	2.0	4.0
	ecl				
2a	stag	R(CC), R(CH), and α(CCH) from 2a	-79.23391	2.2	5.9
	ecl				
2b	stag	R(CC), R(CH)[d] and α(CCH)[d] from 2b	-79.23429	2.4	
	ecl				
		corrected for $\tau = 25.5$[e]		1.5	3.9

[a] Distances R in Å, angles α and τ in deg, energies in hartree, rotational barriers V_3 and Pitzer strain in kcal/mol. For the geometries of 1 and 2 see Table I. [b] Conformations of **4** are staggered and eclipsed. [c] Barrier values have been divided by 3 and, then multiplied by 6 (1) and 8 (2) to obtain Pitzer strain. [d] Averaged values have been used. [e] Corrected according to $0.5 V_3(1 + \cos 3\tau)$.

pared with the difference E(THEO,4) - E(THEO,3). The two values are identical since deviations (ca. 0.4 kcal/mol) between the corresponding $\Delta H_f°$ values and vibrational corrections cancel each other out, i.e., the homodesmotic reactions at 0 K for the motionless molecules happen to reproduce the strain energies of cycloalkanes relative to **6** as the "strain-free" reference molecule. At room temperature the two sets of SEs differ by 1-2 kcal/mol.

From Table III it can be seen that the HF/6-31G** TSEs of **1** and **2** are both 1 kcal/mol smaller than SE values. However, for reasons of consistency we will continue to use the calculated TSEs. Although we have shed some light on the choice of the appropriate reference molecule in order to define ring strain, it is by no means clear whether we can discuss the TSEs of **1** and **2** with regard to the same CH$_2$ reference group. The energies of both **2**, **3**, and **6** comprise contributions resulting from nonbonded CC interactions while that of **1** does not. This fact has to be given special consideration when comparing the TSEs of **1** and **2**.

(III) Pitzer Strain

The barrier for rotation at the CC bond of ethane is close to 3 kcal/mol,[21] suggesting that eclipsing of two vicinal CH bonds leads to Pitzer strain of 1 kcal/mol. Accordingly, a first estimate of Pitzer strain in **1** and **2** yields values of 6 and 8 kcal/mol, respectively. These values have to be corrected for the fact that (a) the CCH angles in **1** and **2** are widened from 111.7° (C$_2$H$_6$, eclipsed, Table IV) to 118.1° and 114.6°, respectively, and (b) **2** in its equilibrium geometry adopts the puckered form **2b** with HCCH dihedral angles of 25.5° (Table I).

The effect of CCH angle widening on the torsional barrier of ethane has been determined at the HF/6-31G** level (Table IV). The barrier values thus obtained suggest that the estimated Pitzer strain of both **1** and **2** has to be reduced by ca. 2.0 kcal/mol.

The torsional potential of ethane varys with cos 3τ where τ is the HCCH dihedral angle. If the calculated τ values of **2b** are used (Tables I and IV), then puckering of **2** is predicted to cause

(19) (a) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *44*, 63-124 and references cited therein. (b) Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *Rep. Prog. Phys.* **1981**, *44*, 893-948 and references cited therein.

(20) Cremer, D. *J. Compt. Chem.* **1982**, *3*, 165-177.

(21) Weiss, S.; Leroi, G. *J. Chem. Phys.* **1968**, *48*, 962-967.

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a further decrease in Pitzer strain by 2 kcal/mol. Considering both effects (a) and (b) we obtain improved estimates of Pitzer strain energies for **1** (4.0), **2a** (5.9), and **2b** (3.9 kcal/mol, Table IV), which are considerably lower than those normally used.[2,7,12]

(IV) CC and CH Bond Energies: The Energetic Consequences of Hybridization Effects on CH Bond Strengths

Coulson and Moffitt[5] were the first to show that the CH bonds of **1** possess considerably more s-character (as a consequence of the high p-character of the CC bonds) than those of a normal alkane. They described the CH bonds of **1** to be formed by sp^2-hybrid orbitals. This was later confirmed by more sophisticated methods,[22,23] which suggest a $C(sp^5)-C(sp^5)$, $C(sp^2)-H$ bonding situation in **1**. Experimental evidence for this description was provided by the geometrical data (see, e.g., Table I), by the $J(^{13}C,^{13}C)$ and $J(^{13}C,H)$ NMR coupling constants,[24] and by the vibrational frequencies of **1**.[25] In Ferguson's review of **1**,[2] a comparison of these properties with those of acyclic alkanes is presented. The conclusion is drawn that the C–H bond of **1** is stronger than that of other alkanes. This is consistent with thermochemical measurements leading to CH bond dissociation enthalpies DH of 106.3 kcal/mol for **1** and 95.1 kcal/mol for the secondary C–H bond in **3**.[26]

In view of these facts, it has repeatedly been suggested that CH bond strengthening in **1** should partially compensate the Baeyer strain of **1**.[27] However, differing suggestions as to the quantitative contribution of this effect to the stability of **1** have been made. For example, in a recent investigation on ring-opening barriers of cycloalkylmethyl radicals, the thermochemical CRSE of **1** was corrected with the difference in the DH(CH) values given above in order to rationalize the observed activation energies for ring fission.[28] If one would follow this line of argument, CH bond strengthening would contribute a total of 67 kcal/mol (!) to the thermodynamical stability of **1**.

However, the DH(CH) value of **1** is of no help in this connection since it reflects the increase in ring strain when converting **1** to a cyclopropyl radical: DH values depend on both the stability of the reactant *and* the stability of the fission products. Therefore, it is unlikely that DH(CH) values are parallel to the corresponding bond energies BE(CH) in the case of ring compounds.

A more conservative estimate on the energetic consequences of CH bond strengthening in **1** has been made by Roberts and Caserio in their textbook on Organic Chemistry.[29] In view of the similarity of the CH bond properties in **1** and in ethylene, they predict the CH bonds of **1** to be stronger by 3 kcal/mol than those of a secondary CH bond in **3**. Hence, the overall stabilization of **1** caused by hybridization effects should be 18 kcal/mol.

Again, a caveat with regard to this estimate is appropriate. For example, CH force constants and CH stretching frequencies reflect the curvature of the potential hypersurface at the global (or a local) minimum, which in turn depends partially on the existence of other local minima (corresponding, e.g., to dissociation products) in the vicinity of the one under investigation. Therefore, it is not surprising that experimental CH stretching frequencies correlate with DH(CH) values as was recently demonstrated by McKean.[30]

There is no unequivocal way of quantitatively deducing bond energies from spectroscopic data. In summary, the known CH bond properties of **1** provide only a qualitative but not a quantitative account of the energetic consequences of hybridization effects in **1**.

Theoretical Calculation of Bond Energies. In view of these difficulties we have approached the problem of determining the CH bond strengths in **1–3** from the theoretical side again utilizing the virial partitioning method.[19] As is described in the Appendix, two atoms can only be bonded if their subspaces Ω are adjacent to each other, i.e., Ω_A and Ω_B are separated by one and only one zero-flux surface $S(A,B)$, which can be determined by analyzing the gradient vector field of the electron density distribution $\rho(r)$. Integration of $\rho(r)$ over the interatomic surface $S(A,B)$ between two bonded atoms A and B yields the quantity $N(A,B)$[31]

$$N(A,B) = R(A,B) \oint_{AB} dS(r)\rho(r)n_A(r) \qquad (II)$$

($R(A,B)$, vector from the nucleus of A to the nucleus of B; n_A, unit vector normal to the surface, outwardly directed from A), which is a measure of the number of electrons involved in the formation of the bond between A and B as determined by the accompanying changes in the properties of the gradient vector field $\nabla\rho(r)$. Since N is related to the sum of atomic averages of the commutator $[\hat{H},r^2]$,[31] its dimension is that of an energy multiplied by the square of a length. Thus division of $N(A,B)$ by R^2 yields an energy quantity which can be used to assess the strength of the bond AB. We assume that the bond energy depends on the number of electrons in the bonding area *and* on the forces exerted on these electrons. For nonpolar or weakly polar bonds, the second factor can be covered by a proportionality constant α that depends on the ordial numbers and the electronic states of A and B. Accordingly, a theoretical bond energy BE-(A,B) can be defined as

$$BE(A,B) = \alpha(A,B)N(A,B)/R^2 \qquad (III)$$

Bader and co-workers[31] have shown that BE(A,B) values thus obtained are similar to averaged thermochemical bond energies. However, these authors chose to evaluate BE(A,B) at the STO-3G level of theory which is inappropriate for the problem under consideration. Also, the same α was used for CC and CH bonds which is too much of a simplification.[32] Therefore, we adopted a somewhat different procedure:

First atomization energies (AE) for CH_4 and C_2H_6 at 0 K for fixed nuclei were derived from experimental $\Delta H_f°(298)$ enthalpies and vibrational frequencies along the lines described in ref 20. From the AE of CH_4 its CH bond energy at 0 K was determined, which in turn was used to evaluate $\alpha(C,H)$ from eq III utilizing the HF/6-31G** values of R and $N(A,B)$ of CH_4 (Table V). Then, in the second step, the BE(C,H) value of C_2H_6 was calculated with $\alpha(C,H)$ and used to determine BE(C,C) from the experimental AE of C_2H_6. By inserting BE(C,C) in eq III, $\alpha(C,C)$ was derived, which together with $\alpha(C,H)$ yielded the CC and CH bond energies of **1–3** from HF/6-31G** values of $N(A,B)$ (Table V).

In addition to using two α values, we refrained from substituting calculated R_e values (Table I) for R in eq III. Strictly speaking, *the interatomic distance R_e is not necessarily identical with the bond length*, which becomes obvious when analyzing bent bonds in strained rings. It is easy to see that in this case the actual length of the bond is larger than the interatomic distance.[33] A quan-

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(26) (a) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532. (b) Baghal-Vayjooee, M. H.; Benson, S. W. *J. Am. Chem. Soc.* **1979**, *101*, 2838–2840. But see also: (c) Tsang, W. *J. Am. Chem. Soc.* **1985**, *107*, 2872–2880.

(27) This suggestion is already inherent in the 1949 work of Coulson and Moffitt.[5] These authors were the first to point out that the CH stretching force constants of **1** and ethylene should be of the same magnitude.

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(29) Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry*; Benjamin: New York, 1965; p 113.

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(31) (a) Bader, R. F. W.; Tang, T.; Tal, Y.; Biegler-König, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 946–952. (b) Bader, R. F. W. *J. Chem. Phys.* **1980**, *73*, 2871–2883. (c) Biegler-König, F. W.; Bader, R. F. W.; Tang, T. *J. Compt. Chem.* **1982**, *3*, 317–328.

(32) See, e.g.: Ehrhardt, C.; Ahlrichs, R. *Theor. Chim. Acta* **1985**, *68*, 231–245. These authors weight the overlap of AOs with the ionization potentials of A and B in order to obtain a BE.

(33) Coulson and Moffitt were the first to distinguish between bond length and interatomic distance.[5] Cremer and Kraka have shown that bent bonds in strained rings may be convex (curved outwardly) or concave (curved inwardly).[10]

Table V. HF/6-31G** Bond Energies (BE), Atomization Energies (AE(CAL)), and Strain Energies (SE) for Cyclopropane (1) and Cyclobutane (2)[a]

molecule	bond	R_b	$N(A,B)$	$BE(A,B)$[b]	$AE(CAL)$[c]	$AE(EXP)$[c]	ΔAE[c]	$SE(CC)$[d]	SE[d]
CH_4	C–H	1.083$_5$	1.970	104.8	419.2	419.2[e]	0	0	0
C_2H_6(4)	C–H	1.086	1.985	105.1	710.7	710.7[e]	0	0	0
	C–C	1.527	3.365	79.9					
1	C–H	1.076	1.976$_5$	106.6	852.7	851.3	1.4	34	28
	C–C	1.506	2.911	71.0					
2a	C–H	1.084	1.994	105.9	1140.0	1144.8	−4.8	31	28
	C–C	1.550	3.174	73.1					
2b	C–H$_{ax}$	1.085	1.996	105.9	1143.0	1146.1	−3.1	29	26
	C–H$_{eq}$	1.084	1.992	105.9					
	C–C	1.547	3.197	73.9					
3	sec-C–H[f]	1.088	1.999	105.5$_5$	1004.8	1004.2	0.6	0	0
	C–H$_i$	1.086	1.985$_5$	105.2					
	C–H$_o$	1.087	1.983	104.8$_5$					
	C–C[f]	1.528	3.456$_5$	81.9$_5$					

[a] Bond path length R_b in Å, $N(A,B)$ in hartree bohr^2 (see formula II), BE, AE, and SE in kcal/mol. For subscripts see Table I. [b] Calculated from $N(A,B)$ and R_b according to formula III with $\alpha(C,H)$ = 223.22 and $\alpha(C,C)$ = 169.12 as described in the text. [c] Atomization energies AE(CAL) are calculated from BE values and compared with experimental atomization energies AE(EXP) at 0 K for fixed nuclei.[20] The error of AE(CAL) is given by ΔAE. [d] Total strain energies SE and strain energies SE(CC) of carbon framework have been calculated using sec-CH(3) and CC(3) as reference bonds and correcting with ΔAE. [e] Used to determine $\alpha(C,H)$ and $\alpha(C,C)$. [f] Reference bonds.
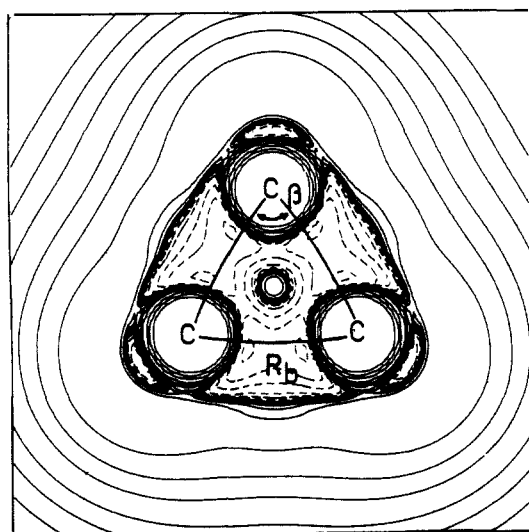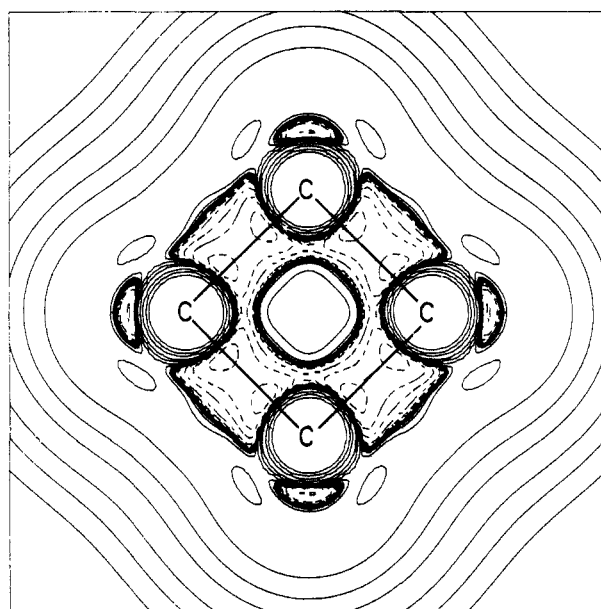
a   b

Figure 1. Contour line diagrams of the HF/6-31G** Laplace concentrations, $\nabla^2\rho(r)$, of cyclopropane (a) and cyclobutane (b). Bond paths (paths of maximum electron density) are indicated by heavy lines. R_b denotes the bond path length and β the interpath angle. Dashed lines are in regions where electronic charge is concentrated ($\nabla^2\rho(r) < 0$) and solid lines in regions where charge is depleted ($\nabla^2\rho(r) > 0$). Inner-shell regions with $\nabla^2\rho(r) < 0$ are not shown.

titative description of the bend of a CC bond in 1 and, hence, the CC bond length is achieved by analyzing $\rho(r)$.[31,34,35] It is an important observation that two bonded atoms are linked by a path of maximum electron density (MED).[36] The existence of a MED path has been considered as a necessary condition for chemical bonding.[34] The MED path, henceforth called bond path, is an image of the chemical bond. Therefore, we define *the bond length to be equal to the calculated bond path length R_b* (Figure 1). Accordingly, we substitute $R_b(A,B)$ (Table V) rather than R_e-(A,B)[37] in eq III, which leads to an improvement of calculated BE(A,B) values in strained systems. In this way, we obtain the bond energies summarized in Table V.

