

MHz) δ 1.50-2.10 (12H, m), 4.68-4.69 (1H, m), 4.84-4.85 (1H, m), 4.95-4.98 (2H, m); ^{13}C NMR δ 21.5, 29.0, 40.0, 72.6, 97.2, 101.0, 155.0; MS m/z 152 (M^+ , 11), 134 (10), 119 (42), 91 (72), 84 (100), 79 (55), 67 (41%); IR ν_{max} 1697 cm^{-1} . **10c**: ^1H NMR δ 1.46-2.26 (14H, m), 4.68-4.69 (1H, m), 4.83-4.85 (1H, m), 4.96-4.98 (2H, m); ^{13}C NMR δ 21.0, 24.4, 28.0, 35.3, 72.5, 96.7, 101.2, 154.1; MS m/z 166 (M^+ , 11), 133 (11), 119 (12), 105 (21), 91 (34), 86 (75), 84 (100), 79 (41), 67 (25%); IR ν_{max} 1697 cm^{-1} . **10d**: ^1H NMR δ 1.50-2.20 (14H, m), 4.79-4.80 (1H, m), 4.92-4.94 (2H, m), 5.06-5.08 (1H, m); ^{13}C NMR δ 26.47, 26.54, 32.3, 33.7, 37.1, 72.4, 97.7, 103.5, 153.1; MS m/z 190 (M^+ , 37), 175 (37), 150 (43), 133 (42), 117 (33), 105 (29), 91 (64), 84 (100), 79 (96), 67 (33), 55 (60%); IR ν_{max} 1688 cm^{-1} . **10e**: ^1H NMR δ 1.81 (3H, s), 4.83-4.86 (1H, m), 4.98-5.01 (1H, m), 5.05-5.18 (2H, m), 7.24-7.51 (5H, m); ^{13}C NMR δ 28.5, 73.7, 94.2, 103.3, 124.0, 127.2, 128.3, 144.8, 152.4; MS m/z 160 (M^+ , 21), 159 (27), 145 (99), 129 (57), 115 (85), 105 (100), 77 (96%); IR ν_{max} 1692 cm^{-1} . **10f**: ^1H NMR δ 5.08-5.09 (1H, m), 5.14-5.15 (1H, m), 5.15-5.19 (2H, m), 7.13-7.47 (10H, m); ^{13}C NMR δ 74.1, 96.9, 106.2, 125.2, 127.6, 127.8, 143.7, 150.5; MS m/z 222 (M^+ , 11), 206 (100), 191 (72), 165 (23), 128 (14), 105 (18), 84 (17%); IR ν_{max} 1698 cm^{-1} .

The Ring Structure and Barrier to Planarity of Oxetane

Soo Gyeong Cho* and Young-Gu Cheun

Agency for Defense Development, P. O. Box 35,
Yuseong, Taejeon 305-600, Korea

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Conformations of 4-membered ring systems have been extensively investigated by a variety of experimental and theoretical methods.¹ Cyclobutane is stable in a puckered conformation with the puckering angle of *ca.* 30° and the barrier

to planarity of 1.5 kcal/mol.¹⁻³ Although planar conformation is favorable in terms of ring strain, the cyclobutane ring structure may alleviate unfavorable eclipsed interactions between vicinal hydrogens by tilting the CH_2 groups in the opposite direction.² Thus, the degree of puckering in 4-membered ring systems is generally accepted as a compromise between ring strain and torsional strain.

The introduction of heteroatom in the cyclic compounds usually changes the equilibrium conformation.⁴ In oxetane, replacement of CH_2 group by O atom can substantially reduce the number of unfavorable eclipsed interactions between vicinal hydrogen. This may cause oxetane to be flatter than cyclobutane. Far-IR⁵ and microwave (MW)⁶ studies have provided that the ring structure of oxetane is planar. However, the planar conformation of oxetane is not the minimum of the puckering potential energy function (PPEF) but is attributed to a rapid equilibrium between two puckered conformers through a small energy barrier. X-ray results at low temperature (90 K and 140 K) have furnished that the oxetane ring exists in a puckered conformation with the puckering angle with *ca.* 10°.⁷ The NMR analyses⁸ using dipolar coupling constants have agreed to the X-ray data. Since both experiments, X-ray and NMR, have been carried out in the condensed phases, the equilibrium conformation may differ from the one in the gas-phase.

