$$\ln\left(1+\frac{k_{rc}}{k_{rt}}+\frac{k_{N_2}}{k_i}\right)$$

which they assumed to be small. Alternatively, it follows from the suggested mechanism[4] (included in Scheme I) that

$$k_{N_2}/k_i = (k_\beta + k_d)/k_{rt} \qquad (1)$$

and

$$\Delta V^\ddagger(k_{N_2}) - \Delta V^\ddagger(k_i) = \Delta V^\ddagger(k_\beta + k_d) - \Delta V^\ddagger(k_{rt}) \qquad (2)$$

The pressure dependencies of k_β, k_d, and k_{rt} will therefore determine the value of $\Delta V^\ddagger(k_{N_2}) - \Delta V^\ddagger(k_i)$ and the validity of the suggested mechanism. If $k_d \gg k_\beta$, then $\Delta V^\ddagger(k_\beta + k_d) \sim \Delta V^\ddagger(k_d)$ and could have a value as large as +18 $cm^3\ mol^{-1}$ for a solvent like hexane, since k_d is inversely proportional to the viscosity of the solvent.[4] On the other hand, if $k_\beta \gg k_d$ then $\Delta V^\ddagger(k_\beta + k_d) \sim \Delta V^\ddagger(k_\beta)$, and we expect this to be very close to $\Delta V^\ddagger(k_{fc})$ due to the similar nature of the reactions involved. A reasonable estimate for $\Delta V^\ddagger(k_{fc})$ is +5 $cm^3\ mol^{-1}$,[4] such that $\Delta V^\ddagger(k_\beta + k_d)$ could have a value between +5 and +18 $cm^3\ mol^{-1}$.

The value of $\Delta V^\ddagger(k_{rt})$ strongly depends on the partial molar volumes of the cis and trans species, i.e., $\bar{V}_c$ and $\bar{V}_t$, respectively, as well as the location of the transition state for this process. Considering the mechanism in Scheme I, it follows that $\Delta\bar{V} = \bar{V}_t - \bar{V}_c = \Delta V^\ddagger(k_{fc}) - \Delta V^\ddagger(k_{ft}) = 0$[22] when $\bar{V}_t = \bar{V}_c$. Under such conditions $\Delta V^\ddagger(k_{rt})$ must be close to zero. Alternatively, $\Delta V^\ddagger(k_{rt}) \sim -\Delta V^\ddagger(k_{fc}) = -5$ $cm^3\ mol^{-1}$ when both processes (denoted by k_{rt} and k_{fc}) have late (product-like) transition states. However, in this study we clearly indicated that $\bar{V}_t$ and $\bar{V}_c$ are not necessarily equal and $\Delta\bar{V}$ could have a value between 10 and 12 $cm^3\ mol^{-1}$. This brings about that $\Delta V^\ddagger(k_{rt})$ could have values between zero and +7 $cm^3\ mol^{-1}$ under the limiting conditions outlined above. It follows that $\Delta V^\ddagger(k_{rt})$ can vary between −5 and +7 $cm^3\ mol^{-1}$ depending on the nature of the transition state and the partial molar volumes of the reactant/product species.

Substitution of these limiting values for $\Delta V^\ddagger(k_\beta + k_d)$ and $\Delta V^\ddagger(k_{rt})$ in eq 2, indicates that $\Delta V^\ddagger(k_{N_2}) - \Delta V^\ddagger(k_i)$ can have values between zero and +23 $cm^3\ mol^{-1}$ for the suggested radical-pair mechanism. The experimental difference[4] of +12 $cm^3\ mol^{-1}$ is therefore no proof for the suggested radical-pair mechanism. On the other hand, we cannot rule out this mechanism on the basis of volume of activation data alone. Our present investigation clearly demonstrated that a very similar $\Delta V^\ddagger(k_i)$ value can be obtained for systems where radical-pair formation can be ruled out. It follows, as mentioned before, that it is unnecessary to invoke a radical-pair mechanism to account for the volume of activation data reportd before[4] and that a semilinearization mechanism can describe the process equally well. Furthermore, the observed volume of activation for the isomerization of *cis*-azonorbornane is in good agreement with the observed overall volume change, which encourages us to extent our arguments to the systems studied by Neuman et al.[4]

