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Registry No. 1-N-1, 274-76-0; 1-N-1·$HClO_4$, 91982-01-3; 2-N-1, 274-47-5; 2-N-1·$HClO_4$, 93966-14-4; 3-N-1, 274-56-6; 3-N-1·$HClO_4$, 93966-15-5; 1,3-N-1, 274-85-1; 1,3-N-1·$HClO_4$, 93966-16-6; 1,4-N-1, 766-55-2; 1,4-N-1·$HClO_4$, 1640-77-3; 1,6-N-1, 274-79-3; 1,6-N-1·$HClO_4$, 1640-75-1; 2,3-N-1, 274-59-9; 2,3-N-1·$HClO_4$, 93966-17-7; 1,2,4-N-1, 274-83-9; 1,2,4-N-1·$HClO_4$, 93966-18-8; 1,2,6-N-1, 274-82-8; 1,2,6-N-1·$HClO_4$, 93966-19-9; 1,2,7-N-1, 274-98-6; 1,2,7-N-1·$HClO_4$, 93966-20-2; 1,3,6-N-1, 399-66-6; 1,3,6-N-1·$HClO_4$, 93966-21-3; 1,3,7-N-1, 275-02-5; 1,3,7-N-1·$HClO_4$, 93966-22-4; 1,2,3,4-N-1, 274-89-5; 1,2,3,4-N-1·$HClO_4$, 93966-23-5; 1,2,3,6-N-1, 13349-87-6; 1,2,3,6-N-1·$HClO_4$, 93966-24-6.

A Theoretical Evaluation of Substituent Effects on the Ionization Potential of Bicyclo[1.1.0]butane

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Molecular orbital calculations in the PRDDO approximation have been made for substituted bicyclo[1.1.0]butanes. The substituents are CH_3, NH_2, OH, F, and CN with all possible isomers for one to six substituents. Ionization potentials from Koopmans' theorem are discussed. In most cases, ionization is predicted to occur from the bond between the bridgehead carbons. All ionization potentials are compared to that of the parent hydrocarbon. The CH_3 substituent lowers the ionization potential in all cases with the largest decrease due to substitution at the bridgehead (1) position. The NH_2 substituent, except where ionization occurs from the amino lone pairs, lowers the ionization potential, and the largest effect is for substitution at the bridgehead carbon. For the OH substituent, ionization usually occurs from the hydroxyl lone pairs. Substitution of OH at the bridgehead carbon leads to a decrease in the ionization potential, and ionization usually occurs from the bond between the bridgehead hydrocarbons. Substitution of F at the bridgehead carbons leads to a decrease in the ionization potential while substitution at the exo or endo positions leads to an increase in the ionization potential. Substitution of CN leads to an increase in the ionization potential with substitution at the bridgehead carbon causing the smallest increase. Relative energetics for all isomers with the same number of substituents are presented. The energetics and ionization potentials are discussed in terms of the thermodynamic and kinetic stability of the compounds. It is shown that kinetic and thermodynamic stability do not necessarily follow the same trends.

Introduction

The electronic structure of strained rings has been of interest for a number of years because of the unique reactivity imparted to these molecules by the presence of bent σ bonds.[2a] One of the most interesting species is bicyclo[1.1.0]butane which has two different types of bent bonds and is highly reactive. Due to the small size of this compound, it has been studied in detail using molecular orbital theory.[2b] For example, the charge deformation density[2] has been studied theoretically as has the inversion process in bicyclo[1.1.0]butane.[3] Previous theoretical studies have shown that the HOMO is localized in the C_1–C_3 region and is composed predominantly of 2p orbitals.[4] This can be considered to be the bond connecting the two bridgeheads. An extensive study of methyl substituent effects on the ionization potential of bicyclo[1.1.0]butane determined from Koopmans' theorem has been made in conjunction with an experimental study of the electrochemical oxidation of a number of these compounds.[4] A plot of ionization potential vs. half-wave oxidation potential showed a linear relationship with correlation coefficient of $R = 0.978$; the experiments thus confirmed the prediction of the calculations at the PRDDO level.

In order to better characterize the nature of the bonding in bicyclo[1.1.0]butane, in general, and the effect of substituents on the ionization potential, in particular, we have carried out an extensive study of substituent effects on the energetics and ionization potentials of this structure in the PRDDO approximation. The substituents studied were NH_2, OH, F, and CN in addition to the previously studied CH_3 group with all possible isomers for one to six substituents having been examined.

Calculations

All calculations were performed by using the PRDDO method.[5] PRDDO is an approximate molecular orbital method employing a minimum basis set of STO's that is computationally efficient yet gives results which compare very well with ab initio minimum basis set calculations.[6] Exponents for the heavy atoms were taken from standard compilations[7] while the exponent for the 1s orbital on H

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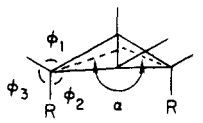
Table I. Bond Angles (deg) for Di-Endo-Substituted Derivatives

R	α	ϕ_1	ϕ_2	ϕ_3
H[a]	122.7	122.9	121.6	115.5
CH_3	135.8	116.7	131.0	112.3
NH_2	123.7	117.5	127.0	115.5
OH	121.6			
CN	123.9			

[a] Reference 8

was set at 1.2. The geometry for bicyclo[1.1.0]butane was taken from the microwave structure of Cox et al.[8] All substituents were placed along the C–H bond axis in the original unsubstituted structure at the appropriate distance except as noted below. The methyl substituents had the following geometric parameters: r(C–CH_3) = 1.54 Å, r(C–H) = 1.09 Å, and all angles at the methyl group were tetrahedral. The C–F distance was optimized at both the bridgehead and exo positions for monofluoro-substituted compounds. These parameters were then employed in all subsequent calculations for fluoro derivatives. The O–H distance in the hydroxy substituent was set at 0.96 Å, and the values for r(C–O) and θ(COH) were then optimized for substituents at both the bridgehead and exo positions. These optimized parameters were then used for the other hydroxy derivatives. The N–H bond distance (1.01 Å), θ(HNH) (105°52′), and θ(HNC) (112°03′) were taken from the experimental structure for CH_3NH_2,[10] and these values were used for all of the amino derivatives. The C–N bond distance was optimized for the bridgehead and exo-substituted mono derivatives. These optimized parameters were employed in subsequent calculations on the remaining amino derivatives. The bond distances for the cyano derivatives were set at r(C–C) = 1.458 Å and r(C–N) = 1.157 Å taken from the experimental parameters for CH_3CN.[11]

The possibility of steric interactions exists for di-endo-substituted species, leading to an increase in the value of the flap angle.