Ab initio methods have been applied to oxetane with the modest basis sets,^{9,10} *i.e.* 3-21G and 4-21G. All the calculations have concluded that the planar form is the equilibrium conformation. Earlier semi-empirical MINDO/2' results have estimated the geometry of oxetane poorly and a zero puckering potential.¹¹ Laane and coworkers have utilized the molecular mechanics (MM2) to examine the PPEF for oxetane.¹² MM2 has deduced that the ring structure of oxetane is planar and, of course, with no puckering potential.

In order to better understand the conformational nature of oxetane, *ab initio* and semi-empirical molecular orbital calculations were performed using the GAUSSIAN 92¹² series of programs on a CRAY Y-MP computer. The equilibrium geometries were fully optimized at four different levels of theories - PM3,¹³ HF/3-21G,¹⁴ HF/6-31G*,¹⁵ and MP2/6-31G*.¹⁶ Semi-empirical method was applied to assess the performance of PM3 hamiltonian for our future studies on highly substituted oxetane derivatives.¹⁷

Table 1 summarizes the geometric parameters optimized

Table 1. Calculated and Observed Geometries^a of Oxetane

	PM3	HF/3-21G	HF/6-31G*	MP2/6-31G*	MW ^b	X-ray ^c
CO	1.453	1.476	1.419	1.451	1.449(2)	1.460(1)
CC	1.544	1.558	1.537	1.533	1.549(3)	1.534(2)
C _o H	1.099	1.079	1.082	1.087	1.091(2)	0.97(2)
C _p H	1.099	1.078	1.084	1.092	1.100(3)	0.97(2)
$\angle\text{COC}$	92.60	92.10	92.78	90.08	91.59(70)	90.18(8)
$\angle\text{CCO}$	90.82	90.95	91.66	91.45	91.44(30)	91.99(7)
$\angle\text{CCC}$	85.76	86.00	83.90	84.13	84.55(10)	84.79(9)
$\angle\text{HC}_o\text{H}$	107.31	110.26	109.26	109.66	110.18(10)	
$\angle\text{HC}_p\text{H}$	109.20	110.74	109.04	109.31	110.44(30)	
Ring puckering angle ^d	0.00	0.00	0.00	17.85	0.00	10.7(1)

^aLengths in Å, and angles in degrees. ^bFrom the rotational constants, ref. 6b. ^cAt 90 K, ref. 7. ^dsee Figure 1 for the definition.

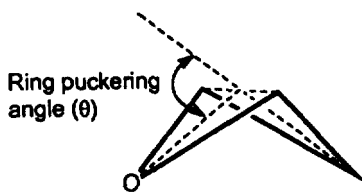


Figure 1. Ring puckering angle (θ) of oxetane.

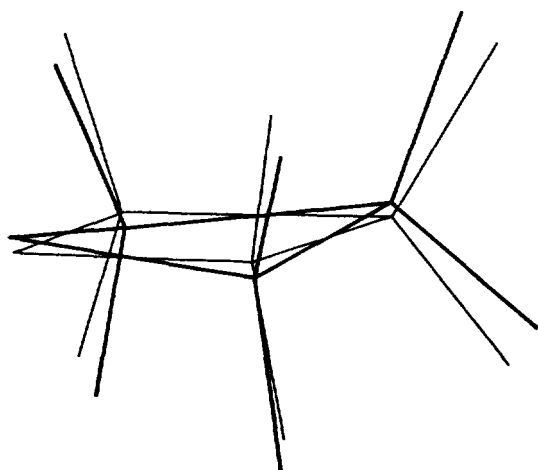


Figure 2. Comparison of the *ab initio* calculated geometries. Thick line represents the MP2/6-31G* optimized geometry, and thin line represents the HF/6-31G* optimized geometry.

at various levels of theories along with the values from MW and X-ray data. Several discrepancies in bond lengths and angles can be found between two sets of experimental values. The C-O bond length from X-ray studies is slightly longer than the one from MW spectra by 0.011 Å, while the C-C bond length from X-ray studies is shorter than the value from MW spectra by 0.015 Å. The C-H bond lengths are significantly underestimated by X-ray crystallographic data, which usually furnish indefinite hydrogen positions. An obvious disagreement can be seen at the ring puckering angle. X-ray data estimate the oxetane ring to be puckered by 10.7°, while MW data predicts the ring to be planar.

