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An *ab initio* Molecular Orbital Study of the Cyclobutyl Anion

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The cyclobutyl anion has been studied with *ab initio* molecular orbital calculation. The structures of two cyclobutyl anion conformers and some related species have been determined by full geometry optimization at the Hartree-Fock level with the diffuse-function augmented basis sets 3-21+G and 6—31+G*. In addition, improved energy comparisons have been obtained at the MP3/6—31+G* level, and vibrational frequency analysis of the various species has been carried out in order to characterize the stationary points as well as to determine the zero-point vibrational energies of these species.

It has been found that the cyclobutyl anion conformer with the lone hydrogen at the anionic center occupying the equatorial position (*1*) is more stable than the one with hydrogen occupying the axial position (*2*) by 13 kJ mol^{-1}. The transition structure for the rearrangement $2 \rightarrow 1$ has an almost completely flattened four-membered ring and a nearly planar geometry at the anionic center. The barrier of the rearrangement is calculated to be 24 kJ mol^{-1}.

In addition, the calculated proton affinities for *1* and *2* are comparable to those of CH_3^-, $C_2H_3^-$, and $C_2H_5^-$. Calculated electron affinities for the cyclobutyl radical indicate that, even if conformers *1* and *2* are stable towards spontaneous electron loss, their ionizations potentials should be very low.

INTRODUCTION

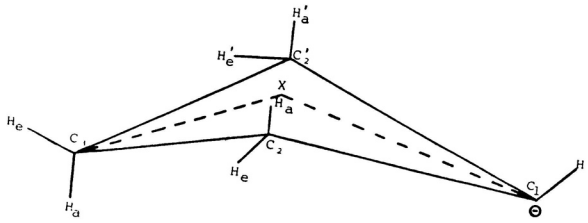
Anions are intrinsically more difficult to treat theoretically than the cations or neutral species: the extra electron is often only weakly bound or not at all. As pointed out in a recent review,[1] in order to obtain reasonable result for anionic systems, it is necessary to employ sufficiently large basis sets (such as diffuse-function augmented sets) and to have adequate incorporation of election correlation. At such levels of theory, properties such as structures and energies of reactions involving closed-shell species may be determined with an accuracy comparable to that achievable for neutral or positively charged species.

In this paper the cyclobutyl anion is studied. As expected, and as shown previously, this anion has two conformers, with the lone hydrogen at the anionic center occupying either the equatorial (*1*) or axial (*2*) position. It is

of interest to determine the barrier between these two conformers. Moreover, once the structure of the transition state linking the two conformers is determined, it may be possible to ascertain whether the transformation proceeds via an inversion at the anionic center or flipping of the four-membered ring. Additionally, the proton affinity of the cyclobutyl anion and the electron affinity of the cyclobutyl radical (*3*) are calculated. The latter can be used to determine whether the cyclobutyl anion conformers are stable towards spontaneous electron loss.

METHOD OF CALCULATION AND RESULTS

The *ab initio* molecular orbital calculations have been carried out using the Gaussian 86 system of program.[3] Geometries of all species have been determfined at the Hartree-Fock (HF) level by employing the gradient optimization technique with basis sets 3—21+G* and 6—31+G*. [The geometry of the cyclobutyl radical (*3*) has been determined at the UHF/6—31G* level.] These diffuse-function augmented basis sets have been shown to yield satisfactory results for anionic systems.[1] It has been demonstrated that the inclusion of



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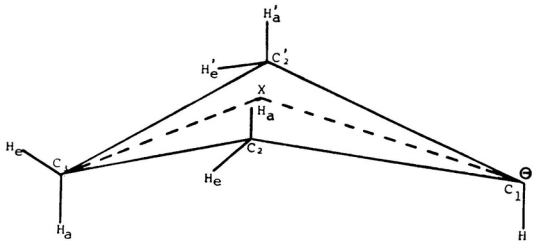

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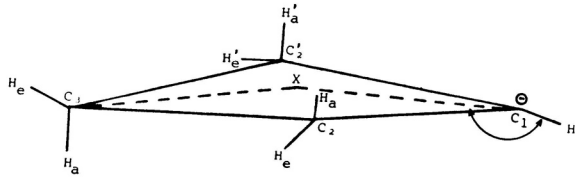

TS : *2* → *1*

Figure 1. Labelling of atoms for cyclobutyl anion conformers *1* and *2* and transition structure TS:*2*→*1*. The labelling for *1* is also applicable to cyclobutyl radical.

diffuse functions to split-valence basis sets improves anion energy calculations significantly.