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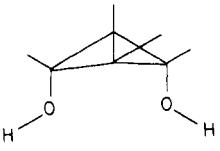
For a number of di-endo derivatives, R = CH_3, NH_2, OH, and CN the value of α was optimized as were the angles ϕ_1 and ϕ_2 as shown in Table I. For these cases, the optimum values were employed in subsequent calculations on the derivatives with two substituents in the endo position.

Results

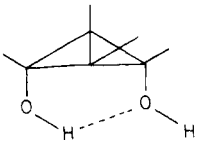
Geometries. The experimental value for the flap angle α which was employed in most of our calculations is 122.7°.[8] Optimization of α constraining the other parameters to their experimental value yields 120.4° while a complete optimization of all of the parameters in bicyclo[1.1.0]butane gives 118.9°. Optimization of α for the di-endo dimethyl derivatives gives 135.8° (see Table I). This is the most stable conformation and the two methyl groups each have two hydrogens pointing toward each other. The angles ϕ_1 and ϕ_2 (see Table I) were optimized which is equivalent to optimizing the R–C–H angle and the rocking angle of the R–C–H group. The methyl and hydrogen both rock up as compared to the parent hydrocarbon while the $C_{Me}CH$ angle decreases in comparison to the H–C–H angle in bicyclo[1.1.0]butane. Rotation barriers for a number of methyl-substituted species were also determined. The rotation barrier for a bridgehead methyl group is 1.6 kcal/mol while the value for an exo methyl group or for an endo methyl group is 2.3 kcal/mol.

The C–N distance for the amino substituent optimized to 1.44 Å independent of whether substitution was at the bridgehead or exo positions. This is similar to the optimized value of 1.45 Å found for r(C–N) in CH_3NH_2. As shown in Table I, for the di-endo derivative, the value of α increases slightly over the hydrocarbon value while ϕ_1 and ϕ_2 also show small changes. The value for α for the di-endo diamino derivative is much smaller than that found for the di-endo dimethyl derivative which demonstrates that there is not a large steric repulsion between two amino groups, when both are in endo positions. The calculated inversion barriers at N in the monosubstituted amino derivatives fall in the range of 6–7 kcal/mol. The calculated value for this barrier in CH_3NH_2 at the PRDDO level is 6.4 kcal/mol[12] in comparison with an experimental value of 4.8 kcal/mol.[13] Thus, the bicyclo[1.1.0]butane fragment has an effect similar to that of a CH_3 group on the inversion barrier at N. The lowest barrier is found for substitution at a bridgehead where the maximum configurative interaction of the lone pair on nitrogen with a p-type orbital (the bond between the bridgehead carbons) of the bicyclo[1.1.0]butane is found. (In vinylamine, conjugation of the lone pair with the π orbital leads to a significant decrease in the inversion barrier at N.[14])

The C–O bond lengths for the hydroxyl derivatives are 1.38 Å (bridgehead) and 1.39 Å (exo) in comparison to the PRDDO optimized value of 1.41 Å found for r(C–O) in CH_3OH.[15] Thus the C–O bonds shorten when the bicyclo[1.1.0]butyl fragment is substituted for methyl. The optimized values for θ(COH) are 107° in good agreement with the calculated value of 106.3° found for θ(COH) in CH_3OH at the PRDDO level.[15] Optimization of θ for the di-endo derivative (Table I) shows very little change from the value in the parent hydrocarbon. This was found for the orientation with the hydrogens pointing away from each other. There is the possibility that a hydrogen bond



2a



2b

can be formed between the H on one OH group and the O on an adjacent group. Such a structure is found to be 4.5 kcal/mol more stable than the one used in our calculations. However, such a structure, **2b**, does not provide as good a measure of the electronic effects of OH group as does structure **2a**. A minimum basis set tends to overestimate charge transfer and hydrogen bond strengths.

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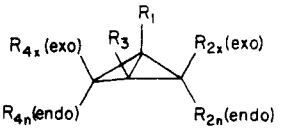
Table II. Ionization Potentials (eV) and Relative Energy Differences (kcal/mol) for Substituted Bicyclo[1.1.0]butanes