A recent paper[3] reported that only a very small fraction of adamantyldiazenyl radicals recombine at the primary end of the dimethylallyl radical. In the diazenylalkyl mechanism obtained for azoadamantane,[4] the observed 57% N_2 yield requires that 43% of the adamantyldiazenyladamantyl radical pairs recombine to give *trans*-azoadamantane. This large difference between the adamantyl and dimethylallyl systems favors the more likely explanation that isomerization proceeds overwhelmingly by inversion while loss of nitrogen goes via diazenyl radicals.[23]

We do not consider the investigated system to be atypical. The fact that the isomerization of azonorbornane occurs at a significantly higher temperature than the other studied systems[4] does not necessarily suggest a change in mechanism. The high reaction temperature results from the low heat of isomerization for this compound, viz., 17.1 compared to 28.4 and 28.2 kcal mol^{-1} for *cis*-1-azoadamantane and *cis*-1-azobicyclo[2.2.2]octane, respectively.[24] Furthermore, it is known from the literature that the relative rates of radical formation decrease in the order 1-adamantyl > 1-bicyclo[2.2.2]octyl > 1-norbornyl.[25]

It follows from this study that $\Delta V^\ddagger$ measurements alone cannot unequivocally pinpoint a mechanism in these systems. Combining such data with partial molar volume data for reactant and product species enables volume equation calculations and the construction of reaction volume profiles which assist the mechanistic assignment. The latter techniques have been applied with significant success in the elucidation of inorganic reaction mechanisms in recent years.[26]

Acknowledgment. We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Registry No. *cis*-Azodi-1-norbornane, 59388-64-6.

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[22] In this treatment it is assumed that the partial molar volume of the radical pair is close to that of the common transition state for both processes.

[23] We are grateful to Prof. P. S. Engel for calling our attention to this fact.

[24] The isomerization enthalpies were calculated by using the MM1 force field method as extended to azo compounds by Crans and Snyder (*Chem. Ber.* 1980, *113*, 1201). Preliminary experimental results in our laboratories support these data.

[25] Golzke, V.; Groeger, F.; Oberlinner, A.; Rüchardt, C. *Nouv. J. Chim.* 1978, *2*, 169. Lomas, J. S.; Dubois, J.-E. *J. Org. Chem.* 1982, *47*, 4505.

[26] van Eldik, R.; Kelm, H. *Rev. Phys. Chem. Jpn.* 1980, *50*, 185. Palmer, D. A.; Kelm, H. *Coord. Chem. Rev.* 1981, *36*, 89. van Eldik, R.; Palmer, D. A.; Kelm, H.; Louw, W. J. *Inorg. Chem.* 1980, *19*, 3551. Doss, R.; van Eldik, R. *Inorg. Chem.* 1982, *21*, 4108. Kitamura, Y.; van Eldik, R.; Kelm, H. *Inorg. Chem.* 1984, *23*, 2038.

Deformation Density and Dissociation Energy of Strained C–C Bonds

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In a covalent bond the shared density binds the nuclei. Thus, the amount of deformation density determines, in some way, the bond strength. Bader et al.[1] have shown that there is a direct relationship between chemical bond strength (dissociation energy) and the magnitude of electrostatic field due to charge redistribution. They have shown that in diatomic homonuclear molecules the plot of the overlap and atomic contributions multiplied by $(1/R_e^2)$ vs. the dissociation energy is described by a linear relationship.

In the deformation density calculated by using IMO (iterative maximum overlap) hybrid functions, the pre-

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[1] Bader, R. F.; Henneker, W. H.; Cade, P. E. *J. Chem. Phys.* 1967, *46*, 3341.

dominant influences have overlap integrals. In accordance with Bader's consideration,[1] some relationship can be expected between IMO calculated bond-deformation densities in polyatomic molecules and corresponding bond-dissociation energies.

The aim of this work is to determine if there is a relationship between the magnitude of bond-deformation densities, calculated with IMO hybrid functions, in polyatomic molecules and corresponding bond-dissociation energies. The molecules considered are strained small hydrocarbon rings: cyclobutene, cyclopentadiene, [2.1.1]propellane, and [2.2.2]propellane.