In order to characterize the stationary points found as minima (equilibrium structures) or saddle points (transition structures) and to include the effects of zero-point vibrational energies (*ZPVEs*) in estimating the relative energies of various structures, harmonic vibrational frequencies have been calculated at the HF level with the 3—21+G and 6—31+G* bases using geometries optimized with the corresponding basis set. In addition, the efects of valence-electron correlation on relative energies have been determined from the third-order Møller-Plesset perturbation theory[4] (MP3) calculations with the 6—13+G* basis set. In other words, our best relative energies are the MP3/6—31+G*//HF/6—31—+G* values.

The labelling of the atoms in conformers *1* and *2*, as well as the transition structure linking them (TS : $2 \rightarrow 1$), is shown in Figure 1. The optimized parameters for these three structures and cyclobutyl radical are summarized in Table I. The optimized geometry for cyclobutane (*4*) is shown in

TABLE I

Energy-optimized structural parameters[a,b] *for the two conformers of cyclobutyl (1 and 2), the transition structure linking them (TS: 2→1), and cyclobutyl radical (3)*

	1	*2*	TS:*2→1*	*3*[c]
C_1—C_2	1.549 (1.588)	1.565 (1.605)	1.508 (1.533)	1.510
C_2—C_3	1.543 (1.566)	1.545 (1.568)	1.544 (1.579)	1.555
C_1—H	1.098 (1.097)	1.100 (1.101)	1.077 (1.073)	1.076
C_3—H_a	1.087 (1.084)	1.091 (1.088)	1.089 (1.086)	1.083
C_3—H_c	1.094 (1.088)	1.100 (1.093)	1.094 (1.088)	1.083
C_2—H_a	1.107 (1.100)	1.094 (1.088)	1.109 (1.102)	1.088
C_2—H_e	1.094 (1.088)	1.096 (1.091)	1.104 (1.097)	1.087
C_1XC_3	146.5 (147.1)	156.9 (157.2)	169.9 (170.6)	171.2
$C_2C_1C'_2$	87.1 (86.6)	86.5 (86.0)	94.3 (93.3)	72.2
HC_1X	125.7 (123.8)	114.2 (113.2)	174.7 (175.0)	164.2[d]
$H_aC_3H_c$	108.7 (110.2)	107.9 (109.2)	107.9 (109.5)	108.4
H_aC_3X	120.1 (119.2)	120.1 (119.9)	123.3 (122.7)	124.2
$H_aC_2H_e$	106.6 (108.3)	106.7 (108.4)	104.7 (106.4)	107.7
H_aC_2X	105.2 (104.8)	110.4 (109.7)	121.5 (121.1)	120.5
H_eC_2X	147.9 (146.7)	142.8 (141.8)	133.3 (132.0)	131.8
$H_aC_2XC_3$	102.1 (102 5)	100.0 (100.6)	90.1 (90.0)	94.4

[a] HF/6—31+G* values; HF/3—21+G values are given in brackets.
[b] Distances are given in Å, angles and dihedral angles in degrees.
[c] HF/6—31G* values.
[d] Dihedral angle HC_1XC_3 is 180°.

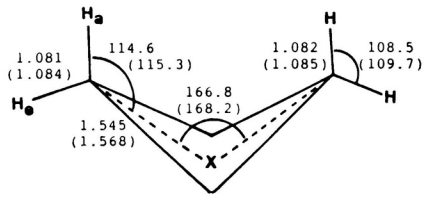

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Figure 2. HF/6—31+G* optimized geometry of cyclobutane. Bond lengths are given in Å and bond angles in degrees. HF/3—21+G parameters are given in brackets.

