of the experimentally accessible molecules, the basis sets that we can afford are rather small.

Electron correlation can influence second-order properties in two ways, either directly in cases of near-degeneracy or indirectly via the theoretical determination of molecular geometries. For the cations investigated in this study, direct correlation effects have been found to play only a minor role. The situation is quite different for molecules containing multiple bonds between second-row atoms like phosphorus or silicon.[50]

The IGLO method has been shown to be a powerful tool for the determination of molecular structures. Providing the complete information about the molecular χ tensor and the shielding tensors of all atoms in a molecule at the expense of at most two additional SCF calculations, an IGLO calculation constitutes a sensitive test for the quality of a theoretically determined structure, if there are no experimental geometries available.

This has been demonstrated for the $C_7H_{11}^+$ and $C_4H_7^+$ cations. Even on the double-ζ SCF level it is possible to decide that nonclassical structure of the 2-norbornyl cation is the correct one.

For $C_4H_7^+$ the disagreement between our calculations for optimized SCF geometries and the experimental data indicates that a reliable equilibrium geometry can be supplied only by using methods that include electron correlation together with a large basis set. Hence indirect correlation effects are important for the determination of σ(C), at least in this case.

This does not automatically imply, however, that direct correlation effects play an imporant role for the calculation of magnetic properties like χ and σ in general.

Note Added in Proof. Very recently an MP2/6-31G* ab initio investigation of the potential hypersurface of $C_4H_7^+$ revealed that the bicyclobutonium ion is more stable than the cyclopropylcarbinyl cation (0.7 kcal/mol at the MP4SDQ/6-31G*//MP2/6-31G* level).[51] This supports our conclusion drawn from the IGLO calculations.

Acknowledgment. The author is grateful to Dr. H. Kollmar for initiating this study, to Prof. P. v. R. Schleyer for supplementary material on MP2 6-31G* geometries of C_1 and C_2 cations, and to Prof. W. Kutzelnigg for numerous helpful discussions. The calculations were performed on the Cyber 205 computer of the Rechenzentrum der Ruhr-Universitat Bochum.

Registry No. 1, 14531-53-4; **2**, 15135-49-6; **6**, 14604-48-9; **8**, 14936-94-8; **10**, 24669-33-8; **12**, 26810-74-2; **13**, 1724-44-3; **14**, 17171-49-2; **15**, 17542-17-5; **16**, 58175-90-9; **17**, 22537-04-8; **18**, 12316-90-4; **19**, 19252-53-0; **20**, 14804-25-2; **21**, 2154-76-9; **22**, 27861-45-6; **24**, 25681-56-5; **25**, 53032-28-3; **28**, 25076-72-6; **29**, 43531-41-5; **35**, 17104-55-1; **36**, 25940-78-7; cyclopropylium, 1724-43-2; 1-methylcyclobutonium, 19394-14-0.

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The Effects of Various Substituents upon the Properties of the Bond between the Bridgehead Carbons in Bicyclobutane

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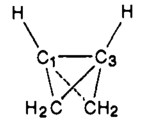
Contribution from the Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148, and the U.S. Army Armament Research, Development and Engineering Center, SMCAR-AEE-WE, Dover, New Jersey 07801-5001. Received July 3, 1986

Abstract: We have used a computational approach to investigate the properties of bicyclobutane and various of its derivatives in which one or more of the groups NH_2, NCO, NO, and NO_2 are substituted on its bridgehead positions. Our primary focus has been upon the bond between the bridgehead carbons. An ab initio self-consistent-field molecular orbital procedure (GAUSSIAN 82) was used to compute optimized structures for these molecules and then to calculate three key properties: molecular electrostatic potentials, bond deviation indices, and bond orders. We find the two three-membered rings in bicyclobutane to show some definite similarities to cyclopropane, but both the reactivity of the molecule toward electrophiles and also its degree of strain are greater than would be expected in terms of an analogy to cyclopropane. All of the substituents except NH_2 are found to diminish the reactivity of the carbon framework toward electrophiles. The bond between the bridgehead carbons is weakened by the presence of either NO or NO_2 as a substituent at these positions. The greatest degree of weakening of this bond occurs for the combination of NH_2 and NO_2 as substituents; the effect is less for NCO and NO_2. These observations can be interpreted in terms of electronic rearrangements and resonance arguments. Thus it appears that isocyanate precursors are to be preferred to amines, in this respect, in the stepwise polynitration of strained C–C bonds.