Method

A brief statement of IMO procedure is given here while the details are available elsewhere.[2]

The aim of the IMO procedure is to construct a set of local hybrid orbitals of the form

$$\Psi_{A\mu} = c_{A\mu}(2s)_A + (1 - c_{A\mu}{}^2)^{1/2}(2p_\mu)_A \tag{1}$$

The hybridization parameters $c_{A\mu}$ are varied to maximize the sum of weighted bond overlap integrals

$$E = k_{CC}\sum_{CC} S_{CC} + k_{CH}\sum_{CH} S_{CH} \tag{2}$$

The resulting hybrid orbitals were applied in evaluation of the total density

$$\rho_v = \sum_{AB} \rho^{\nu}_{AB} = \sum_{AB} (\Psi^2_{A\mu} + \Psi^2_{B\nu} + 2S_{AB}\Psi_{A\mu}\Psi_{B\nu})/(1 + S^2_{AB}) \tag{3}$$

and deformation density

$$\Delta\rho_v(\vec{r}) = \sum_{AB} \rho^{\nu}_{AB}(\vec{r}) - \sum_{A} \rho^{\nu}_{A}(\vec{r})_{sph} \tag{4}$$

The position of the vector $\vec{r}$ refers to the bond midpoint, and $\Delta\rho_\nu$ is calculated over the region of charge buildup. The details of calculation were given earlier.[3]

Results and Discussion

Deformation densities and hybrid functions of cyclobutene and cyclopentadiene were calculated earlier.[2,3] The hybrid functions of [2.1.1]propellane and [2.2.2]propellane were also calculated earlier,[5] while their deformation densities are calculated by us and will be published.

All bonds in considered molecules are homonuclear covalent bonds. Formation of homonuclear covalent bond is the buildup of a large overlap population of shared density between the nuclei. Quantitative magnitude of shared (overlap) density of covalent bonds are given by the values of deformation density. It can be assumed that the value of deformation density per unit of the bond length is a measure of the bond strength. Because of that, the relationship between bond deformation density and bond dissociation energy can be established.

Experimental values of bond dissociation energies of these molecules are not available in literature. Thus, instead of dissociation energies, the calculated values of IMO instantaneous bond-dissociation energies (E_{IBD}) have been chosen. Instantaneous bond-dissociation energies were calculated by using the relationship established earlier:[4]

$$E(CC)_{IBD} = (372.3S_{CC} - 143.7)\ \text{kcal mol}^{-1} \tag{5}$$

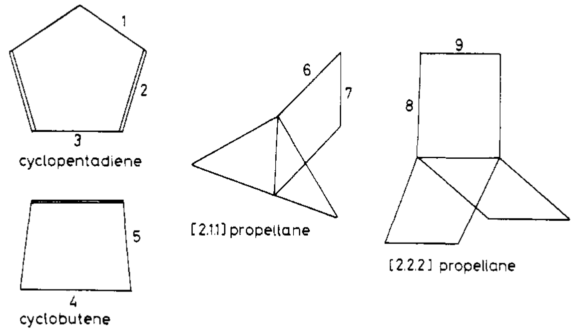

Figure 1. Schematic diagrams for considered molecules and numbering of bonds.

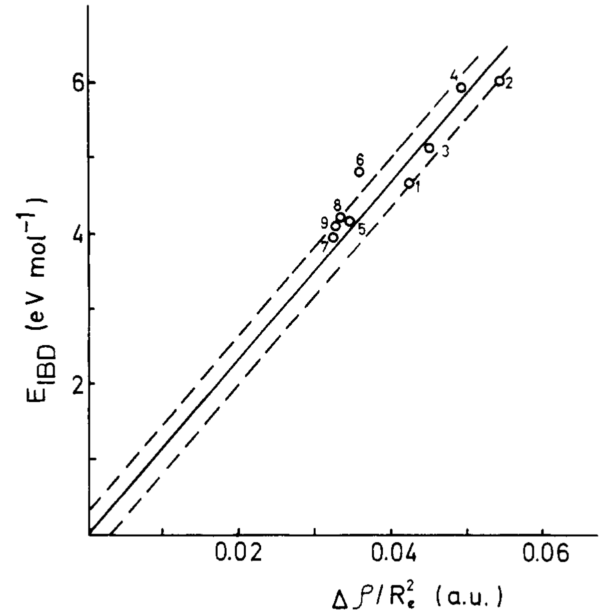

Figure 2. Plot of instantaneous bond-dissociation energies (E_{IBD}) vs. unit deformation densities ($\Delta\rho/R_e{}^2$). The solid line is a least-squares line and the dashed lines are standard deviation. Numbers denote corresponding bonds given in Figure 1.