substitution pattern						X = methyl		X = amino		X = hydroxyl		X = fluoro		X = cyano	
1	2x	2n	3	4x	4n	IP[a]	ΔE[b]	IP[a]	ΔE[b]	IP[a]	ΔE[b]	IP[a]	ΔE[b]	IP[a]	ΔE[b]
H	H	H	H	H	H	8.97		8.97		8.97		8.97		8.97	
monosubstituted															
X	H	H	H	H	H	8.66	0.0	7.46	3.5	8.59	0.4	8.66	6.7	9.32	0.0
H	X	H	H	H	H	8.92	2.0	8.65	1.7	9.03	1.1	9.30	2.2	9.80	5.5
H	H	X	H	H	H	8.80	6.6	8.95	0.0	9.13	0.0	9.42	0.0	9.86	5.8
disubstituted															
X	H	H	X	H	H	8.24	0.0	6.35	8.2	8.10	2.8	8.15	17.2	9.54	0.0
X	X	H	H	H	H	8.58	2.2	7.32	4.3	8.61	2.3	8.95	11.0	9.93	4.7
H	X	H	H	X	H	8.88	3.2	8.53	2.3	9.00 (9.09)[c]	2.5	9.65	5.3	10.57	8.4
X	H	X	H	H	H	8.48	6.0	7.39	2.9	8.71	0.5	9.04	7.4	10.00	4.4
H	X	X	H	H	H	8.77	7.7	8.68 (8.98)[c]	0.0	9.26 (9.27)[c]	0.2	9.74	0.0	10.59	13.6
H	X	H	H	H	X	8.77	8.8	8.47	0.6	9.13 (9.17)[c]	0.8	9.75	2.9	10.63	8.9
H	H	X	H	H	X	8.58	16.6	7.89 (9.17)[c]	1.1	9.07 (9.41)[c]	0.0	9.91	1.2	10.77	9.3
trisubstituted															
X	X	H	H	X	H	8.53	0.0	7.20	4.5	8.58 (8.64)[c]	5.2	9.25	15.5	10.50	4.3
X	X	H	X	H	H	8.20	0.8	6.26	8.6	8.15	6.0	8.46	21.7	10.06	1.1
X	H	X	X	H	H	8.15	1.2	6.35	6.9	8.30	2.6	8.60	16.4	10.17	0.0
X	X	X	H	H	H	8.46	3.6	7.35	2.3	8.79	1.8	9.34	7.6	10.54	8.6
X	X	H	H	H	X	8.44	3.7	7.28	3.0	8.66 (8.74)[c]	2.5	9.34	10.5	10.58	4.1
H	X	X	H	X	H	8.75	4.5	8.43 (9.38)[c]	0.0	8.85 (9.30)[c]	1.4	10.06	1.7	11.29	11.8
X	H	X	H	H	X	8.31	12.6	7.54	3.2	8.60 (8.93)[c]	0.7	9.46	7.5	10.70	3.9
H	X	X	H	H	X	8.58	15.0	7.96 (9.19)[c]	1.2	8.87 (9.56)[c]	0.0	10.24	0.0	11.37 (11.49)[c]	13.4
tetrasubstituted															
X	X	H	X	X	H	8.16	0.0	6.18	7.7	8.20	9.1	8.77	27.4	10.55	1.5
X	X	X	X	H	H	8.12	2.6	6.31	5.7	8.42	4.5	8.88	18.9	10.62	5.0
X	X	H	X	H	X	8.12	2.7	6.27	6.0	8.29 (8.34)[c]	5.1	8.90	21.9	10.66	0.6
X	X	X	H	X	H	8.43	4.2	7.24	1.0	8.36 (8.85)[c]	3.6	9.64	11.8	11.07	7.8
X	H	X	X	H	X	8.02	11.6	6.53	5.7	8.24 (8.58)[c]	2.2	9.04	17.3	10.80	0.0
H	X	X	H	X	X	8.60	16.2	7.93 (9.22)[c]	0.0	8.58 (9.71)[c]	0.0	10.57	0.0	11.59 (12.13)[c]	17.1
X	X	X	H	H	X	8.31	17.2	7.50	1.6	8.38 (9.05)[c]	1.1	9.77	8.6	11.22	9.0
pentasubstituted															
X	X	X	X	X	H	8.10	0.0	6.24	4.7	7.98 (8.46)[c]	5.3	9.19	14.7	11.08	0.0
X	X	X	X	H	X	8.01	15.7	6.49	4.9	8.00 (8.71)[c]	1.6	9.33	9.8	11.23	0.7
X	X	X	H	X	X	8.31	17.9	7.46	0.0	8.12 (9.16)[c]	0.0	10.08	0.0	11.69	8.6
hexasubstituted															
X	X	X	X	X	X	8.00		6.45		7.74 (8.84)		9.63		11.63	

[a] Ionization potential in eV. [b] ΔE is calculated relative to the most stable isomer with the same number of substituents in kcal/mol. [c] Values in parentheses are for ionization from the bridgehead bond. Ionization for these molecules is predicted to occur from the substituent orbitals.

This can lead to variations in the ionization potentials of the oxygen lone pairs that are too large. Furthermore, structure **2a** will be a better model for the ether-type substituents where hydrogen bonds will not form that are most likely to be encountered experimentally. For the trisubstituted hydroxy derivative with one bridgehead and an exo-2, endo-2 substitution pattern the rotation barrier was found to be 3.8 kcal/mol for the exo hydroxyl.

Optimization of the C–F bond length gives a value of 1.36 Å at either the bridgehead or the exo position. No optimization of was carried out since only a small interaction of the two fluorines was expected.

Optimization of α for the di-endo cyano derivative gives 123.9°, slightly larger than the value found for bicyclo[1.1.0]butane. The rocking motion of the CHCN fragments is highly coupled to the value of α with the exo hydrogen moving toward the bridgehead bond.

Energetics and Ionization Potentials. The relative energetics and ionization potentials determined from Koopmans' theorem for the different substituents are given in Table II. Only qualitative predictions of the energetics can be made since full geometry optimization of each isomer was not performed and large basis sets were not employed. However, we do expect that the general trends will be correct. We note that the ionization potential from Koopmans' theorem is a vertical ionization potential and assumes that the geometry does not change significantly during the ionization process. As discussed below, this is a reasonable assumption for bicyclo[1.1.0]butane. Whether this will hold true for all substituted species will be discussed below. The substituents can affect both the thermodynamic and kinetic stability of the substituted bicyclo[1.1.0]butanes. In what follows we define thermodynamic stability in terms of the relative energetics for a given set of isomers. Kinetic stability or reactivity, in part, is related to the ease of oxidation of these molecules, and thus a lower ionization potential corresponds to a molecule that is more easily oxidized and is more reactive.

The results for the methyl substituent are summarized in Table II. The general energetic trend for all isomers with the same number of substituents is that substitution at the bridgehead leads to the most thermodynamically

stable isomer while substitution at the endo position leads to the most thermodynamically unstable isomer. Compounds with two endo substituents are always the most unstable isomers. Steric repulsions between the two methyl groups force the flap angle to increase. The energy required to increase α from 118.9 to 138.9° with subsequent optimization of all remaining geometric parameters is 15.5 kcal/mol at the Hartree-Fock level in the PRDDO approximation. This angular distortion accounts for the increase in energy found for the di-endo derivatives. The Hartree-Fock calculation is an overestimate of the actual energy increase since a generalized valence bone (GVB) calculation where the bridgehead bond pair is split leads to an energy increase of only 9.5 kcal/mol.[3]

The general trend in ionization potentials is that methyl substitution lowers the ionization potential. Substitution of a methyl at the bridgehead position lowers the ionization potential by the largest amount. Substitution at the endo position also leads to a decrease while substitution at the exo position only introduces a small change in the ionization potential. The various effects are approximately additive, and the lowest ionization potential is expected for the hexamethyl derivative with a decrease of 0.97 eV relative to that of the parent bicyclo[1.1.0]butane. Rotation of a methyl group causes only a small change in the ionization potential. The largest effect due to rotation observed for the monosubstituted derivatives was a decrease of 0.05 eV for bridgehead substitution. However, these changes imply that the measurement of a sharp onset in a photoelectron spectrum may be difficult.