Figure 2. The calculated total energies, relative energies, and zero-point vibrational energies are given in Table II, while the vibrational frequencies are listed in Table III. The electron affinities of the cyclobutyl radical calculated by different methods are given in Table IV. Unless otherwise noted, relative energies quoted in the text correspond to MP3/6—31+G* values, together with *ZPVE* contribution.

TABLE II

Calculated total energies (E, hartrees), relative energies (ΔE, kJ mol⁻¹), and zero-point vibrational energies (ZPVEs, kJ mol⁻¹) of the two conformers of cyclobutyl anion (1 and 2), the transition structure linking them (TS₁ : 2 → 1), and cyclobutane (4)

	1	*2*	TS : *2* → *1*	*4*
E(3—21+G//3—21+G)	—154.54455	—154.54118	—154.52904	—155.23715
Δ*E*(3—21+G//3—21+G)	0	9	41	—1818
ZPVE(3—21+G)	263	263	258	310
Δ*E*[a]	0	9	36	—1717
E(6—31+G*//6—31+G*)	—155.40535	—155.40089	—155.38879	—156.09874
Δ*E*(6—31+G*//6—31+G*)	0	12	43	—1821
ZPVE(6—31+G*)	264	264	258	311
E(MP2/6—31+G*//6—31+G*)	—155.94901	—155.94347	—155.93376	—156.62344
Δ*E*(MP2/6—31+G*//6—31+G*)	0	15	40	—1717
E(*MP3*/6—31+G*//6—31+G*)	—155.97938	—155.97454	—155.96326	—156.66117
Δ*E*(MP3/6—31+G*//6—31+G*)	0	13	42	—1790
best Δ*E*[b]	0	13	37	—1742

[a] HF/3—21+G//HF/3—21+G values together with *ZVPE* correction.
[b] MP3/6—31+G*//HF/6—31+G* values together with *ZVPE* correction.

DISCUSSION

The Two Conformers of the Cyclobutyl Anion and Their Interconversion

There are two conformers for the cyclobutyl anion, with the lone hydrogen at the anionic center occupying either the equatorial (*1*) or axial (*2*) position. Energetically, *1* is calculated to be 13 kJ mol⁻¹ more stable than *2*. This result is not very different from the value of 12 kJ mol⁻¹ obtained at the HF/4—21G level.[2]

As far as the optimized geometries are concerned, some of the present results are slightly different from the previous[2] (HF/4—21G) ones. For *1* at the HF/6—31+G* level, bond length C_1—C_2, bond angle HC_1X, dihedral angle $H_aC_2XC_3$ have been calculated to be 1.549 Å, 125.7 °, and 102.1 °, respectively. The corresponding values at the HF/4—21G level are 1.597 Å, 120.3 °, and 106.1 °, respectively. For *2*, the largest differences are the following: C_1—C_2, 1.565 Å *vs.* 1.617 Å; C_1XC_3, 156.9 ° *vs.* 160.7 °; HC_1X, 114.2 ° *vs.* 109.8 °; H_aC_2X, 110.4 ° *vs.* 120.6 °; and H_cC_2X, 142.8 ° *vs.* 149.2 °, where the first number in each pair is the present result. From these comparisons it can be seen that the inclusion of diffuse and polarizations functions does make a difference. Furthermore, upon comparing the HF/3—21+G and HF/6—31+G* results, it may be concluded that the inclusion of diffuse functions is more important than that of polarization functions for these anionic species.

TABLE III

Calculated harmonic vibrational frequencies (cm^{-1})[a] of the two conformers of cyclobutyl anion (1 and 2), tranistion structure linking them (TS : 2 → 1), and cyclobutane (4)