Bicyclo[1.1.0]butane (I) is a strained cyclic hydrocarbon, containing two types of C–C bonds. Our present focus is upon the one between the two bridgehead positions, C_1 and C_3, as an example of a strained linkage between two tertiary carbons. We wish to determine how the stability and other reactive properties of this bond are affected by the presence of various substituents on the bridgehead carbons. The substituting groups that will be considered, alone or in combination, are NH_2, NO, NCO, and NO_2. Derivatives involving the first three of these are possible precursors in nitration processes; thus the results of this work will be of direct relevance to synthetic approaches to the polynitration of strained hydrocarbons.



I

A question of particular interest is whether the combination of NH_2 and NO_2 will weaken the C_1–C_3 bond. Equation 1 shows a mechanism by which, in the extreme case, rupture of this bond would occur.

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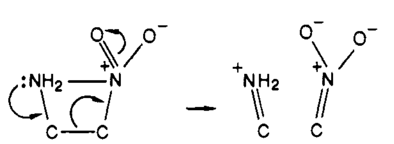
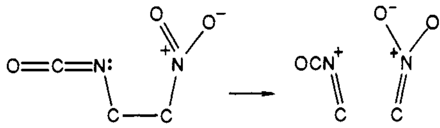
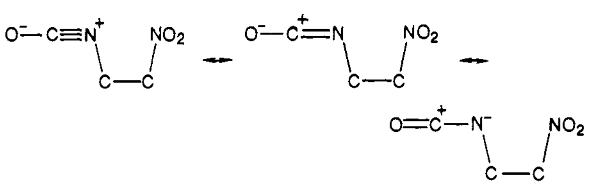

(1)

The key to this bond destabilization is the availability of the lone pair on the amine nitrogen. It would accordingly be predicted that the effect will be diminished if the NH_2 is replaced by a substituent having a less available lone pair. This requirement may be met by NCO. The latter group can still give rise to a mechanism analogous to eq 1, as is shown below in eq 2a; however, there are also several resonance possibilities, including one in which the nitrogen lone pair is delocalized in the direction away from the bicyclobutane framework (eq 2b). Accordingly, the bond-weakening mechanism may play a smaller role in the case of NCO. The validity of this reasoning is examined in this work.


(2a)


(2b)

Methods

(1) General. Our approach is a computational one, which uses an ab initio self-consistent-field molecular orbital procedure (GAUSSIAN 82).[1] The initial step is to calculate an optimized geometry for each molecule of interest. This has been done at the 3-21G level, which has been shown to be effective for this purpose.[2] The resulting structures are then used to compute some key properties, including molecular electrostatic potentials, bond deviation indices, and bond orders. Each of these shall be briefly described.

(2) Molecular Electrostatic Potentials. The electrons and nuclei of any molecule create a potential in the surrounding space, with a magnitude $V(\bar{r})$ at any point $\bar{r}$ that is given rigorously by

$$V(\bar{r}) = \sum_{A} \frac{Z_A}{|\bar{R}_A - \bar{r}|} - \int \frac{\rho(\bar{r}')\,d\bar{r}'}{|\bar{r}' - \bar{r}|} \tag{3}$$

Z_A is the charge on nucleus A, located at R_A, and $\rho(\bar{r})$ is the electronic density function of the molecule, which we obtain from the molecular wave function.

The electrostatic potential is well-established as a means of interpreting and predicting chemical reactive behavior, especially toward electrophiles.[3-5] Equation 3 shows that $V(\bar{r})$ is negative in those regions where the effects of the molecule's electrons are dominant. It is to these regions that an approaching electrophile is initially attracted, especially to these points at which $V(\bar{r})$ attains its most negative values (the local minima).