In order to examine whether the prediction of changes in ionization potentials due to substituent effects would be strongly dependent on the geometry of the parent hydrocarbon, we optimized the geometry of bicyclo[1.1.0]-butane. The calculated ionization potential using this geometry is 9.46 eV. Methyl substitutents were then added at the exo, endo, or bridgehead positions, and the ionization potentials were calculated. The changes in ionization potential relative to that of the parent hydrocarbon are decreases of 0.31, 0.04, and 0.18 eV for the bridgehead, exo, and endo isomers, respectively. These decreases should be compared to the changes of 0.31, 0.08, and 0.17 eV determined using the experimental bicyclo[1.1.0]butane geometry. This demonstrates that our predictions are not strongly dependent on the structure of the parent hydrocarbon.

The results for amino substitution can be found in Table II. Substitution of one amino group leads to the endo isomer being the most thermodynamically stable and the bridgehead isomer being the least thermodynamically stable. This pattern continues for the disubstituted compounds and the derivative with two amino groups substituted at the bridgehead is the least thermodynamically stable. In general, compounds with exo groups are energetically less stable than compounds with endo amino substituents. For isomers with only one bridgehead amino group, the energy differences are quite small.

Substitution of an amino group in the endo position leads to essentially no change in the ionization potential (a small increase of 0.02 eV) while substitution at the exo position introduces a decrease of 0.34 eV. Monosubstitution at the bridgehead leads to a very large decrease of 1.51 eV. The disubstituted compounds show a similar trend with the compound with two bridgehead amino groups having the lowest ionization potential, a decrease of 1.11 eV over the monosubstituted bridgehead compound. For two of the disubstituted compounds, the di-endo derivative and the exo-2, endo-2 derivative, ionization is predicted to occur from an orbital composed essentially of nitrogen atomic orbitals (lone pair orbitals) rather than from the bridgehead C–C bond. The ionization potential for CH_3NH_2 (8.97 eV, experiment 16; 8.97 eV, PRDDO) is comparable to that of bicyclo[1.1.0]butane. Thus competition for ionization between the amino group lone pair and the bond between the bridgehead atoms will occur. In the cases where ionization is from the amino substituent, which occur only if the amino is not substituted at a bridgehead carbon, the bicyclo[1.1.0]butane skeleton is acting as more of an electronic donor than does a methyl group. The ionization potential for removal of an electron from the C_1–C_3 bond of the bicyclo[1.1.0]butane structure is given in parentheses and is comparable to or slightly larger than the ionization potential of the parent hydrocarbon. This is not inconsistent with the results discussed above where endo substitution has little effect on the ionization potential and the effect of the exo substituents is moderated somewhat because the C_1–C_3 bond is no longer associated with the HOMO. The increase is presumably due to the electron-withdrawing properties of the amino group when the amino group is in a position that would not allow donation of the nonbonding electron on nitrogen to the cation radical generated by removal of an electron from the C_1–C_3 bond. Both the tri- and tetrasubstituted compounds show a similar phenomena of ionization from nitrogen orbitals when there are no bridgehead amino groups. The ionization potential for electrons from the bridgehead bonding orbitals tend to be somewhat higher than that for bicyclo[1.1.0]butane. This result reinforces the above arguments. The lowest ionization potential for all of the amino derivatives is for the tetrasubstituted (dibridgehead, di-exo) derivative where the ionization potential (from the C_1–C_3 bond) has decreased by 2.79 eV over that for the parent hydrocarbon. For amino substitution, the decreases in ionization potential correlate for the most part with the decreases in stability within a group of isomers. The change in ionization potential due to planarity at nitrogen was also investigated for the monosubstituted amino derivatives. The ionization potentials all decrease by a significant amount: bridgehead, 0.51 eV; exo, 0.37 eV; endo, 0.69 eV. The ionization in the planar form now occurs from an orbital composed of predominantly nitrogen character for the endo and exo isomers while the orbital for the bridgehead isomer (at C_1) is composed of nitrogen and C_2 bridgehead bond character. Such a decrease in ionization potential has been previously observed in other planar amines.[12,16]

The results for substitution of hydroxyl groups are given in Table II. Substitution of a hydroxyl group leads to very small energy differences for the mono- and disubstituted derivatives. Substitution of two OH groups at the bridge-head leads to the most thermodynamically unstable isomer for the disubstituted derivatives. The di-endo derivative is the most thermodynamically stable. This thermodynamic stability can be enhanced by up to 4.5 kcal/mol by forming a hydrogen bond between the two endo OH groups. For the remaining isomers with three to five OH groups, the compounds with two endo hydroxyl groups remain the most thermodynamically stable. The substitution of two OH groups at the bridgehead positions leads to the least thermodynamically stable compounds as long as the maximum number of exo hydroxyl groups are also present within a set of isomers.