(34) Cremer, D.; Kraka, E. *Croat. Chem. Acta* **1984**, *57*, 1265–1287.
(35) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061–5068.
(36) Any lateral displacement from the MED path leads to a decrease in $\rho(r)$. See ref 19 and 35. See also Appendix.
(37) For acyclic systems or n-membered rings with $n \geq 5$, R_b is equal to R_e within calculational accuracy.

If all calculated BE(A,B) values of a molecule are added, theoretical atomization energies AE(CAL) result (Table V), which differ by 0.2 (1) 0.4 (2a), 0.3 (2b), and 0.1% (3) from experimental atomization energies AE(EXP) at 0 K. Since experimental atomization energies AE(EXP) at 0 K are considerably larger than AE(EXP) values at 298 K,[1a] theoretical BE(CH) values exceed those normally used in thermochemistry by ca. 5 kcal/mol. This would also hold for theoretical BE(CC) values if the reference energy would have been obtained by an averaging procedure.[1a] However, by using CH_4 and 4 as reference compounds and determining BE(CC) of 4 dependently of CH_4, CC BEs result which are ca. 2 kcal/mol smaller than averaged thermochemical values for 298 K.

Due to calculational uncertainties of the numerical integration method applied for getting N,[31c] calculated BEs are only accurate within ±0.5 kcal/mol, i.e., theoretical BE(CH) and BE(CC) values for CH_4, C_2H_6, and C_3H_8 are essentially the same. Although a discussion of individual BE values is not appropriate in view of these uncertainties, it is interesting to note that all BEs of 3 but

one are larger than the corresponding BEs of **4**. Investigation of experimental AE values reveals that *either CC or CH BE values have to be larger than those of **4** in order to reproduce the correct AE of **3**.* On the other side, ab initio CH and CC bond lengths of **3** are equal or longer than those of **4**. Obviously, the longer bond possesses the higher bond energy contrary to what is normally assumed.

It is a common believe in chemistry that the strength of bond AB depends on the overlap of the orbitals of atoms A and B. The overlap, in turn, decreases with increasing bond length. While this may be true in the majority of all bonding situations, it is hardly possible to verify the bond energy, bond length relationship when BE values differ by a few tenths of a kcal/mol. In these cases experimentally based BE schemes prefer to operate with just one averaged BE value and to "explain" deviations of predicted AEs from AE(EXP) by correction parameters needed to account for nonbonded interactions. However, in the theoretical approach used in this work, the calculated BE contains *all* effects influencing the bond strength. Therefore, the sum of BEs has to be equal to AE, no matter whether nonbonded interactions are important or not. In this situation, it cannot be excluded that a longer bond indeed possesses a larger BE as in the case of **3**.

Influence of Hybridization Effects on Strain Energies. A straightforward discussion of CC and CH BEs of **1** and **2** would require the HF/6-31G** reference values calculated for **6**. Since these calculations, although in principle possible, are too expensive, in particular with regard to the numerical integrations needed to obtain $N(A,B)$, we revert to **3** as a reference molecule and compare the bond energies of **1** and **2** (Table V) with BE(CC,3) and BE(*sec*-CH,3).

As can be seen from Table V, the calculated BE(CC) of **1** is 11 kcal/mol lower than that of the CC reference bond in **3**. Accordingly, the carbon ring is strained by 33 kcal/mol which increases to 34 kcal/mol if the error ΔAE in AE(CAL) is considered. On the other hand, a CH bond in **1** is stronger by 1 kcal/mol than a *sec*-CH bond in **3** (Table V).

If one assumes that the BE of the latter bond could be overestimated and the one of the former, however, underestimated by 0.5 kcal/mol (vide infra), than the two BE values would differ by 2 kcal/mol. Hence, the strain of **1** is reduced by 6 or maximally 12 kcal/mol due to CH bond strengthening.

The BE(CC) value of **2b** is 8 kcal/mol lower than BE(CC) of **3**, thus leading to a SE of 32 kcal/mol and a corrected SE of 29 kcal/mol (ΔAE = -3, Table V). As already predicted by Coulson and Moffitt,[5] the CH bonds of **2** are also slightly strengthened. We calculate 105.9 (**2b**) -105.5$_5$ (**3**) = 0.3$_5$ kcal/mol (Table V). This means that the energy contribution of the rehybridization effect in **2b** is 2.8 kcal/mol, almost 50% of that calculated for **1**. Similar values are calculated for planar **2a** (Table V).

(V) Dunitz–Schomaker Strain

Bauld and co-workers[7] have calculated nonbonding CC interaction energies at the semiempirical CNDO/2 level by dropping all Fock matrix elements representing 1,3 CC interactions and comparing the energy thus obtained with that of a normal calculation. In this way, 1,3 CC interaction energies of 33.5, 29.7, and 7.6 kcal/mol for **2a**, **2b**, and **3**, respectively, have been derived. If one assumes that these energies, although probably too large, provide at least a consistent description of repulsive 1,3 interactions in **2** and **3**, then the energetic contribution of Dunitz–Schomaker strain (ΔE(DS)) to the total TSE as defined by the homodesmotic reaction 2 will be vanishing small

$$\Delta E(DS,2) = 4 \times 7.6 - 29.7 = 0 \pm 1 \text{ kcal/mol} \quad (IV)$$

If one further assumes that 1,3 CC interactions in **5** (n = 5), **6** (n = 6), and larger n-membered cycloalkanes are similar to those in **3**, then the conclusion can be drawn that *DS strain does not perceptibly contribute to the TSE or CRSE of **2** and larger cyclic homologues.*

This conclusion, however, is not valid for **1** since **3** does but **1** does not suffer from repulsive 1,3 CC interactions. Hence, TSE(1) has to be corrected by three times the value of E(DS,3).

In other words, a comparison of TSE(1) and TSE(2) according to reaction 3 (= reaction 1 - reaction 2)

$$1 + 3 \rightarrow 2b + 4 \quad (3)$$

requires a correction term $\Delta E(DS) = E(DS,2b) - E(DS,3)$ that decreases $\Delta E_R(3)$ = TSE(2) - TSE(1) considerably. We conclude that *neither TSE(1) nor CRSE(1) are good values when comparing the ring strain in cycloalkanes.*

The correction ΔE(DS) are derived from the energies given in ref 7 (22 kcal/mol) is certainly too large.[38] For example, the barrier to ring inversion of **2** is overestimated by a factor of 3 by the difference $E(DS,2a) - E(DS,2b)$ = 3.8 kcal/mol.[7] Employing a scaling factor $f = \frac{1}{3}$, ΔE(DS) is predicted to be 7.3 kcal/mol. This means that the corrected TSE(1) might be close to 35 kcal/mol.

Even if one would agree with the simplified way of estimating ΔE(DS) presented above, the question of the correct TSE(1) to be compared with TSE(2) would not be solved since two additional problems arise from the discussion of DS strain: (a) What is the energetic influence of nonbonded 1,3 CH interactions on TSE(1) and TSE(2)? (b) Is $CH_2(6)$ (or $-CH_2-$) still a good reference state when comparing **1** and **2**?

The work of Bauld and co-workers[7] seems to suggest that 1,3 CH interactions can be neglected when discussing TSEs. The former are calculated to be repulsive by 3 kcal/mol and to be of the same magnitude in **3** and **4**.[7] Assuming similar values for **1** and **2**, it is easy to show that 1,3 CH interactions in reactions 1, 2, and 3 cancel each other out since there are 12 in **1**, 16 in **2**, 10 in **3**, and 6 in **4**.