The electrostatic potential is a real physical property, which can be determined experimentally as well as computationally.[5] Extensive studies have shown that ab initio SCF methods, such as that used in this work, produce generally reliable representations of $V(\bar{r})$.[3,6-8]

(3) Bond Deviation Index. The ridge of maximum electronic density linking two chemically bonded nuclei is called the "bond path".[9] It often lies along the internuclear axis, as in the C-C bonds of cyclohexane and propane; in some instances, however, including strained bonds, it is curved.[9-12] As a quantitative measure of the degree of this curvature, we have introduced the "bond deviation index", λ, defined by eq 4.[11] The

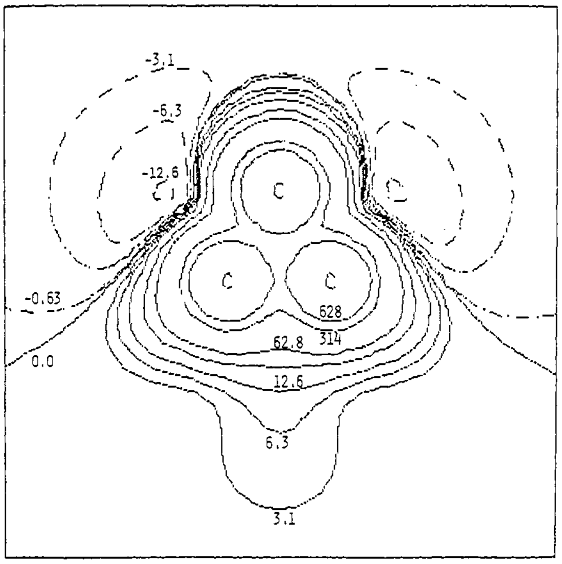


Figure 1. Electrostatic potential of bicyclobutane in the plane of one of the three-membered rings. Dashed contours represent negative potentials. Values are in kcal/mol.

$$\lambda = \left[\frac{1}{N}\sum_{i}^{N} r_i^2\right]^{1/2} \Big/ R \tag{4}$$

r_i are the lengths of N equally spaced lines drawn between the actual bond path and a reference path defined in terms of the superposed electronic densities of the corresponding free atoms placed at the same positions as they occupy in the molecule. N is taken to be 320, which is well beyond the value at which further increases in its magnitude produce no significant change in λ. R is the internuclear distance.

The bond deviation index has proven to be effective for characterizing and comparing strained chemical bonds.[11-14] It has the particular advantage of focusing specifically upon an individual bond in a molecule, rather than being a property of the molecule as a whole.

(4) Bond Orders. We have recently demonstrated that bond orders calculated from force constants and bond lengths via eq 5 correlate well with experimentally determined bond dissociation energies.[15] This is accordingly a practical method for assessing the relative strengths of

$$\text{bond order} = 0.55747\sqrt{k/R_e} \tag{5}$$

chemical bonds. In eq 5, k is the force constant in mdyn/Å and R is the equilibrium bond length in Å. Both of these can be obtained with the GAUSSIAN 82 program.

Results and Discussion

(1) Structures. Our calculated structures are summarized in Table I. Experimentally determined data were found only for bicyclobutane itself;[16] these are generally in good agreement with the computed values.

In all instances, the NO_2 groups are planar and perpendicular to the symmetry plane through the C_1–C_3 axis. In the NO, NO combination, the oxygens are on opposite sides of this plane. The NH_2 groups are usually pyramidal, with the hydrogens pointing

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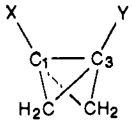
Table I. Calculated Structures[a]