1	285 (261) (a′)	681 (674) (a′)	762 (721) (a′)	870 (822) (a″)
	955 (911) (a′)	985 (916) (a″)	994 (962) (a″)	995 (978) (a′)
	1048 (990) (a′)	1082 (1083) (a″)	1197 (1171) (a′)	1242 (1226) (a″)
	1300 (1299) (a′)	1347 (1351) (a″)	1363 (1354) (a″)	1395 (1385) (a″)
	1399 (1368) (a′)	1606 (1604) (a′)	1623 (1621) (a″)	1649 (1642) (a′)
	2928 (2970) (a′)	2928 (2985) (a″)	3037 (3031) (a′)	3087 (3129) (a′)
	3088 (3130) (a″)	3122 (3149) (a′)	3208 (3230) (a′)	
2	194 (179) (a′)	678 (680) (a′)	838 (771) (a′)	844 (806) (a″)
	874 (853) (a′)	918 (842) (a″)	929 (923) (a′)	986 (933) (a″)
	1041 (985) (a′)	1053 (1066) (a″)	1229 (1203) (a′)	1270 (1245) (a″)
	1327 (1312) (a′)	1355 (1353) (a″)	1377 (1370) (a″)	1379 (1350) (a′)
	1403 (1402) (a″)	1603 (1604) (a′)	1617 (1614) (a″)	1645 (1636) (a′)
	3002 (2983) (a′)	3031 (3076) (a′)	3087 (3113) (a″)	3091 (3120) (a′)
	3092 (3143) (a″)	3098 (3140) (a′)	3160 (3184) (a′)	
TS:	661i (612i) (a′)	104 (88) (a′)	761 (768) (a′)	870 (877) (a′)
2 → *1*	949 (888) (a′)	952 (912) (a″)	997 (971) (a″)	1040 (980) (a″)
	1071 (1012) (a′)	1126 (1105) (a′)	1159 (1153) (a″)	1265 (1272) (a′)
	1283 (1239) (a″)	1324 (1331) (a″)	1371 (1360) (a″)	1410 (1380) (a″)
	1418 (1377) (a″)	1610 (1609) (a′)	1647 (1651) (a″)	1670 (1669) (a′)
	2825 (2896) (a′)	2834 (2901) (a″)	2951 (2987) (a″)	2953 (2991) (a′)
	3114 (3147) (a′)	3175 (3201) (a′)	3322 (3336) (a′)	
4	204 (168) (a_1)	685 (698) (b_2)	815 (813) (e)	963 (955) (b_2)
	987 (934) (e)	1015 (967) (b_1)	1042 (1084) (a_2)	1080 (1021) (a_1)
	1284 (1283) (b_1)	1292 (1271) (a_1)	1362 (1363) (e)	1388 (1380) (b_1)
	1391 (1413) (a_2)	1432 (1413) (e)	1625 (1625) (b_2)	1626 (1623) (e)
	1670 (1655) (a_1)	3213 (3221) (b_2)	3217 (3226) (e)	3225 (3236) (a_1)
	3251 (3263) (a_1)	3262 (3278) (e)	3282 (3278) (b_2)	

[a] HF/6—31+G* frequencies; 3—21+G values are given in brackets.

TABLE IV

Calculated total energies[a] (hartrees) and electron affinities[b] (kJ mol^{-1}) of CH_3^-, $CH_3^\cdot$, and $C_4H_7^\cdot$

Species	HF/6—31+G*	MP2/6—31+G*	MP3/6—31+G*	*EA*[c]	*EA*[d]
CH_3^-	—39.50415	—39.65424	—39.66539	---	---
$CH_3^\cdot$	—39.56110	—39.67230	—39.68811	---	---
				—66[e]	2[e]
$C_4H_7^\cdot$	—155.46953	—155.96593	—156.00453		
				—79[f]	—11[f]

[a] Based on HF/6—31+G* structure for CH_3 and HF/6—31G* structure for the radicals [b] Evaluated at the MP3/6—31+G* leval. [c] Calculated by direct subtraction. [d] Evaluated *via* equation (1). [e] Yielding *1*. [f] Yielding *2*.

Attention is now turned to the interconversion of *1* and *2*. The barrier for the reaction *2* → *1* has been calculated to be 24 kJ mol^{-1}. Hence, conformer *2* should be observable only at low temperatures.