As for the second question the answer is not as easy. The choice of $CH_2(6)$ as an appropriate reference is only valid for **2**, **5**, and larger cycloalkanes but not for **1**. For example, the energy required for CCC bending in either **6** or **3** is partially caused by 1,3 CC interactions, which is reflected by the magnitudes of the corresponding force constants k. If one suppresses repulsive 1,3 CC interactions, k will decrease to the value k^* appropriate for evaluating Baeyer strain in **1**. Unfortunately, there is no direct way of determining k^* for a hypothetical CH_2 group in a C-H_2-CH_2-CH_2 environment without repulsive 1,3 CC interactions. Therefore, we have to find an indirect way of evaluating k^* which will be discussed in the next section.

(VI) Baeyer Strain

As discussed in the introduction, the use of the geometrical angles α in conjunction with formula 1 leads to unreasonably high Baeyer SEs. In section IV we have already pointed out the chemical significance of the MED or bond paths linking the atoms of a molecule in space. Because of this significance we have set the bond length to be equal to the bond path length R_b. For the same reason, this definition can be extended in the following way: *The bond angle is equal to the angle between two bond paths, i.e., the interpath angle β.*[10] The use of β rather than α is chemically more meaningful, in particular when discussing Baeyer strain in small rings.

In Table VI, calculated HF/6-31G** interpath angles β of **1-3** are listed, together with the corresponding Baeyer SEs derived by inserting β, n, and the bending force constants of **3** in formula I. The CCC bending SEs of **1** and **2** are put into parentheses in Table VI since they have been determined with force constant $k(3)$, which is either too high due to the absence of 1,3 CC interactions (**1**) or too low due to an increase of the latter as a result of relatively small bond angles (**2**).

One could try to improve CCC bending SEs by simply adjusting k(CCC) for **1** and **2** in a way that leads to total Baeyer SEs, which, combined with the other energetic contributions to ring strain, yield CRSE (**1**) and CRSE (**2**). In this way, one would get four force constants k(CCC), the values of which would increase approximately in the order **1**, **3**, **2** as $1:\sqrt{3}:3$ whereby k(2a) and

(38) For example, molecular mechanics calculations predict nonbonded strain to be just 4 kcal/mol in the case of **2**.[12] Unfortunately, a reevaluation of E(DS) at the ab initio level by simply dropping relevant F- and S-matrix elements is not possible for principal reasons.

Table VI. Baeyer Strain of Cyclopropane (**1**), Cyclobutane (**2**), and Propane (**3**)[a]

molecule	angle	BS(α)[b]	β	BS(β)[c]
1	CCC	172.6	78.8	(66.4)
	CCH	12.8	113.8	3.2
	HCH	0.8	117.0	2.0
2a	CCC	35.7	96.5	(15.9)
	CCH	6.0	112.5	2.1
	HCH	0.2	109.7	0
2b	CCC	41.0	95.6	(18.1)
	CCH$_{ax}$	7.7	114.6	3.0
	CCH$_{eq}$	0.6	110.6	0.1$_5$
	HCH	0.1	110.0	0
3	CCC	0.3	112.9	0.3
	CCH$_i$	0.1	106.3	0.1
	CCH$_i$	0.1	111.3	0.1
	CCH$_o$	0.1$_5$	111.1	0.1$_5$
	H$_i$CH$_i$	0	109.4	0
	H$_i$CH$_o$	0.1$_5$	107.8	0.1$_5$
	H$_o$CH$_o$	0.1	107.6	0.1

[a] Baeyer strain (BS) in kcal/mol and interpath angles β in deg. For angle notations see Table I. Experimental bending force constants k-(CCC) = 1.071, k(CCH) = 0.656, and k(HCH) = 0.550 (mdyn·Å)/rad^2 from **3**[4] have been used. [b] BS(α) values calculated from geometrical angles α are included for reasons of comparison. [c] BS(β) values in parentheses indicate wrong force constant.

k(**2b**) would have to differ by 10% in order to reproduce the inversion barrier of **2**.

Clearly, this is not a satisfactory solution since it "explains" the anomaly of the SEs of **1** and **2** by an unreasonably large spread in CCC bending force constants caused by a variation in 1,3 CC interactions. Peculiarities of experimentally determined properties of **1**[9] as well as the theoretical indications for surface delocalization of electrons remain unexplained.[10]

Therefore, it seems to be more rewarding to reconsider the question of the CH$_2$ reference group and to determine a force constant k^*(CCC) (section V) which applies when 1,3 CC interactions are suppressed in the reference molecule.
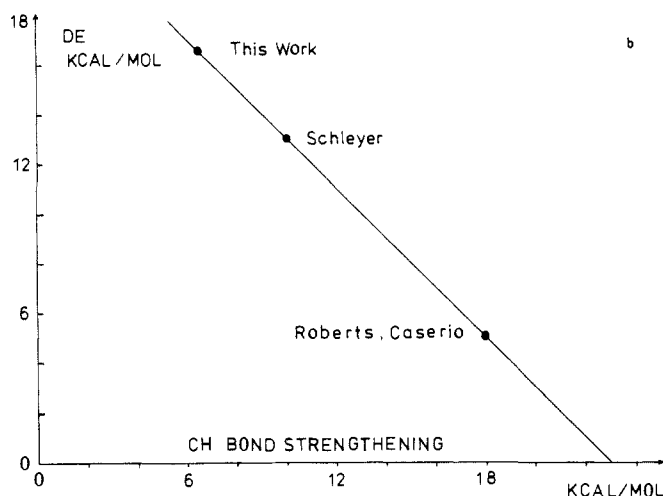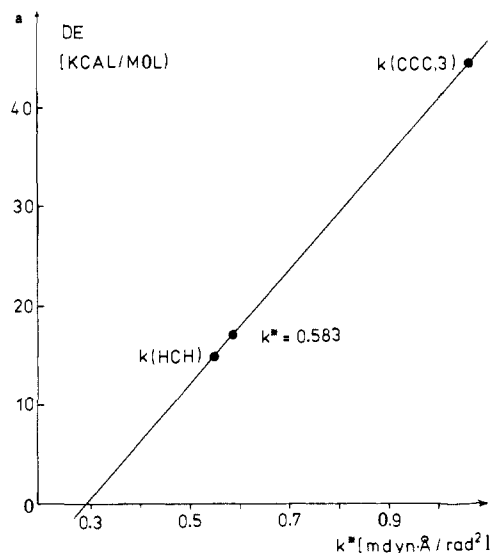
Determination of the CCC Bending Force Constant k^*. In a first estimate, k^* may be simply set equal to k(HCH) = 0.550 (mdyn·Å)/rad^2, i.e., about one-half of the value of k(CCC).[4] This estimate, henceforth called alternative I, leads to CCC bending SEs of 34.1 (**1**) and 9.3 kcal/mol (**2**), applicable in the absence of DS strain. Accordingly, the total Baeyer strain BS* of **2** (12.4 kcal/mol) has to be added to the DS strain to obtain CRSE(**2**). With f = 0.33 (section V) the latter comes out too small by ca. 3 kcal/mol which can be corrected by adjusting f to 0.42 (see Table IX).

Clearly, the values of k^* and f couple: the larger is the energetic contribution of DS strain to the total SE of **2** or **3**, i.e., the larger the scaling factor f defined in the preceding section, the smaller is the force constant k^*. The relation between k^* and f can be expressed analytically by setting up two equations which contain k^* and f as unknowns. Solution of these equations leads to improved estimates of k^* and f (alternative II).

Figure 2. Dependence of the σ-delocalization energy DE on (a) the value of the CCC bending force constant k^* and (b) CH bond strengthening (hybridization effect) in **1**.