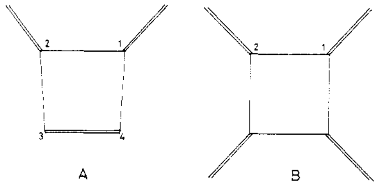

Figure 3. Schematic diagrams and numbering of atoms for 1,2-dimethylenecyclobutene (A) and tetramethylenecyclobutane (B).

Molecules and bonds taken in consideration are denoted in Figure 1. A plot of unit deformation density[6] ($\Delta\rho/R_e{}^2$) vs. E_{IBD} is given in Figure 2.

Correlation between these two quantities is indeed obtained and can be described by a linear relationship. By a least-squares method the following relationship is obtained:

$$E_{IBD} = (119.2 \pm 2.4)(\Delta\rho/R_e{}^2)\ \text{eV mol}^{-1} \tag{6}$$

It is obvious that the standard deviation is very small.

To verify the validity of the established relationship 1,2-dimethylenecyclobutene and tetramethylenecyclobutane were chosen (Figure 3). Both molecules are highly

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(2) Vujisić, Lj.; Maksić, Z. B. *J. Mol. Struct.* **1976**, *33*, 49.

(3) Vujisić, Lj.; Vučković, D. Lj.; Maksić, Z. B. *THEOCHEM* **1984**, *106*, 323.

(4) Vujisić, Lj.; Maksić, Z. B. *J. Mol. Struct.* **1971**, *7*, 431.

(5) Vučković, D. Lj.; Vujisić, Lj. *Croat. Chem. Acta* **1984**, *57*, 801.

(6) Unit deformation density is the value of bond-deformation density divided by the square of equilibrium bond distance.

Table I. Values for the Instantaneous Bond-Dissociation Energies (E_{IBD}) for 1,2-Dimethylenecyclobutene and Tetramethylenecyclobutane

	E_{IBD}, eV mol^{-1}	
bond[a]	eq 5	eq 6
	1,2-dimethylenecyclobutene	
C_1C_2	4.98	5.05
C_2C_3	5.32	5.20
C_3C_4	5.68	5.88
	tetramethylenecyclobutane	
C_1C_2	4.86	4.80

[a] Notation is given in Figure 3.

strained four-membered rings.

By the IMO procedure the bond overlaps (eq 1 and 2) and the deformation densities (eq 3 and 4) for 1,2-dimethylenecyclobutene and tetramethylenecyclobutane were calculated. With the values of bond overlaps and bond-deformation densities, instantaneous bond-dissociation energies were calculated by eq 5 and 6. Notation of the atoms in the molecules is given in Figure 3, and the values of both E_{IBD}'s are given in Table I.

It can be seen, from Table I, that agreement between instantaneous bond-dissociation energies calculated by unit deformation densities (eq 6) and by the bond overlaps (eq 5) is within the standard deviation error.

Established relationship 6 gives satisfactory results for covalent bonds in strained four- and five-membered rings. Also it can be said that the unit deformation density is a measure of binding power of molecular orbitals.

Registry No. Cyclobutene, 822-35-5; cyclopentadiene, 542-92-7; [2.1.1]propellane, 36120-91-9; [2.2.2]propellane, 36120-88-4; 1,2-dimethylenecyclobutene, 5291-90-7; tetramethylenecyclobutane, 3227-91-6.