Upon examining the geometry of TS : $2 \rightarrow 1$, it is seen that the at the transition state, the structure around the anionic carbon is almost a planar one ($C_1XC_3 = 174.7$ °). Also, the four-membered ring is nearly completely flattened ($C_1XC_3 = 169.9$ °). So, it may be concluded that the rearrangement proceeds *via* a pathway which is a combination of hydrogenic motion at the anionic center and ring flattening. Other geometric parameters that have undergone significant change during the $2 \rightarrow 1$ process include bond length C_i—C_2 (from 1.565 Å to 1.508 Å), bond angles H_aC_2X (from 110.4 ° to 121.5 °) and H_eC_2X (from 142.8 ° to 133.3 °), and dihedral angle $H_aC_2XC_3$ (from 100.0 ° to 90.1 °).

The Proton Affinity of the Cyclobutyl Anion Conformers

Without taking temperature correction into account, the proton affinity (*PA*) of anion X^- is simply the energy difference between X^- and its protonated counterpart, HX. Examining Table II, it can be seen that the *PA*s for *1* and *2* are 1742 and 1755 kJ mol^{-1}, respectively. These values are comparable to those methyl, ethenyl, and ethyl anions. The calculated (MP2/4—31+G//HF/4—31 + G) values[5] for these anions are 1779, 1748, and 1807 kJ mol^{-1}, respectively. The experimental values[6] for CH_3^- and $C_2H_3^-$ are 1743 and $>$ 1690 kJ mol^{-1}, respectively.

Referring to Figure 2, the structure of cyclobutane optimized at the HF/6—31+G* level is in fairly good agreement with the experimental results.[7] The more interesting experimental parameters are given here for comparison: C—C = 1.548 Å, CXC = 145 °, and HCH = 112 °.

Electron Affinity of the Cyclobutyl Radical

In this section, we address the question of whether the anion conformers are stable towards the spontaneous loss of an electron. Additionally, if the answer is in the affirmative, what is the electron affinity (*EA*) of the cyclobutyl radical?

The *EA* of a radical $X^{\cdot}$ is the energy difference between the radical and its anion X^-. However, the *EA*s obtained this way are not always very accurate,[1] especially for species leading to localized anions. Hence, in the results reported below, we have also included the approach of Schleyer and coworkers[8] by calculating the enthalpy change for the isogyric[9] reaction

$$CH_3^{\cdot} + H^- \rightarrow CH_3^- + X^{\cdot} \qquad (1)$$

This enthalpy change gives the *EA* of $X^{\cdot}$ relative to that of $CH_3^{\cdot}$. Taking the experimental value[10] (8 ± 2 kJ mol^{-1}) for the *EA* of $CH_3^{\cdot}$ allows the *EA* of $X^{\cdot}$ to be calculated. In principle, evaluation of *EA*s in this manner should be most effective when $X^{\cdot}$ is similar to $CH_3^{\cdot}$. Thus, it is not certain whether the *EA* for $C_4H_7^{\cdot}$ obtained *via* reaction (1) is more or less accurate than the directly calculated value.

Examining the results given in Table IV, it is seen that, for *1* and *2*, the *EA*s obtained *via* reaction (1) are more positive than the *EA*s obtained by direct subtraction by 68 kJ mol^{-1}. More importantly, the two methods yield qualitatively different results. Direct subtraction results indicate that the two conformers of cyclobutyl anions are unstable towards spontaneous electron

loss. On the other hand, results obtained *via* reaction (1) give either positive or only slightly negative values for the *EA*s, signifying that the two conformers may be stable towards spontaneous loss of electron. In view of the fact that *EA* is probably the most difficult quantity in anion chemistry to be evaluated accurately,[1] and the present computed *EA*s are fairly close to zero, it is not prudent to conclude whether the conformers are stable towards spontaneous electron loss or not. However, it is safe to say that, even if the conformers are stable towards spontaneous electron loss, their ionization potentials would be very low.