The ionization potentials for hydroxyl substitution show some interesting trends. Substitution of a single hydroxyl

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group at the bridgehead leads to a decrease of 0.38 eV while substitution at the exo and endo positions leads to an increase of 0.06 and 0.16 eV, respectively. Increasing the number of substituents at bridgehead positions to two lowers the ionization potential by an additional 0.49 eV while hydroxyl substitution at the exo or endo positions with one bridgehead hydroxyl group raises the ionization potential above the value found with a single bridgehead hydroxyl substituent. Substitution at the endo position leads to a larger increase than does substitution at the exo position. This is presumably due to the electron-withdrawing power of the hydroxyl group when it is not directly bonded to C_1 or C_3. If no bridgehead substituents are present, ionization is predicted to occur from orbitals localized on the oxygen for the disubstituted compounds. This is consistent with the result observed for amino substitution although it may arise from a somewhat different physical phenomenon. The ionization potential of CH_3OH (10.83 eV, experiment 16; 10.11, PRDDO) is much higher than that of CH_3NH_2 or bicyclo[1.1.0]butane. It must be the antibonding combination of the large number of lone pairs present on more than one oxygen that leads to the significant decrease in ionization potential and to the switch of the HOMO from the C_1–C_3 bond to the lone pairs on the oxygens. Ionization occurs from the bridgehead C–C bond for trisubstituted hydroxyl derivatives only if two bridgehead groups are present or for the monobridgehead, exo-2, endo-2 isomer. Otherwise, ionization is predicted to occur from oxygen orbitals. A similar result is observed for the tetrasubstituted species while for the penta- and hexasubstituted derivatives, ionization is only observed from oxygen orbitals.

Formation of the hydrogen bond in the di-endo isomer leads to a large decrease in the ionization potential (0.62 eV) although ionization is still predicted to occur from oxygen orbitals. Rotation of the exo OH group (which does not form a strong hydrogen bond) in the bridgehead-1, exo-2, endo-2 trisubstituted derivative leads to a much smaller change with a maximum increase of 0.13 eV.

The fluorine substituent exhibits simple trends as shown in Table II. The endo-substituted compound is the most thermodynamically stable energetically while the bridgehead-substituted compound is the least stable. This pattern continues for the other higher substituted derivatives. A very large energy difference is observed for the dibridgehead, di-exo tetrasubstituted derivative as compared to the di-exo, di-endo tetrasubstituted derivative.

Substitution of fluorine at the bridgehead also leads to a decrease in the ionization potential, 0.33 eV for one substituent and an additional 0.49 eV for a second fluorine. Substitution at the endo and exo positions leads to increases in the ionization potential of 0.45 and 0.33 eV, respectively. This is consistent with expectation given above based on electronegativity considerations and the ability of the heteroatom to donate nonbonding electrons to stabilize the cation radical when directly attached to the bridgehead position. Derivatives with more substituents show the same patterns, and the results are essentially additive. In general, this leads to an increase in the ionization potential over that of the hydrocarbons, and, thus, the lowest ionization potential is found for the dibridgehead-substituted derivative.

The results for the cyano substituent are shown in Table II. It is energetically most favorable for the cyano to be substituted at the bridgehead position for monosubstitution while substitution at the endo or exo positions produces derivatives with significantly higher energies. A similar result is found for disubstituted compounds with the exo-2, endo-2 derivative being the least stable. The same pattern is followed for the higher substituted derivatives.

Substitution of cyano for hydrogen results in an increase in the ionization potential. The smallest increase is observed for substitution at the bridgehead (0.35 eV) while much larger increases are found for substitution at the exo (0.83 eV) and endo (0.89 eV) positions. This pattern is continued for the systems with a higher degree of substitution except for the exo-2, endo-2, endo-4 trisubstituted derivative and the di-exo, di-endo tetrasubstituted derivative. For these compounds, ionization is predicted to occur from the cyano orbitals, equally from all cyanos for the latter and predominantly from the endo-4-position for the former. For these compounds bridgehead cyano groups are absent and they are the most unstable isomers of their respective groups. Furthermore, ionization from the C_1–C_3 bond should be competitive with ionization from the cyano groups in the trisubstituted compound. In the penta- and hexasubstituted cyano derivatives, the trends observed above are followed. Since a bridgehead substituent is always present, ionization will occur from the C_1–C_3 bond. The presence of the bridgehead substituent also moderates the effects of the endo and exo substituents on the increase in the ionization potential, and the largest ionization potential is actually predicted for a pentasubstituted isomer.

Discussion

Koopmans' theorem corresponds to a vertical process where there is no geometry change on ionization. An important consideration is the difference between the vertical and adiabatic energies where the latter energy is the difference between the optimal structures of the neutral and the ion. For bicyclo[1.1.0]butane, calculations were performed on the radical ion at the RHF level. The ion with the neutral geometry was 4 kcal/mol lower in energy than an ion with planar bridgehead carbons (a radical center and a cation center) and 11 kcal/mol lower than an ion with a planar carbon ring structure. The vertical process yields a structure quite close to that of the optimal structure of the radical cation and the vertical, and adiabatic IP's should be very similar. The wave function for the radical ion has the unpaired electron still localized in the orbital between the bridgehead carbons. This provides further support for the identification and location of the HOMO in the bicyclo[1.1.0]butanes.[3,4] The nonplanarity of the bridgehead carbons is not surprising since the one electron bond is retained.[4] A similar result of nonplanar radical centers is also found in the diradical corresponding to the planar carbon ring leading to inversion in bicyclo[1.1.0]butane.[3]

Calculations were performed on the radical cations of the monomethyl-substituted bicyclo[1.1.0]butanes in order to demonstrate that the dependence of the ionization potential on the substituents remains in a direct calculation of the vertical process. The direct calculation of the ionization process shows that the vertical IP for the exo isomer is 0.13 eV below that of bicyclo[1.1.0]butane while that of the endo isomer is 0.26 eV below that of the parent hydrocarbon. The vertical IP of the bridgehead isomer is 0.38 eV below that of bicyclo[1.1.0]butane. Exactly the same trends are given by the use of Koopmans' theorem further justifying our use of Koopmans' theorem for describing the vertical ionization process.