X, Y	distances (Å)		angles (deg)	
H, H	C_1–C_3:	1.48 (1.497)	C_1–C_3–H:	135 (128°22′)
	C_1–C_2:	1.51 (1.498)	H–C_2–H:	115 (115°34′)
	C_1–H:	1.06 (1.071)	C_4–C_3–C_1–C_2:	118 (121°40′)
	C_2–H:	1.07 (1.093)		
NH_2, H	C_1–C_3:	1.49	C_1–C_3–H:	140
	C_1–C_2:	1.50	C_1–N–H:	116
	C_3–C_2:	1.52	N–C_1–C_3:	141
	C_1–N:	1.40	C_1–C_3–C_4:	60
	C_3–H:	1.06	C_2–C_1–C_3:	61
	C_2–H:	1.08	H–C_2–H:	115
			C_4–C_3–C_1–C_2:	118
NH_2, NH_2	C_1–C_3:	1.49	C_3–C_1–C_2:	60
	C_1–C_2:	1.51	N–C_1–C_3:	147
	C_1–N:	1.41	C_1–N–H:	115
	N–H:	1.00	H–C_2–H:	114
	C_2–H:	1.08	C_4–C_3–C_1–C_2:	117
NO, H	C_1–C_3:	1.50	C_3–C_1–C_2:	60
	C_1–C_2:	1.51	N–C_1–C_3:	130
	C_1–N:	1.40	O–N–C_1:	114
	N–O:	1.23	C_1–C_3–H:	131
	C_3–H:	1.06	H–C_2–H:	116
	C_2–H:	1.07	C_4–C_3–C_1–C_2:	121
NO, NO[b]	C_1–C_3:	1.51	C_3–C_1–C_2:	60
	C_1–C_2:	1.50	N–C_1–C_3:	129
	C_1–C_4:	1.51	O–N–C_1:	113
	C_1–N:	1.42	H–C_2–H:	116
	N–O:	1.22	C_4–C_3–C_1–C_2:	124
	C_2–H:	1.07		
NO_2, H	C_1–C_3:	1.49	C_3–C_1–C_2:	61
	C_1–C_2:	1.50	C_4–C_3–C_1:	60
	C_3–C_2:	1.51	N–C_1–C_3:	130
	C_1–N:	1.41	O–N–C_1:	117
	N–O:	1.25	O–N–O:	126
	C_3–H:	1.06	C_1–C_3–H:	131
	C_2–H:	1.07	H–C_2–H:	116
			C_4–C_3–C_1–C_2:	122

X, Y	distances (Å)		angles (deg)	
NO_2, NO_2	C_1–C_3:	1.50	C_3–C_1–C_2:	60
	C_1–C_2:	1.50	N–C_1–C_3:	130
	C_1–N:	1.42	O–N–C_1:	117
	N–O:	1.24	O–N–O:	127
	C_2–H:	1.07	H–C_2–H:	117
			C_4–C_3–C_1–C_2:	125
NH_2, NO_2	C_1–C_3:	1.61	C_3–C_1–C_2:	58
	C_1–C_2:	1.49	C_4–C_3–C_1:	57
	C_3–C_2:	1.51	N–C_1C_3:	136
	C_1–NH_2:	1.35	N–C_3–C_1:	130
	C_3–NO_2:	1.37	H–N–C_1:	120
	N–H:	1.00	H–N–H:	117
	N–O:	1.26	O–N–C_3:	118
			O–N–O:	125
			H–C_2–H:	115
			C_4–C_3–C_1–C_2:	128
NCO, H	C_1–C_3:	1.48	C_3–C_1–C_2:	61
	C_1–C_2:	1.51	C_4–C_3–C_1:	60
	C_3–C_2:	1.52	N–C_1–C_3:	137
	C_1–N:	1.36	O–C–N:	179
	N–CO:	1.16	C–N–C_1:	175
	C–O:	1.18	C_1–C_3–H_5:	136
	C_3–H:	1.06	H–C_2–H:	116
			C_4–C_3–C_1–C_2:	118
NCO, NO_2	C_1–C_3:	1.50	C_3–C_1–C_2:	60
	C_1–C_2:	1.51	C_4–C_3–C_1:	60
	C_3–C_2:	1.50	N–C_1–C_3:	135
	C_1–NCO:	1.35	N–C_3–C_1:	133
	C_3–NO_2:	1.40	O–C–N:	180
	N–CO:	1.16	C–N–C_1:	176
	C–O:	1.17	O–N–C_3:	117
	N–O:	1.25	O–N–O:	126
	C_2–H:	1.07	H–C_2–H:	116
			C_4–C_3–C_1–C_2:	122

[a] The experimentally determined distances and angles for bicyclobutane are given in parentheses. These were taken from ref 16. [b] The oxygen of the NO group attached to C_1 is on the same side of the plane bisecting the angle between the three-membered rings as is C_2.