Finally, it is interesting to note that, for the cyclobutyl radical, only one equilibrium structure has been found upon optimization. In other words, no axial-equatorial conformational isomerism exists for this radical. Comparing the structure of the free radical *3* with those of *1* and *2*, it is seen that the four-menbered ring of *3* is nearly planar ($C_1XC_3 = 171.2\ ^\circ$), and geometry around the radical center is also almost planar ($HC_1X = 164.2\ ^\circ$). Additionally, the C_1—C_2 bonds are noticeably shorter (1.510 Å in *3 vs.* 1.549—1.565 Å in *1* and *2*). In fact, the structure of *3* resembles that of TS : *2* → *1*, the only significant difference being the $C_2C_1C_2'$ angle (72.2 ° in *3 vs.* 87 ° in *1* and *2*).

CONCLUDING REMARKS

Upon applying *ab initio* molecular orbital theory to the cyclobutyl anion, it has been found that there are two stable conformers of this anion, *i.e.*, the lone hydrogen at the anionic center can occupy either the equatorial (*1*) or the axial (*2*) position. Conformer *1* is found to be more stable than *2* by 13 kJ mol^{-1}. The barrier for the rearrangement *2* → *1* is calculated to be 24 kJ mol^{-1}, indicating *2* can be observed only at low temperatures. Furthermore, upon studying TS : *2* → *1*, it may be concluded that the rearrangement proceeds *via* a pathway involving both the motion of the hydrogen atom at the anionic center and ring flattening.

The proton affinities for *1* and *2* have been calculated to be 1742 and 1755 kJ mol^{-1}, respectively. These *PA* values are similar to those of CH_3^-, $C_2H_3^-$ and $C_2H_5^-$. Finally, the calculated electron affinities for the cyclobutyl radical indicate that, if conformers *1* and *2* are stable towards spontaneous electron loss, their ionization potentials should be very low.

REFERENCES

1. R. H. Nobes, D. Poppinger, W.-K. Li, and L. Radom, in *Comprehensive Carbanion Chemistry*, Part C, E. Buncel and T. Durst (Eds.), Elsevier, Amsterdam 1987, Ch. 1.
2. T. Jonvik and J. E. Boggs, *J. Mol. Struct.* **85** (1981) 293.
3. M. J. Frisch, J. S. Brinkley, H B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. DeFrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuder, and J. A. Pople, *Gaussian 86*, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, U.S.A., 1984.
4. C. Møller and M. S. Plesset, *Phys. Rev.* **46** (1934) 618; J. A. Pople, J. S. Brinkley, and R. Seeger, *Int. J. Quantum Chem. Symp.* **10** (1976) 1.
5. J. Chandrasekhar, J. G. Andrade, and P. v. R. Schleyer, *J. Amer. Chem. Soc.* **103** (1981) 5609.
6. J. E. Bartmess and R. T. McIver, *Gas Phase Ion Chem.* **2** (1979) 88.
7. A. Wilson and D. Goldhammer, *J. Chem. Educ.* **40** (1963) 504.

8. G. Winkelhofer, R. Janoschek, F. Frater, G. M. Spitznagel, J. Chandrasehkar, and P. v. R. Schleyer, *J. Amer. Chem. Soc.* **107** (1985) 332.
9. J. A. Pople, M. J. Frisch, B. T. Luke, and J. S. Brinkley, *Int. J. Quantum Chem. Symp.* **17** (1983) 307.
10. G. B. Ellison, P. C. Engelking, and W. C. Lineberger, *J. Amer. Chem. Soc.* **100** (1978) 2556.

SAŽETAK

Ab initio molekularno-orbitalni račun za ciklobutilni anion

Wai-Kee Li

Proveden je *ab initio* molekularno-orbitalni račun za ciklobutilni anion. Nađena su dva konformera. U jednom konformeru vodik na anionskom središtu zauzima ekvatorijalni položaj, a u drugom aksijalni položaj. Prvi je konformer *(I)* stabilniji za 13 kJ mol^{-1} od drugoga *(II)*. Struktura prijelaznog stanja za pregradnju *II* → *I* je gotovo planaran četveročlani prsten. Energijska barijera za tu pregradnju iznosi 24 kJ mol^{-1}. Ta vrijednost energijske barijere upućuje na to da bi *II* eventualno mogao biti eksperimentalno opažen jedino pri vrlo niskim temperaturama.