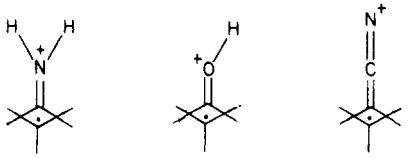
Although the vertical and adiabatic IP's should be similar for the methyl and fluoro substituents, a larger difference between the two values may be found for the monosubstituted compounds with amino, hydroxyl, and cyano groups at the bridgehead. This arises because al-

Table III. Trends in Ionization Potential and Energies for the Monosubstituted Derivatives

subst	IP[a,b]	energy ordering[b,c]
CH_3	BH < endo < exo	endo < exo < BH
NH_2	BH < exo < endo	BH < exo < endo
OH	BH < exo < endo	exo < BH < endo
F	BH < exo < endo	BH < exo < endo
CN	BH < exo < endo	endo < exo < BH

[a] BH = bridgehead. [b] Lowest ionization potential (IP) given first. [c] Least stable compound given first.

ternate resonance structures can be found for these compounds as shown in **3–5**. In these cases, the positive charge



3 **4** **5**

can be stabilized on an alternate center to form an iminium ion, **3**, and an oxonium ion, **4**. The resonance structure **5** will only be a partial contributor as has previously established for simple cyano-substituted carbonium ions.[17] For R_2C^+CN ions, the C_N–C bond has partial double-bond character while the $C_N{\equiv}N$bond has less than triple-bond character. The strain in the ring may not favor formation of an exocyclic double bond leading to a smaller contribution from resonance structure **5**. The additional strain of an exocyclic double bond may also play a role in lowering the contribution of the iminium and onium resonance structures. It is well established that the $R_2C{=}NH_2^+$ and $R_2C{=}OH^+$ do have essentially C=N and C=O bonds.[14,18] Thus, the actual interplay between ring strain, radical stabilization, and the desire to have iminium and onium resonance structures will lead to the best description of the ionic structures.

Examination of the trends in IP's for the monosubstituted derivatives, as shown in Table III, shows the following order *bridgehead* < *exo* < *endo*. The only exception is found in the methyl derivatives where the ordering of the exo and endo isomers is reversed. In all cases, the lowest ionization potential is always for the bridgehead substituents. This does not necessarily imply that the bridgehead substituent has the largest effect on the IP when compared to the parent hydrocarbon. The bridgehead cyano substitutent has the smallest effect on the IP while the fluoro substituents change the IP's by approximately the same amount. We note that in these latter two cases the exo and endo substituents actually increase the IP when compared to that of bicyclo[1.1.0]butane.

The variation in relative stabilization energies for the monosubstituted derivatives shows that the exo substituent occupies the central position (for the hydroxy case, the energies are all within ~1 kcal/mol). For the methyl and cyano substituents, bridgehead substitution gives the most stable structure, while for the amino and fluoro substituents, the endo-substituted compounds are the most stable. These results illustrate that energetic thermodynamic stability and chemical reactivity (i.e., oxidative reactivity) do not necessarily follow the same trends.

Dill et al.[19] have discussed the effect of substituents on strain energies and have performed some ab initio STO-3G calculations on simple substituted bicyclo[1.1.0]butanes. For the monosubstituted derivatives, they find that the strain energies for the methyl and fluoro substituents at the bridgehead are greater than those at the exo position. For the cyano substituent the strain energies are reversed. Our relative stabilization energies give the bridgehead more stable than the exo position for the methyl and cyano substituents and the reverse for the fluoro substituents. Our energy differences are also larger than their values. For the difluoro-substituted compounds Dill et al.[19] find the strain energies of the 1,2, 1,3, and 2,4 isomers to be within 4 kcal/mol. We find that the energy differences between the isomers is ~12 kcal/mol. Whether we are comparing the same quantities is difficult to judge since their strain energies may be based on different fluorobutane isomers. We note that Dill et al. focus on substituent effects on the strain energy while our focus has been on the oxidation related properties of these molecules. Dill et al. show that all substituents lower the strain energy of bicyclo[1.1.0]butane relative to hydrogen as a substituent. We find that only cyano raises the IP (increases oxidative stability) for the bicyclo[1.1.0]butanes. This simply illustrates that changes in strain energy may not correlate well with the oxidative stability (or with other types of chemical reactivity) of a compound. Furthermore, simple models based on σ and π donation and acceptance in the ground state may not accurately predict variations in ionization potentials since stabilizations in the ion must also be considered.

In summary, our calculations have provided an insight into the influence of a series of "first-row" substituents on the stability and reactivity of the bicyclo[1.1.0]butane ring system. In many regards, our data support the concept, which is based on limited experimental data, that there is not a direct relationship between thermodynamic stability of a strained polycyclic molecule and its chemical reactivity. Many types of chemical reactivity (e.g., ease of oxidation) depend on the energy of the highest occupied molecular orbital (HOMO). What should be stressed is that there is not a uniform or direct relationship between the energy of the HOMO and the overall energy of the molecule. We believe that our calculations on the bicyclo[1.1.0]butane system clearly illustrate the point for this system.

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Registry No. Bicyclo[1.1.0]butane, 157-33-5; 1-methylbicyclo[1.1.0]butane, 30494-08-7; *exo*-2-methylbicyclo[1.1.0]butane, 20831-04-3; *endo*-2-methylbicyclo[1.1.0]butane, 20831-03-2; 1,3-dimethylbicyclo[1.1.0]butane, 930-25-6; *exo*-1,2-dimethylbicyclo[1.1.0]butane, 72213-01-5; *exo,exo*-2,4-dimethylbicyclo[1.1.0]butane, 20831-02-1; *endo*-1,2-dimethylbicyclo[1.1.0]butane, 72244-53-2; 2,2-dimethylbicyclo[1.1.0]butane, 72213-00-4; *exo,endo*-2,4-dimethylbicyclo[1.1.0]butane, 20991-80-4; *endo,endo*-