away from the C_1–C_3 axis; in the presence of the strongly electron-withdrawing NO_2; however, the NH_2 group becomes planar, a tendency that we have observed earlier.[13,17]

The most notable features of the structures in Table I are the marked changes that are observed when NH_2 and NO_2 are the bridgehead substituents. The C_1–C_3 bond length increases quite considerably, from 1.48 to 1.61 Å, while the C–NH_2 and C–NO_2 distances decrease significantly and the N–O distances increase, compared to their values in the other molecules. These changes reflect corresponding ones in relative bond strengths, as shall be discussed.

(2) Molecular Electrostatic Potentials. Figures 1 and 2 show the calculated electrostatic potentials of unsubstituted bicyclobutane in two different planes through the molecule. There are seen to be negative potentials associated with the C–C bond regions. This is a rather unusual feature, but one that we have observed previously in a variety of strained hydrocarbons. This negative bond potential is rather small and weak for the C_1–C_3 bond (Figure 2) but much larger and stronger for the other bonds in the three-membered rings, reaching minima (most negative values) of −13.2 kcal/mol. These observations are consistent with the fact that the dipole moment of bicyclobutane is relatively large

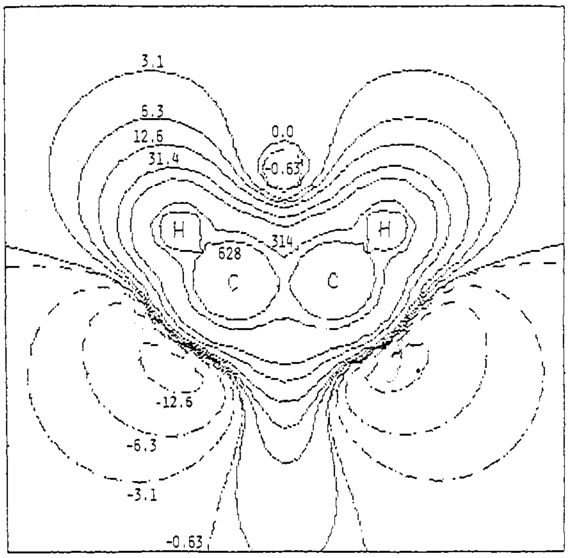


Figure 2. Electrostatic potential of bicyclobutane in the plane through the bridgehead carbons and bisecting the angle between the two three-membered rings. Dashed contours represent negative potentials. Values are in kcal/mol.

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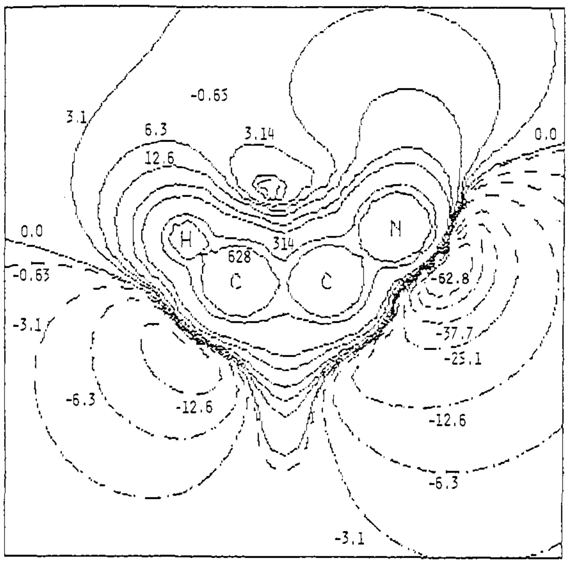


Figure 3. Electrostatic potential of aminobicyclobutane in the plane of bridgehead carbons and nitrogen. Dashed contours represent negative potentials. Values are in kcal/mol.