Hydroboration. 72. Hydroboration–Oxidation of 1,4-Epoxy-1,4-dihydronaphthalene with and without Ring Opening

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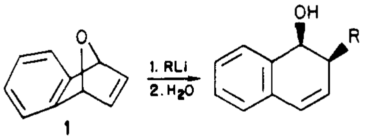
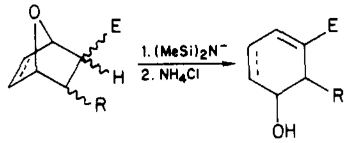
Recently we reported the hydroboration of heterocyclic olefins with representative hydroborating agents such as borane–methyl sulfide (BMS), 9-borabicyclo[3.3.1]nonane (9-BBN), dicyclohexylborane (Chx_2BH), and disiamylborane (Sia_2BH) providing a highly convenient and efficient method for the synthesis of heterocyclic alcohols.[2] β-Substituted organoboranes readily undergo elimination. However, in these reactions we were able to avoid the ring cleavage by careful selection of reagent and conditions. In continuation of these studies, we selected 1,4-epoxy-1,4-dihydronaphthalene (1), an unusual heterocycle, in order to study the stability and synthetic utility of organoboranes produced in the hydroboration of the 7-oxabicyclo[2.2.1]heptene system.

There are reports in the literature that 1, on treatment with alkyllithiums, yield 1,2-dihydro-2-alkylnaphthalenes via ring opening of the initially formed addition products[3,4] (eq 1). Similarly, a base-promoted β-elimination in the 7-oxabicyclo[2.2.1]heptyl system, yielding cyclohexanols and cyclohexadienols, has been reported[5] (eq 2). Previously we reported that cyclic ethers undergo ready cleavage in the presence of lithium tri-*tert*-butoxyaluminum hydride and triethylborane.[6,7] Extension of this reaction to 1 has recently been reported to yield 1-hydroxy-1,4-dihydronaphthalene[8] (eq 3).

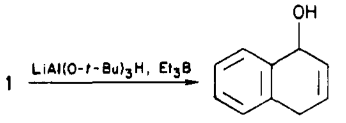


1

(1)



(2)

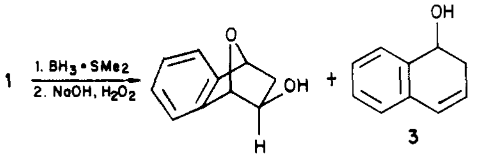


(3)

Results and Discussion

Compound 1 was hydroborated with BMS, 9-BBN, Chx_2BH, and Sia_2BH, and the products were oxidized with alkaline hydrogen peroxide. The results are shown in Table I.

BMS. Compound 1 was hydroborated with BMS (3:1 mol ratio) in THF at 25 °C. The ^{11}B NMR spectrum of the reaction mixture showed a signal at δ 27.6, which, on methanolysis, transformed itself into a new signal at δ 18.3. Oxidation of the reaction mixture afforded 7-oxa-*exo*-2-benznorborneol (2) and 1-hydroxy-1,2-dihydronaphthalene (3) in a 1:5 ratio (eq 4). It should be noted that 3 is isomeric with the compound synthesized by the reaction shown in eq 3.



2 3

(4)

It appears that the latter product might have arisen from a cleavage of the organoborane initially formed. Lowering the reaction temperature to 0 °C did not avoid this cleavage. The ^{11}B NMR spectra and the product analysis after oxidation were essentially the same as in the reaction at 25 °C. However, in these two cases, only 2 mol of olefin per mol of BMS were consumed. A longer reaction time did not achieve the utilization of a third mole of olefin. However, reaction in refluxing THF (65 °C) consumed all of the olefin. The ^{11}B NMR of the reaction mixture following reaction at 65 °C for 1 h showed a signal at δ 20.2, characteristic of $B(OR)_3$ species. Oxidation of the reaction

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(1) Postdoctoral research associate on Grant GM 10937-22 from the National Institutes of Health.

(2) Brown, H. C.; Vara Prasad, J. V. N.; Zee, S.-H. *J. Org. Chem.* **1985**, *50*, 1582.

(3) Caple, R.; Chen, G. M. S.; Nelson, J. D. *J. Org. Chem.* **1971**, *36*, 2874.

(4) Jeffrey, A. M.; Yeh, H. J. C.; Jerina, D. M.; DeMarinis, R. M.; Foster, C. H.; Piccolo, D. E.; Berchtold, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 6929.

(5) Brion, F. *Tetrahedron Lett.* **1982**, 5299.

(6) Brown, H. C.; Krishnamurthy, S.; Coleman, R. A. *J. Am. Chem. Soc.* **1972**, *94*, 1750.

(7) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1979**, *44*, 3678.

(8) Moss, R. J.; Rickborn, B. *J. Org. Chem.* **1985**, *50*, 1381.