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2,4-dimethylbicyclo[1.1.0]butane, 72244-54-3; *exo,exo*-1,2,4-trimethylbicyclo[1.1.0]butane, 72213-02-6; *exo*-1,2,3-trimethylbicyclo[1.1.0]butane, 72213-03-7; *endo*-1,2,3-trimethylbicyclo[1.1.0]butane, 94130-86-6; 1,2,2-trimethylbicyclo[1.1.0]butane, 28569-96-2; *exo,endo*-1,2,4-trimethylbicyclo[1.1.0]butane, 72244-55-4; *exo*-2,2,4-trimethylbicyclo[1.1.0]butane, 72213-04-8; *endo,endo*-1,2,4-trimethylbicyclo[1.1.0]butane, 72244-56-5; *endo*-2,2,4-trimethylbicyclo[1.1.0]butane, 72244-57-6; *exo,exo*-1,2,3,4-tetramethylbicyclo[1.1.0]butane, 72213-05-9; 1,2,2,3-tetramethylbicyclo[1.1.0]butane, 32348-64-4; *exo,endo*-1,2,3,4-tetramethylbicyclo[1.1.0]butane, 72257-48-8; *exo*-1,2,2,4-tetramethylbicyclo[1.1.0]butane, 72213-06-0; *endo,endo*-1,2,3,4-tetramethylbicyclo[1.1.0]butane, 72257-49-9; 2,2,4,4-tetramethylbicyclo[1.1.0]butane, 30494-12-3; *endo*-1,2,2,4-tetramethylbicyclo[1.1.0]butane, 72257-50-2; *exo*-1,2,2,3,4-pentamethylbicyclo[1.1.0]butane, 72213-07-1; *endo*-1,2,2,3,4-pentamethylbicyclo[1.1.0]butane, 72257-51-3; 1,2,2,4,4-pentamethylbicyclo[1.1.0]butane, 24133-00-4; hexamethylbicyclo[1.1.0]butane, 20019-13-0; 1-aminobicyclo[1.1.0]butane, 72540-66-0; *exo*-2-aminobicyclo[1.1.0]butane, 94024-07-4; *endo*-2-aminobicyclo[1.1.0]butane, 94130-87-7; 1,3-diaminobicyclo[1.1.0]butane, 94024-08-5; *exo*-1,2-diaminobicyclo[1.1.0]butane, 94024-09-6; *exo,exo*-2,4-diaminobicyclo[1.1.0]butane, 94024-10-9; *endo*-1,2-diaminobicyclo[1.1.0]butane, 94130-88-8; 2,2-diaminobicyclo[1.1.0]butane, 94024-11-0; *exo,endo*-2,4-diaminobicyclo[1.1.0]butane, 94130-89-9; *endo,endo*-2,4-diaminobicyclo[1.1.0]butane, 94130-90-2; *exo,exo*-1,2,4-triaminobicyclo[1.1.0]butane, 94024-12-1; *exo*-1,2,3-triaminobicyclo[1.1.0]butane, 94024-13-2; *endo*-1,2,3-triaminobicyclo[1.1.0]butane, 94130-91-3; 1,2,2,-triaminobicyclo[1.1.0]butane, 94024-14-3; *exo,endo*-1,2,4-triaminobicyclo[1.1.0]butane, 94130-92-4; *exo*-2,2,4-triaminobicyclo[1.1.0]butane, 94024-15-4; *endo,endo*-1,2,4-triaminobicyclo[1.1.0]butane, 94130-93-5; *endo*-2,2,4-triaminobicyclo[1.1.0]butane, 94130-94-6; *exo,exo*-1,2,3,4-tetraaminobicyclo[1.1.0]butane, 94024-16-5; 1,2,2,3-tetraaminobicyclo[1.1.0]butane, 94024-17-6; *exo,endo*-1,2,3,4-tetraaminobicyclo[1.1.0]butane, 94130-95-7; *exo*-1,2,2,4-tetraaminobicyclo[1.1.0]butane, 94024-18-7; *endo,endo*-1,2,3,4-tetraaminobicyclo[1.1.0]butane, 94130-96-8; 2,2,4,4-tetraaminobicyclo[1.1.0]butane, 94024-19-8; *endo*-1,2,2,4-tetraaminobicyclo[1.1.0]butane, 94130-97-9; *exo*-1,2,2,3,4-pentaaminobicyclo[1.1.0]butane, 94024-20-1; *endo*-1,2,2,3,4-pentaaminobicyclo[1.1.0]butane, 94130-98-0; 1,2,2,4,4-pentaaminobicyclo[1.1.0]butane, 94024-21-2; hexaaminobicyclo[1.1.0]butane, 94024-22-3; 1-hydroxybicyclo[1.1.0]butane, 72507-62-1; *exo*-2-hydroxybicyclo[1.1.0]butane, 94024-23-4; *endo*-2-hydroxybicyclo[1.1.0]butane, 94130-99-1; 1,3-dihydroxybicyclo[1.1.0]butane, 94024-24-5; *exo*-1,2-dihydroxybicyclo[1.1.0]butane, 94024-25-6; *exo,exo*-2,4-dihydroxybicyclo[1.1.0]butane, 94024-26-7; *endo*-1,2-dihydroxybicyclo[1.1.0]butane, 94131-00-7; 2,2-dihydroxybicyclo[1.1.0]butane, 94024-27-8; *exo,endo*-2,4-dihydroxybicyclo[1.1.0]butane, 94131-01-8; *endo,endo*-2,4-dihydroxybicyclo[1.1.0]butane, 94131-02-9; *exo,exo*-1,2,4-trihydroxybicyclo[1.1.0]butane, 94131-75-6; *exo*-1,2,3-trihydroxybicyclo[1.1.0]butane, 94024-28-9; *endo*-1,2,3-trihydroxybicyclo[1.1.0]butane, 94131-03-0; 1,2,2-trihydroxybicyclo[1.1.0]butane, 94024-29-0; *exo,endo*-1,2,4-trihydroxybicyclo[1.1.0]butane, 94024-30-3; *exo*-2,4,4-trihydroxybicyclo[1.1.0]butane, 94024-31-4; *endo,endo*-1,2,4-trihydroxybicyclo[1.1.0]butane, 94131-04-1; *endo*-2,2,4-trihydroxybicyclo[1.1.0]butane, 94131-05-2; *exo,exo*-1,2,3,4-tetrahydroxybicyclo[1.1.0]butane, 