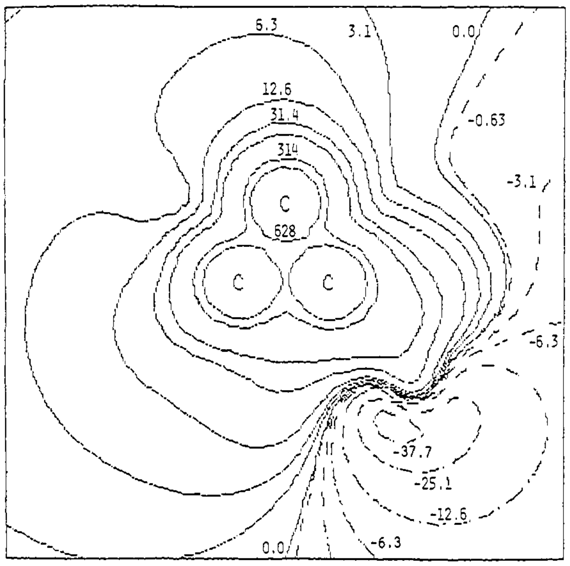


Figure 4. Electrostatic potential of nitrobicyclobutane in the plane of one of the three-membered rings. Dashed contours represent negative potentials. Values are in kcal/mol.

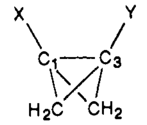
for a saturated hydrocarbon, 0.68 D,[18] and has a polarity such that the C_1–C_3 bond is at the positive end.[19]

The negative potentials associated with the bonds other than C_1–C_3 bear a marked resemblance to analogous ones in cyclopropane, which have minima of −13.0 kcal/mol.[10] In the case of bicyclobutane, however, the angle between the two three-membered rings is small enough (calculated to be 118°) that these negative regions overlap and reinforce each other, so that minima of −16.2 kcal/mol are found within this dihedral angle (Figure 2). This may account for the high degree of stabilization that has been attributed, on the basis of experimental studies, to the protonated form of bicyclobutane.[20,21]

The C–C bonds retain negative electrostatic potentials when an NH_2 is substituted on one of the bridgehead carbons, although now the dominant feature is the very strong negative regions due to the nitrogen lone pair, with a minimum of −84 kcal/mol. (See Figure 3.) Indeed in 1,3-diaminobicyclobutane, the C–C bond potentials are no longer separately discernible, being engulfed by the widely extended lone pair potentials. In both of these amine derivatives, the nitrogens have pyramidal configurations.

In contrast to NH_2, the nitro group completely eliminates the negative C–C potentials (Figure 4); this is a characteristic of NO_2 as a substituent that has been observed in the past,[10,22] and it presumably reflects the strong electron-attracting inductive effect of NO_2. The only negative regions associated with nitrobicyclobutane are those by the oxygens; thus the carbon framework

Table II. Calculated Properties[a]



X, Y	bond orders		bond deviation indices		electrostatic potentials[b]	
H, H	C_1–C_3:	1.43	C_1–C_3:	0.084	C_1–C_3:	−2.3
	C_1–C_2:	1.32	C_1–C_2:	0.080	C_1–C_2:	−13.2
						(−16.2)
NH_2, H	C_1–C_3:	1.41	C_1–C_3:	0.090	C_1–C_3:	−1.4
	C_1–N:	1.42	C_1–C_2:	0.077	N:	−84.0
			C_3–C_2:	0.081	C_1–C_2:	−15.8
						(−19.0)
NH_2, NH_2	C_1–C_3:	1.42	C_1–C_3:	0.095	N:	−88.0
	C–N:	1.40	C_1–C_2:	0.078		
NO, H	C_1–C_3:	1.35	C_1–C_3:	0.078	C_1–C_2:	−4.3
	C_1–N:	1.36	C_1–C_2:	0.077		(−4.7)
					C_3–C_2:	−1.2 (−3.9)
	N–O:	2.14	C_3–C_2:	0.007	N:	−65.8
					O:	−34.0, −46.5
NO, NO	C_1–C_3:	1.32	C_1–C_3:	0.075	N:	−57.1
	C–N:	1.32	C_1–C_2:	0.075	O:	−25.2, −38.5
	N–O:	2.17	C_1–C_4:	0.076		
NO_2, H	C_1–C_3:	1.38	C_1–C_3:	0.080	0:	−43.6, −56.7
	C_1–N:	1.41	C_1–C_2:	0.077		
	N–O:	1.89	C_3–C_2:	0.080		
NO_2, NO_2	C_1–C_3:	1.36	C_1–C_3:	0.080	O:	−31.6, −46.8
	C–N:	1.37	C_1–C_2:	0.078		
	N–O:	1.91				
NH_2, NO_2	C_1–C_3:	1.12	C_1–C_3:	0.072	C_3:[c]	−9.0
	C_1–NH_2:	1.57	C_1–C_2:	0.064	H_2N:	−29.6
	C_3–NO_2:	1.53	C_3–C_2:	0.064	O:	−53.9, −68.6
NCO, H	C_1–C_3:	1.43	C_1–C_3:	0.086	C_1–C_2:	−2.6
	C_1–NCO:	1.51	C_1–C_2:	0.080		(−3.4)
					C_3–C_2:	−3.6
	N–CO:	2.64	C_3–C_2:	0.081		(−6.0)
	C–O:	2.24			N:	−2.9
					O:	−50.2
NCO, NO_2	C_1–C_3:	1.35	C_1–C_3:	0.082	O(NCO):	−40.5
	C_1–NCO:	1.56	C_1–C_2:	0.078	O(NO_2):	−39.6, −53.7
	N–CO:	2.60	C_3–C_2:	0.076		
	C–O:	2.31				
	C_3–NO_2:	1.41				
	N–O:	1.89				