In Table VII, the two equations (a and e), on which alternative II is based, are shown. They express the SEs of **2a** and **2b** (or equivalently the inversion barrier SE(**2a**)–SE(**2b**)) as the sum of the energetic contributions arising from PS, BS*, HE, and DS (for explanation of the abbreviations see Table VII). In addition, corrections SS for CC bond stretching in **2**, employing **4** as a suitable reference molecule (Table VIII), are included. With the experimental inversion barrier of **2** (1.3 kcal/mol[18]), the SE of **2b** (27.3 kcal/mol, section II), the relevant PS (Table IV), HE (Table V), BS (Table VI, HCH and CCH bending), and SS contributions (Table VIII) as well as the bond angles β(CCC) (Table VI) and the DS energies of ref 7, eq a and e of Table VII

Table VII. Determination of the Bending Force Constant k^*(CCC) and the Scaling Factor f for 1,3 CC Interaction Energies[a]

	equation	comment[b]
a	SE(**2a**) = PS + BS' + X_1 + SS + HE + Y_2	SE(**2a**) = 27.3 + 1.3 = 28.6, PS = 5.9, BS' = 2.1,
b	X_1 = $^1/_2 nk^*[109.5 - \beta(CCC,\mathbf{2a})]^2$ = 14.820k^*	SS = 1.2, HE = -2.8, X_1, Y_1 substituted in (a) leads
c	Y_1 = 33.5f	to (d)
d	22.2 = 14.820k^* + 33.5f	
e	SE(**2a**) - SE(**2b**) = ΔPS + ΔBS' + ΔX_2 + ΔSS + ΔHE + ΔY_2	SE(**2a**) - SE(**2b**) = 1.3, ΔPS = 2.0, ΔBS' = -1.1,
f	ΔX_2 = $^1/_2 nk^*[(109.5 - \beta(CCC,\mathbf{2a}))^2 - (109.5 - \beta(CCC,\mathbf{2b}))^2]$	ΔSS = 0.1, ΔHE = 0, ΔX_2, ΔY_2 substituted in (e)
g	ΔY_2 = (33.5 - 29.7)f = 3.8f	leads to (h)
h	0.3 = -2.123k^* + 3.8f	
i	k^*(CCC) = 0.583 (mdyn·Å)/rad^2; f = 0.405	Alternative II (from d and h)

[a] All energies in kcal/mol, interpath angles β in deg, force constant k^* in (mdyn·Å)/rad^2. The following symbols are used: PS, Pitzer strain; BS', Baeyer strain from CCH and HCH angle deformations; X, Baeyer strain from CCC angle deformations in the absence of 1,3 CC interactions (DS); BS* = BS' + X, total Baeyer strain for a molecule *without* DS; SS, bond stretching strain; HE, CH bond strengthening due to hybridization effects; DS = Y, Dunitz–Schomaker strain due to 1,3 CC interactions. [b] Values from Tables III–VI and VIII.

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Table VIII. Bond-Stretching Strain of Cyclopropane (1) and Cyclobutane (2)[a]

molecule	bond	R_b	SS
1	C–C	1.5064	0.4
	C–H	1.0761	0.1
2a	C–C	1.5503	1.2
2b	C–C	1.5468	1.0_5

[a] Bond lengths R_b in Å, bond-stretching strain (SS) in kcal/mol. Ethane has been used as a reference: $R_b(CC) = 1.5268$, $R_b(CH) = 1.0858$ Å (HF/6-31G**); $k(CC) = 4.57$, $k(CH) = 4.88$ mdyn/Å (exptl values[4]).

Table IX. Determination of the Stabilization of Cyclopropane (1) due to σ-Delocalization. SE(1) and SE(2) Are Compared with the Aid of Reaction 3[a]

SE[b] contributions	reaction 1	+	3 →	2b	+ 4	TSE(2) –TSE(1) = $\Delta E_R(3)$ = –0.7
Alternative I (k^* = 0.550, f = 0.419)						
PS	4.0	0	3.9	0		
BS*	39.3	0.9	12.4	0		
SS	0.5	0	1.0	0		
HE	–6.4	1.1	–2.8	0		
DS	0	3.2	12.5	0		
DE	Z	0	0	0		
SE	37.4 + Z	5.2	27.0	0		$\Delta E_R(3)$ = –15.6 – Z DE = –14.9
Alternative II (k^* = 0.583, f = 0.405)						
PS	4.0	0	3.9	0		
BS*	41.3	0.9	13.0	0		
SS	0.5	0	1.0	0		
HE	–6.4	1.1	–2.8	0		
DS	0	3.1	12.0	0		
DE	Z	0	0	0		
SE	39.4 + Z	5.1	27.1	0		$\Delta E_R(3)$ = –17.4 – Z DE = –16.7

[a] All energy values in kcal/mol. [b] For symbols see Table VII. DE is the σ-delocalization energy. Energy contributions have been taken from Tables IV–VIII.

Table X. Reliability of the Calculated σ-Delocalization Energy of Cyclopropane

no.	possible source of error	consequence
1	inversion barrier of 2 is too high (see Table I)	DE is too low
2	SE of 2b is too low (see Table III)	DE is too low
3	H,H van der Waals attractions contribute to the stability of 2b	DE is too low
4	PS of 2b is overestimated since τ (Table IV) is too small	DE is too low
5	HE effects are underestimated in 2b (s character of CH hybrid orbitals increases with puckering)	DE is too low
6	k^* is too small for 1 because of anharmonicity effects	DE is too low
7	CCC reference angle is too small	DE is too low
8	BS of 2b is underestimated since puckering is underestimated (β decreases with increasing q)	DE is too high
9	DS of 2a is too high compared to DS(2b)	DE is too high
10	2 is destabilized by σ-antiaromaticity	DE is too high
11	calculated BE values underestimate CH bond strengthening in 1	DE is too high

It is appealing to attribute these peculiarities of 1 to a specific electronic effect, namely to a delocalization of its σ-electrons as suggested by Dewar[9] and Cremer and Kraka.[10]

In Figure 1, contour line diagrams of the HF/6-31G** Laplace concentrations $\nabla^2\rho(r)$[40] of 1 and 2 with regard to the plane of the C nuclei are shown. Concentrations of electrons ($\nabla^2\rho(r) < 0$, dashed contour lines) are found in the CC bonding regions of both molecules. For 2 the interior of the four-membered ring is largely depleted of electronic charge while for 1 concentration of electronic charge is also found inside the ring. As a consequence, $\rho(r)$ at the center of the three-membered ring is of about the same magnitude as at the CC bond critical points[10,36] while it is only one-third of this value at the center of 2. These observations have led Cremer and Kraka to speak of σ-delocalization in the case of 1.[10]

The analysis of $\rho(r)$ alone does not provide an answer to the question of whether σ-delocalization in 1 leads to significant energetic consequences. The latter can only be assessed by comparison with the energies of appropriate reference compounds as has been done in the preceding sections. The résumé of this analysis is summarized in Table IX.

If we compare the TSE of 1 with that of 2 with the aid of reaction 3, which is simply the difference of the homodesmotic reactions 1 and 2, then the reaction energy $\Delta E_R(3) = TSE(2) - TSE(1) = -0.7$ kcal/mol (HF/6-31G**, Table IX) can be considered to comprise the corresponding differences of PS, BS*, SS, HE, and DS contributions to the SEs of 1, 2, and 3.[41] These are listed in Table IX both for a crude estimate of k^* (alternative I) and a direct calculation of k^* and f (alternative II). In both cases, the various energy contributions add to an $\Delta E_R(3)$ which is lower than the ab initio value by 15–17 kcal/mol. We consider this discrepancy to arise from surface delocalization of the σ-electrons of 1 and, therefore, call it the σ-delocalization energy DE of 1.

In view of the discussion presented in Section VI, it is mandatory to assess the error margins of the calculated DE. From Table

can be solved. The values of k^* and f thus obtained (Table VII) are close to the estimates of alternative I. They lead to BS* values of 41.3 (1) and 13.0 kcal/mol (2) (see also Table IX).