94024-32-5; 1,2,2,3-tetrahydroxybicyclo[1.1.0]butane, 94024-33-6; *exo,endo*-1,2,3,4-tetrahydroxybicyclo[1.1.0]butane, 94131-06-3; *exo*-1,2,2,4-tetrahydroxybicyclo[1.1.0]butane, 94024-34-7; *endo,endo*-1,2,3,4-tetrahydroxybicyclo[1.1.0]butane, 94131-07-4; 2,2,4,4-tetrahydroxybicyclo[1.1.0]butane, 94024-35-8; *endo*-1,2,2,4-tetrahydroxybicyclo[1.1.0]butane, 94131-08-5; *exo*-1,2,2,3,4-pentahydroxybicyclo[1.1.0]butane, 94024-36-9; *endo*-1,2,2,3,4-pentahydroxybicyclo[1.1.0]butane, 94131-09-6; 1,2,2,4,4-pentahydroxybicyclo[1.1.0]butane, 94024-37-0; hexahydroxybicyclo[1.1.0]butane, 94024-63-2; 1-fluorobicyclo[1.1.0]butane, 72507-63-2; *exo*-2-fluorobicyclo[1.1.0]butane, 72507-64-3; *endo*-2-fluorobicyclo[1.1.0]butane, 94131-76-7; 1,3-difluorobicyclo[1.1.0]butane, 72507-81-4; *exo*-1,2-difluorobicyclo[1.1.0]butane, 94131-10-9; *exo,exo*-2,4-difluorobicyclo[1.1.0]butane, 94131-11-0; *endo*-1,2-difluorobicyclo[1.1.0]butane, 94131-12-1; 2,2-difluorobicyclo[1.1.0]butane, 94024-38-1; *exo,endo*-2,4-difluorobicyclo[1.1.0]butane, 94131-13-2; *endo,endo*-2,4-difluorobicyclo[1.1.0]butane, 94131-14-3; *exo,exo*-1,2,4-trifluorobicyclo[1.1.0]butane, 94131-77-8; *exo*-1,2,3-trifluorobicyclo[1.1.0]butane, 94024-39-2; *endo*-1,2,3-trifluorobicyclo[1.1.0]butane, 94131-15-4; 1,2,2-trifluorobicyclo[1.1.0]butane, 94024-40-5; *exo,endo*-1,2,4-trifluorobicyclo[1.1.0]butane, 94024-41-6; *exo*-2,2,4-trifluorobicyclo[1.1.0]butane, 94024-42-7; *endo,endo*-1,2,4-trifluorobicyclo[1.1.0]butane, 94131-16-5; *endo*-2,2,4-trifluorobicyclo[1.1.0]butane, 94131-17-6; *exo,exo*-1,2,3,4-tetrafluorobicyclo[1.1.0]butane, 94024-43-8; 1,2,2,3-tetrafluorobicyclo[1.1.0]butane, 94024-44-9; *exo,endo*-1,2,3,4-tetrafluorobicyclo[1.1.0]butane, 94131-18-7; *exo*-1,2,2,4-tetrafluorobicyclo[1.1.0]butane, 94024-45-0; *endo,endo*-1,2,3,4-tetrafluorobicyclo[1.1.0]butane, 94131-19-8; 2,2,4,4-tetrafluorobicyclo[1.1.0]butane, 94024-46-1; *endo*-1,2,2,4-tetrafluorobicyclo[1.1.0]butane, 94131-20-1; *exo*-1,2,2,3,4-pentafluorobicyclo[1.1.0]butane, 94024-47-2; *endo*-1,2,2,3,4-pentafluorobicyclo[1.1.0]butane, 94131-21-2; 1,2,2,4,4-pentafluorobicyclo[1.1.0]butane, 94024-48-3; hexafluorobicyclo[1.1.0]butane, 94024-64-3; 1-cyanobicyclo[1.1.0]butane, 16955-35-4; *exo*-2-cyanobicyclo[1.1.0]butane, 72507-60-9; *endo*-2-cyanobicyclo[1.1.0]butane, 72523-90-1; 1,3-dicyanobicyclo[1.1.0]butane, 27184-67-4; *exo*-1,2-dicyanobicyclo[1.1.0]butane, 94024-49-4; *exo,exo*-2,4-dicyanobicyclo[1.1.0]butane, 94024-50-7; *endo*-1,2-dicyanobicyclo[1.1.0]butane, 94131-22-3; 2,2-dicyanobicyclo[1.1.0]butane, 94024-51-8; *exo,endo*-2,4-dicyanobicyclo[1.1.0]butane, 94131-23-4; *endo,endo*-2,4-dicyanobicyclo[1.1.0]butane, 94131-24-5; *exo,exo*-1,2,4-tricyanobicyclo[1.1.0]butane, 94024-52-9; *exo*-1,2,3-tricyanobicyclo[1.1.0]butane, 94024-53-0; *endo*-1,2,3-tricyanobicyclo[1.1.0]butane, 94131-25-6; 1,2,2-tricyanobicyclo[1.1.0]butane, 94024-54-1; *exo,endo*-1,2,4-tricyanobicyclo[1.1.0]butane, 94131-26-7; *exo*-2,2,4-tricyanobicyclo[1.1.0]butane, 94024-55-2; *endo,endo*-1,2,4-tricyanobicyclo[1.1.0]butane, 94131-27-8; *endo*-2,2,4-tricyanobicyclo[1.1.0]butane, 94131-28-9; *exo,exo*-1,2,3,4-tetracyanobicyclo[1.1.0]butane, 94024-56-3; 1,2,2,3-tetracyanobicyclo[1.1.0]butane, 94024-57-4; *exo,endo*-1,2,3,4-tetracyanobicyclo[1.1.0]butane, 94131-29-0; *exo*-1,2,2,4-tetracyanobicyclo[1.1.0]butane, 94024-58-5; *endo,endo*-1,2,3,4-tetracyanobicyclo[1.1.0]butane, 94131-30-3; 2,2,4,4-tetracyanobicyclo[1.1.0]butane, 94024-59-6; *endo*-1,2,2,4-tetracyanobicyclo[1.1.0]butane, 94131-31-4; *exo*-1,2,2,3,4-pentacyanobicyclo[1.1.0]butane, 94024-60-9; *endo*-1,2,2,3,4-pentacyanobicyclo[1.1.0]butane, 94131-32-5; 1,2,2,4,4-pentacyanobicyclo[1.1.0]butane, 94024-61-0; hexacyanobicyclo[1.1.0]butane, 94024-62-1.