[a] These properties were computed with our 3-21G optimized geometries. The electrostatic potentials and bond deviation indices were obtained by single runs at the STO-5G and STO-6G levels, respectively; we have found these two basis sets to give satisfactory and virtually identical results for one-electron properties. The bond orders were calculated at the STO-3G level, which we have found to give very nearly the same relative magnitudes as the 3-21G. [b] These are the electrostatic potentials, in kcal/mol, at those points at which $V(\bar{r})$ attains its most negative values (the local minima). They are indicated as being associated with specific bonds or specific atoms. The values given in parentheses in a few cases are due to the overlap of the negative C_1–C_2 and C_3–C_2 regions. [c] This minimum is near C_3, on the plane that bisects the dihedral angle between the three-membered rings.

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should be much less susceptible to electrophilic attack than is the parent hydrocarbon. In proceeding to 1,3-dinitrobicyclobutane, the oxygen potentials are seen to become less negative (Table II). Again, this is a tendency that has been observed previously, for various electron-withdrawing groups;[22-24] it is due to the fact that there are now two substituent groups competing for the same polarizable charge.

For all of the molecules studied, the electrostatic potential minima are summarized in Table II. In the singly substituted nitroso and isocyanate derivatives, there are again negative potentials associated with the C–C bonds, but they are rather weak.

(3) Bond Deviation Indices. The bond deviation indices of the C–C bonds in bicyclobutane, given in Table II, also bring out a degree of similarity of its three-membered rings to cyclopropane. For the bonds to the methylene carbons, λ is exactly the same as for cyclopropane, 0.080;[11] for the bond between the bridgehead positions, λ is 0.084. Thus the degree of curvature is slightly greater in the C_1–C_3 bond. This is consistent with the conclusion that this is the most strained bond in bicyclobutane,[25] and with the estimated strain energy of the molecule being somewhat more than twice the cyclopropane value.[20,21,25,26]

Cyclopropane is known to have certain olefin-like chemical properties, such as the ability to undergo some addition reactions.[27-29] These are believed to be associated with the curved, or "bent", nature of its C–C bonds. By extending this reasoning, one would expect the C_1–C_3 bond in bicyclobutane, in particular, to also show olefin-like reactive behavior. This is indeed true; for instance, bicyclobutane undergoes addition across this bond with both H_2O and I_2, producing cyclobutane derivatives.[20,21]

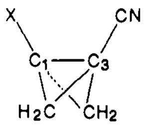
For the various bicyclobutane derivatives, Table II shows that the bond deviation indices of the bonds to the methylene carbons remain quite close to the cyclopropane value, 0.080; the one exception is their relatively low values for the NH_2, NO_2 combination. λ is considerably more variable for the bond between the bridgehead positions; its smallest magnitude, however, is also for the NH_2, NO_2 derivative. The lesser degrees of curvature of the C–C bonds in this molecule may be related to the rather long C_1–C_3 bond length, 1.61 Å.