Although the results of alternatives I and II seem to suggest that a useful way of determining Baeyer and DS strain in 1 and 2 has been found, one has to stress that the whole analysis presented is based on a model that naturally involves a number of assumptions, e.g., that no other effects influence the SEs of 2 and that the energy contributions evaluated are truly additive. Although such a model approach is common practice in discussions of SEs,[1,2] it may become problematic when using it in a quantitative rather than qualitative or semiquantitative fashion.

Another problem stems from the fact that relatively large energy terms are evaluated with the aid of two SEs, which differ by somewhat more than 1 kcal/mol. One could avoid this problem by analyzing the SEs of 5 and 6 (Table III) in the same way as those of 1 and 2. For this purpose, however, one would have to know the energetic contributions of 1,3 CC interactions and, possibly, those of other nonbonded interactions exactly to carry out a quantitative analysis.

In view of the lack of appropriate data, the analysis presented in this work can only be carried out for 1 and 2, i.e., the known SE of 2 and its inversion barrier have to be used to get k^* and f. This, of course, entails rather large uncertainties in the final BS* and DS values of 1, which makes it essential to establish the error margins of k^* and f, respectively (see section VII).

(VII) Energetic Consequences of Surface Delocalization

A number of unusual molecular properties have been observed for 1, e.g., its SE (as discussed), its exceptionally short CC bond lengths (see Tables I and V), its rather high CC dissociation enthalpy, or the unexpected upfield shift of its NMR signals.[39]

(39) For a detailed discussion see ref 9. See also ref 11.

(40) The Laplace field indicates where electron density concentrates ($\nabla^2\rho(r) < 0$) or is depleted ($\nabla^2\rho(r) > 0$). This becomes obvious when considering the definition of second derivatives. (a) Bader, R. F. W.; Essén, H. *J. Chem. Phys.* **1984**, *80*, 1943–1960. (b) Bader, R. F. W.; McDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc.* **1984**, *106*, 1594–1605. (c) Cremer, D.; Kraka, E., *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 627–628.

(41) Note that 3 is slightly strained if DS strain is explicitly taken into account (Table IX).

(42) See, e.g., ref 5 and the following: (a) Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179–190. (b) Hoffmann, R. *Tetrahedron Lett.* **1970**, *2907–2909*. (c) Günther, H. *Tetrahedron Lett.* **1970**, 5173–5176. (d) Hoffmann, R.; Davidson, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 5699–5704. (e) Honegger, E.; Heilbronner, E.; Schmelzer, A. *Nouv. J. Chim.* **1982**, *6*, 519–526. (f) Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic: New York, 1973.

IX it becomes obvious that a relatively small change in k^* leads to a change of 2 kcal/mol in DE. The dependence of DE on the value of k^* is shown in Figure 2a. If k^* is set equal to $k(3)$ then a DE of ca. 50 kcal/mol will result.[9,10] If, on the other hand, k^* is chosen to be equal or lower than 0.28 (mdyn·Å)/rad^2, a zero or a negative DE value will be obtained. Since k^* cannot be determined directly, it is essential to outline those factors which may alter the magnitude of k^* (alternative II, Table IX). To shorten the discussion, relevant sources of errors in the calculation of k^* and, hence, DE are listed in Table X. Of these all but 8–11 (for numbering see Table X) would lead to a *higher* DE if indeed appropriate corrections would become necessary. Therefore, we can concentrate on those factors that would lead to a decrease of DE.

As noted above, the calculated puckering amplitude q of **2b** is still somewhat too small compared to experimental results. If we increase q to the experimental value,[17,18] then the CCC angle β decreases slightly leading to a somewhat higher BS value for **2b**. At the same time, PS of **2b** decreases slightly (No. 4, Table X). As a consequence, the overall effect becomes negligible, leading to a change in DE of less than 0.5 kcal/mol. As for points 9 and 10 of Table X, it is difficult to make any quantitative predictions. We just note that the results of Bauld and co-workers[7] give no indication of an inconsistent evaluation of DS strain in **2a** and **2b**. Also, there are no experimental observations that support a description of **2** as being a σ-antiaromatic compound.[9]

One might also argue that CH bond strengthening in **1** is underestimated by the BEs presented in Table V (point 11, Table X). In Figure 2b it is shown how the DE of **1** changes dependently with CH bond strengthening. Assuming values given by Schleyer (10 kcal/mol, ref 12) or Roberts and Caserio (18 kcal/mol, ref 29), DE values of 13 and 5 kcal/mol, respectively, result (Figure 2b). A DE $\leq$ 0 kcal/mol would result if the total effect of CH bond strengthening would be $\geq$23 kcal/mol. However, this is unlikely in view of the similarity of the bonds in $CH_2(3)$ and $CH_2(1)$ (Table V).

More likely as sources of error are the neglect of van der Waals attractions in **2b** and the neglect of anharmonicity effects when going from **2** (β = 96°) to **1** (β = 79°). If, in addition, a CCC reference angle of 112° rather than 109.5° is chosen as has been suggested by Schleyer and co-workers,[2e] then BS* of **1** will increase considerably entailing a DE higher by 6 kcal/mol. We conclude that any correction taking 3, 6, and 7 into account will lead to a significant increase of DE. Therefore, *the calculated DE value of 17 kcal/mol should be considered as a lower bound to the correct value.*

(VIII) Chemical Relevance of σ-Electron Delocalization: σ-Aromaticity

In Figure 3, the CC bonding MOs of **1** and **2** are schematically shown. Since MOs of both molecules have been discussed many times before,[42] we confine ourselves to pointing out just some essential features of the MOs of **1** and **2**:

(1) If one considers **1, 2, 5, 6**, etc., to be made up of CH_2 fragments each possessing two singly occupied orbitals, then two sets of MOs can be distinguished: first, the r set, which consists of linear combinations of radially (toward the ring center) oriented sp^2 hybrid orbitals, and, second, the t set, which consists of linear combinations of (with regard to the ring perimeter) tangentially oriented p orbitals.

(2) The r orbitals always form a Hückel system while the t orbitals lead to a Möbius system for **1, 5**, etc. (n odd), and a Hückel system for **2, 6**, etc. (n even).

(3) Mixing of r and t orbitals possessing the same symmetry yields the final MOs. Electrons are transferred from the r (t) to the t (r) set. A closed-shell system is formed with Hückel ($4q$ + 2) and Möbius ($4q$) "aromatic" subshells (Figure 3).

(4) There is always a totally symmetric doubly occupied low lying r MO (a_1' and a_{1g} in Figure 3) that stems from the in-phase overlap of all sp^2 orbitals inside the ring. The nature of this orbital changes dramatically with the size of the ring (Figure 4): For **1**, it is a "surface" orbital covering the ring surface due to strong
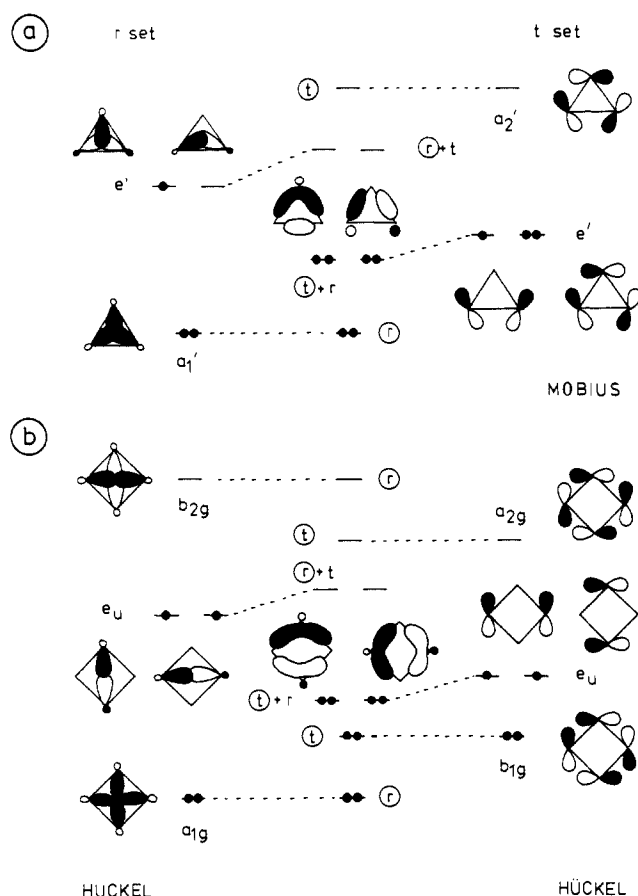

Figure 3. MOs of (a) **1** and (b) **2**. The predominant nature of the final MOs, r to t, is indicated by $\bigcirc$ and $\bigcirc$, respectively.
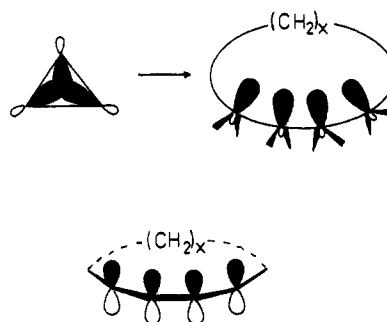

Figure 4. Equivalence of the r MOs in a large n-membered ring and the $p\pi$-MOs of a cyclopolyene.

overlap of the three sp^2 orbitals in the ring center. This overlap decreases exponentially with the size of the ring, thereby changing the surface orbital to a "ribbon" orbital which allows electron delocalization along the ring framework similar as in the case of a π orbital in cyclopolyenes (Figure 4). We note that for ethylene ("cycloethane") and **1**, the r and t orbitals should be classified as σ and π orbitals while for a large n-membered ring (with $n \geq$ 5) the r orbitals are topologically equivalent with π orbitals and the t orbitals with σ orbitals. This classification collapses in the case of **2** since both r and t orbitals enclose angles of 45° with CC connection lines.

(5) The mixing of r and t MOs, apart from improving 1,2 bonding interactions in the ring, causes across ring antibonding interactions. Again, these decrease rapidly with the size of the ring. They are strongest for **2**, leading to relatively large DS strain (1,3 CC repulsion).

On the basis of 1–5 some interesting conclusions with regard to CC bonding in cycloalkanes can be drawn.

(6) Since all cycloalkanes possess "aromatic" subshells of electrons, their ring bonds are all equivalent. However, it would

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be both trivial and misleading to term an n-membered ring with $n > 4$ "σ-aromatic" since (a) the r orbitals are always occupied by $4q + 2$ electrons and (b) are topologically equivalent with π rather than σ-orbitals (see point 4).

(7) Due to its topology, **1** differs from all other cycloalkanes. *Occupation of its surface orbital leads to a 2-electron 3-center bond* similar to that in H_3^+ or B_2H_6 and other boranes. As a consequence, CC bonding in **1** is much stronger as one would expect in view of the poor overlap of its t orbitals (π orbitals). In **2**, however, the totally symmetric r orbital is already more a ribbon than a surface orbital in nature since sp^2–sp^2 overlap is much smaller. This description is confirmed by the calculated Laplace concentrations of **1** and **2** (Figure 1) and the fact that inside the ring of **1** there is a relatively large plateau of electron density.

(8) In view of the fact that the σ-orbital set of **1** (i.e., the r set, see point 4) is occupied by $4q + 2$ ($q = 0$) completely delocalized electrons, it is justified to term **1** as being σ-aromatic and to distinguish it from all other cycloalkanes.[43]

(9) σ-Aromaticity will be bound to systems with appropriate surface orbitals which in turn depend on the topology of the molecule and the magnitude of the overlap.

Further conclusions can be drawn from 1–9.

(10) A substituent with σ-electron acceptor capacity withdraws electrons from the surface orbital of **1**, thus decreasing σ-aromaticity and destabilizing **1**. In the case of **2**, electrons are withdrawn from the 1,3-antibonding orbitals. Accordingly, DS strain is decreased and the overall stability of **2** increased. (b) Substituents with σ-donor capacity should cause the opposite effects.

(11) When replacing the C atoms of **1** by Si, Ge, etc., threefold overlap inside the ring is reduced by (a) an increase of the ring dimensions and (b) a decreasing tendency of these atoms to form sp^2 hybrid orbitals. In addition, H has to be considered as a relatively strong σ-electron acceptor in these cases. Accordingly, σ-delocalization is less developed in trisilacyclopropane, etc. We predict that the Si, Ge, etc. analogues of **1** exhibit larger SEs than **1**. For the same reasons, 1,3 interactions (DS strain) should be lower in the Si, Ge, etc., analogues of **2**. Therefore, tetrasilacyclobutane, etc., should be less strained than **2**.

(12) The SE in bicyclic and tricyclic compounds which contain **1** and **2** as subunits cannot be expected to be the sum of the SEs of its subunits.[2] Electronic interactions between the subunits will either enlarge or reduce the SE arising from the subunits.

(13) In a cage compound formed by three-membered ring subunits, σ-electrons may be delocalized inside the cage, forming a cloud of negative charge which attracts the nuclei of the cage atoms thus improving bonding. Such a situation may be described by the term "volume" delocalization of electrons.

Prediction 10 is in line with known substituent effects on **1**[44-46] and **2**.[47] For example, it has been shown that 1,1-difluoro-**1** is 12[46b] and hexafluoro-**1** 26 kcal/mol[46c] more strained than **1** as a result of the strong σ-acceptor capacity of fluorine. On the other hand, octafluoro-**2** is less strained than **2** by 9–12.5 kcal/mol.[46b] Prediction 11 is in line with theoretical calculations carried out by Schleyer[12] and by Sax,[48] who predict the SEs of trisila-**1** and tetrasila-**2** to be 38 and 18 kcal/mol, respectively.

Prediction 12 is easily confirmed by considering the SE of bicyclo[1.1.0]butane (66 kcal/mol[2]), which is higher by 10 kcal/mol than twice the SE of **1** (56 kcal/mol). This increase in SE results from the fact that σ-aromaticity of the subunits is partially offset by an increase in BS and DS strain between the subunits. Prediction 13 has been checked so far only for tetrahedrane.[49] Calculation of β(CCC) suggests that BS of this cage compound should be considerably larger than four times the BS of **1**. However, the theoretical SE of 127 kcal/mol[23] is just 15 kcal/mol above the sum of the SEs of its subunits. Work is in progress to test whether σ-delocalization is of relevance in cage compounds like tetrahedrane.[49] In this connection, it is interesting to note that σ-donor (acceptor) substituents have a similar influence on tetrahedrane as on **1**. The former decrease the SE of tetrahedrane and the latter decrease it.[47]

(IX) Conclusions

In this work we have presented a way (a) of calculating theoretical strain energies (SE) of cycloalkanes; (b) of evaluating Pitzer strain (PS) of cyclopropane (**1**) and cyclobutane (**2**); (c) of getting reasonable ab initio bond energies of **1**, **2**, and propane (**3**); (d) of determining the length R_b of a bent bond and the angle β between two bent bonds; (e) of defining a CCC bending force constant k^* appropriate for the calculation of Baeyer strain (BS) in the absence of repulsive 1,3 CC interactions (Dunitz–Schomaker (DS) strain); (f) of estimating DS strain in **2** and **3**; and (g) of comparing the SEs of **1** and **2**.

Our results lead to the following conclusions:

(1) The SEs of **1** and **2** cannot directly be compared since **1** is the only cycloalkane that does not suffer from DS strain. By correcting the SE of **1** for DS strain present in **2** and all other cycloalkanes, a value of 37 rather than 28 kcal/mol results.

(2) The PS of **1** and **2** is of the same magnitude and much lower than has previously been assumed (4 kcal/mol).

(3) The calculated CH bond energies of **1** and **2** reveal a stabilization of the ring molecules by 6 (maximally 12) and 3 kcal/mol, respectively, due to increased s character in the CH bonds. Hence, hybridization effects are far less important for an exact evaluation of SE(1) than one would expect on the basis of observed NMR coupling constants, CH stretching frequencies, CH force constants, or CH dissociation enthalpies. *It is difficult to make an assessment of the magnitude of bond energies from the latter quantities.*

(4) The calculated bond angles β (CCC) of **1** (79°) and **2** (96°) differ by just 17° rather than the 30° derived from geometrical data.