(4) Bond Orders. On the basis of the calculated bond orders, which are also presented in Table II, the bond between the bridgehead carbons in bicyclobutane is predicted to be somewhat stronger than the other C–C bonds in this molecule and those in cyclopropane, all of which have essentially the same bond order.[30] The same conclusion has been reached, tentatively, through an analysis of experimental studies of the thermal isomerizations of bicyclobutane derivatives.[20,21]

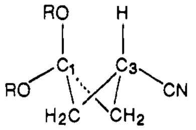
The bond orders of the C–C bonds to the methylene carbons are affected very little by substitutions at the bridgehead positions. However, the C_1–C_3 bond is again much more sensitive to this factor. The NH_2 and NCO groups, in themselves, do not significantly alter the C_1–C_3 bond order. Nitro and nitroso substitution, on the other hand, does weaken this bond, the effect increasing in going from the singly to the doubly substituted molecules.

The NH_2, NO_2 and NCO, NO_2 derivatives are of special interest because they reveal the relative roles played by the mechanisms depicted in eq 1 and 2. Our results (Table II) fully support the analysis given earlier in this paper. The NH_2, NO_2 combination produces a very marked lowering of the C_1–C_3 bond order, indicating a considerable weakening of this bond. Furthermore, the C–NH_2 and C–NO_2 bond orders are greater than their normal values, while the N–O bond orders are lower. All of this is consistent with eq 1. In contrast, a much lesser degree of bond-weakening occurs for the NCO, NO_2 derivative, as expected on the basis of the anticipated lesser availability of its nitrogen lone pair (see eq 2 and the related discussion).

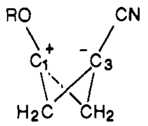
It is interesting to note a recent experimental study of the reactions of 3-halobicyclobutanecarbonitrile (II) with various alkoxides, RO^-, forming primarily the ketals III.[31] It was concluded that these processes proceed through a zwitterionic intermediate, IV, in which the original bond between the bridgehead carbons has been broken. Such a mechanism, involving electron-donor and -acceptor substituents on these carbons (RO^- and CN, respectively), is fully consistent with that shown in eq 1.



II X = Cl, Br



III



IV

Finally, it is noteworthy that the bridgehead C–H bonds are consistently stronger than the other C–H, with bond orders of approximately 1.56 for the former and 1.51 for the latter. This is in accord with the view that the bridgehead protons have some degree of vinylic character.[16]

Summary and Conclusions

By various quantitative measures—electrostatic potentials, bond deviation indices, and bond orders—the two three-membered rings in bicyclobutane have been shown to bear certain distinct similarities to cyclopropane. However, both the reactivity of bicyclobutane toward electrophiles and also the degree of strain in the molecule are greater than would be predicted on the basis of an analogy to cyclopropane. These conclusions are in accord with experimental observations.

The reactivity toward electrophiles of the carbon framework of bicyclobutane is diminished, to various extents, by all of the substituents investigated except NH_2. On the other hand, these groups introduce new reactive regions, as exemplified by the strong negative electrostatic potentials associated with the nitrogen in NH_2 and NO.

The bond between the bridgehead carbons, C_1 and C_3, is significantly weakened by the substitution of either NO or NO_2 at these positions. The most marked degree of weakening occurs, however, for the combination of NH_2 and NO_2. This finding argues against the effectiveness of amine precursors in the stepwise polynitration of strained C–C bonds. We find the isocyanate group to be clearly preferable in this respect.

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Registry No. I (X = Y = H), 157-33-5; I (X = NH_2; Y = H), 72540-66-0; I (X = Y = NH_2), 94024-08-5; I (X = NO; Y = H), 104835-36-1; I (X = Y = NO), 104835-37-2; I (X = NO_2; Y = H), 104835-38-3; I (X = Y = NO_2), 104835-39-4; I (X = NH_2; Y = NO_2), 104835-40-7; I (X = NCO; Y = H), 104835-41-8; I (X = NCO; Y = NO_2), 104835-42-9.

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