(5) The Baeyer strain of **1** is with 41 kcal/mol 28 kcal/mol larger than that of **2**. These values have been evaluated with a CCC bending force constant $k^* = 0.583$ mdyn·Å/rad² suitable for **1**, **2**, and **3** (and other (cyclo)alkanes) in the absence of DS strain (1,3 CC repulsion).

(6) **1** *is stabilized by a 2-electron-3-center bond*[50] which leads to significant changes in both the electron distribution and the stability of **1**. σ-Electrons are delocalized in the surface of the ring (surface delocalization). We estimate the delocalization energy (DE) of **1** to be equal or higher than 17 kcal/mol. In our view, it is appropriate to consider **1** as being σ-aromatic.[9,10] An estimate of DE with k(CCC) of 3 leads to 50 kcal/mol. However, this value is at best an upper bound of DE.

(7) σ-Aromaticity is responsible for the properties of **1**, in particular its unusually short CC distances.

(8) σ-Aromaticity of **1** is enhanced by σ-donor substituents but decreased by σ-acceptor substituents. As a consequence, the former stabilize, the latter destabilize **1**. Opposite effects are predicted for **2**: σ-acceptors reduce, σ-donors enhance DS strain, and, thereby, total strain in **2**.

(9) Sila and germa analogues of **1** are predicted to be more strained, those of **2** less strained due to a decrease of (stabilizing)

(43) If one also considers that the π-set constitutes a Möbius system occupied by 4 electrons, one comes to the same electron count as Dewar[9] does. However, we feel that this might be somewhat misleading since all cycloalkanes possess "aromatic" electron ensembles in their subshells.

(44) See, e.g., Table VII in ref 10b. One has to note that the description of substituent effects based on MOs differs somewhat from that based on electron density patterns. The latter show that it is, e.g., a simplification to expect σ-donor (acceptor) substituents to influence just the σ-aromatic character of **1**. Of course, they influence also the Baeyer strain of **1**.

(45) Clark, T.; Spitznagel, G. W.; Klose, R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 4412-4419.

(46) (a) Greenberg, A.; Liebman, J. F.; Dolbier, W. R., Jr.; Medinger, K. S.; Skancke, A. *Tetrahedron* **1983**, *39*, 1533-1538. (b) Liebman, J. F.; Dolbier, W. R., Jr.; Greenberg, A. *J. Phys. Chem.* **1986**, *90*, 394-397.

(47) Dill, J. D.; Greenberg, A.; Liebman, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 6814-6826.

(48) Sax, A. *Chem. Phys. Lett.* **1986**, *127*, 163-168.

(49) Gauss, J.; Cremer, D., to be published.

(50) It is interesting to note that Ahrichs and Ehrhardt (Ahlrichs, R.; Ehrhardt, C. *Chem. Z.* **1985**, *19*, 120-124) calculate a CCC shared electron number of 0.3 for **1** indicative of three-center bonding.

σ-aromaticity in the former and a decrease of (destabilizing) DS strain in the latter case.

(10) We predict "volume-delocalization" of σ-electrons in the case of cage compounds like tetrahedrane. Investigation of the energetic implications of this effect is in progress.[49]

Appendix

Bader and co-workers[19] have shown that molecular space can be divided into a collection of quantum-mechanically well-defined subspaces Ω with the aid of the topological properties of the total one-electron density distribution $\rho(\mathbf{r})$ of a molecule. These properties are made evident by those of the gradient vector field $\nabla\rho(\mathbf{r})$. The vector $\nabla\rho(\mathbf{r})$ always points into the direction of maximum increase in $\rho(\mathbf{r})$. The paths traversed by the vectors $\nabla\rho(\mathbf{r})$, the gradient paths, originate and terminate at critical points $\rho(\mathbf{r}_c)$ where $\nabla\rho(\mathbf{r}) = 0$. A critical point in the internuclear region of two bonded atoms A and B corresponds to a minimum of the path of maximum electron density (MED) linking A and B; at the same time it corresponds also to a maximum in all directions perpendicular to the MED path. The MED path is defined by exactly two gradient paths springing from $\mathbf{r}_c$ and ending at A and B. It has been termed "bond path" and the associated critical point $\mathbf{r}_c$ "bond critical point".[19]

All gradient paths terminating at the bond critical point between A and B form the zero-flux surface $S(A,B)$, through which the flux of $\nabla\rho(\mathbf{r})$ is everywhere zero:

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) = 0;\ \forall\mathbf{r} \in S(\mathbf{r})$$

$n(r)$ is the vector normal to $S(r)$.[19]

The surfaces S partition the space of the molecule in a unique way to yield subspaces Ω. As has been shown by Bader it is reasonable to assign a subspace Ω to the atom, the nucleus of which is embedded in Ω, and to consider Ω as the basin of the atom.[19] In this way, an atom in a molecule is defined.

With the definition of Ω(A) it is straightforward to calculate atomic expectation values $F_\Omega = \langle\hat{F}\rangle_\Omega$ where $\hat{F}$ is an appropriate operator. By summing values F_Ω over all atomic basins Ω(A) of a molecule, the molecular expectation value $F = \langle\hat{F}\rangle$ is obtained. For example, the sum of all atomic charges and energies obtained by the virial partitioning method is equal to the molecular charge and the molecular energy, respectively.

Temperature Dependence of Proton Recombination and Proton-Induced Quenching for 2-Naphtholate

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Abstract: Lifetime and quantum yield measurements in aqueous solutions have been performed on the anion (RO*⁻) of electronically excited 2-naphthol (ROH*). Measurements were made at moderately low pH in order to determine the temperature dependence of the rate of proton recombination, k_{rec}, with this anion. As predicted by recently proposed absolute rate expressions for weak acid dissociation/recombination, k_{rec}^{-1} has the same temperature dependence and magnitude as the Debye (transverse) rotational relaxation time of the pure water solvent. It is also likely that the rate for the proton-quenching reaction, H⁺ + RO*⁻ → ROH (ground state), has the same temperature dependence as k_{rec}. These types of experiments are of great importance toward the fundamental understanding of ion-hydration reactions, since up to now purely theoretical considerations have indicated that it is the much shorter longitudinal relaxation time that sets the time scale for ion solvation in water.

Beginning with the classic work of Förster and Weller,[1-3] proton dissociation (dis) and recombination (rec) of the photon-initiated, moderately weak acid 2-naphthol ($pK_a^* \approx 2.7$) in aqueous solutions have been extensively studied.[4,5] Temperature-dependent measurements of the rate k_{dis} give an activation energy of ~2.6 kcal mol⁻¹.[6-9] However, no information about the temperature dependence of k_{rec} is known.

A hydration model has been proposed[8] that correlates k_{dis} and k_{rec} for weak acids ($\Delta G_i^\circ \gtrsim 0$) with thermodynamic ionization enthalpies (ΔH_i°) and entropies (ΔS_i°). Absolute rate expressions were derived that give a good representation of the rate and equilibrium constant data for ground-state and photon-initiated univalent weak acids. If $\Delta H_i^\circ \geq 0$, both the enthalpy and entropy create barriers for the dissociation reaction, and $\Delta G^\ddagger_{dis} = \Delta G_i^\circ$. In contrast, no barriers stand in the way of the recombination reaction, and $\Delta G^\ddagger_{rec} = 0$ (see ref 8, section 12, case II). The rate expressions reduce to

$$k_{dis}\ (\text{s}^{-1}) = \tau_D^{-1}\Omega e^{+\Delta S_i^\circ/R}e^{-\Delta H_i^\circ/RT} \qquad (1)$$

$$k_{rec}\ (\text{M}^{-1}\ \text{s}^{-1}) = \tau_D^{-1}\Omega \qquad (2)$$

where reactants are at 1 M and where Ω is a steric/mobility factor introduced by Eigen and Kustin[10] and is equal to 0.45 ± 0.05 for protons from a fairly large precursor molecule such as 2-naphthol.[7,8]

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