In general, the bond lengths and angles calculated by various levels of theories including PM3 are in fairly good agreement with the values observed experimentally. The C-O bond length varies significantly with the levels of calculations. The HF/3-21G calculations overestimate the C-O bond length measured experimentally by 0.02-0.03 Å, and the HF/6-31G* calculations substantially underestimate by 0.03-0.04 Å. The C-O bond length becomes close to experimental values when electron correlation effects are taken into account. The ring puckering angle is a controversial geometric parameter in oxetane. All Hartree-Fock results, including semi-empirical PM3 hamiltonian, predict that oxetane is most stable in the planar conformation. On the other hand, MP2/6-31G* results show that the equilibrium conformation of oxetane is puckered by 17.9° (see Figure 2).

At MP2/6-31G* theory, the planar conformation is a transition structure with only one imaginary frequency ($-91.2i$ cm⁻¹), and the barrier to planarity is 0.14 kcal/mol. This

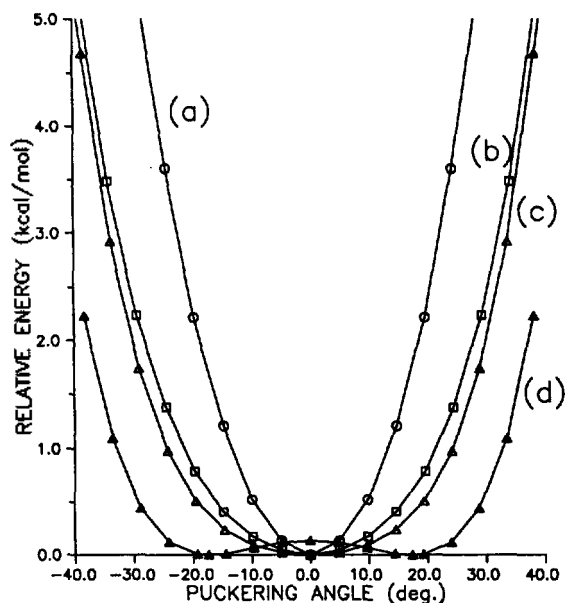


Figure 3. Calculated PPEF curves for oxetane: (a) PM3; (b) HF/3-21G; (c) HF/6-31G*; (d) MP2/6-31G*.

barrier has also been estimated as 0.10 kcal/mol by MW,⁶ and 0.04 kcal/mol by far-IR,^{5e} respectively. The MP2/6-31G* calculated barrier appears to be quite consistent with the values observed by experimental methods. Zero point vibrational energy (ZPVE) corrections further reduce the barrier of planarity to be exactly none.¹⁸ ZPVE corrections may also alter the equilibrium conformation significantly from the MP2/6-31G* optimized one. We can locate the minimum by calculating both geometries and frequencies in each point of puckering potential energy surface. We have not attempted to employ this tedious method in order to find the equilibrium conformation, since (1) PPEF of oxetane is quite flat, and (2) the tiny energy difference between the puckered and planar conformations is far beyond the accuracy of the current state-of-art *ab initio* methods.¹⁹

Figure 3 shows the PPEF calculated by various levels of theories. The MP2/6-31G* calculations provide a flat PPEF with the minimum at 17.9° and the barrier of planarity of 0.14 kcal/mol. In contrast, other *ab initio* HF and semi-empirical PM3 results furnish the PPEF with the minimum at 0°. In this study, we feel that the shape of the PPEF is more important than the location of the minimum. The trend in Figure 3 convinces us that the PPEF becomes flatter, as the larger basis sets are employed and the electron correlation effect is incorporated.

Accordingly, puzzlement of experimental analyses of the oxetane geometry may come from the extremely flattened PPEF which cause the oxetane ring to be deformed easily without the significant increase in potential energy. The MP2/6-31G* calculations predict that the potential energy is only 0.44 kcal/mol higher than the minimum even at the conformation of the puckering angle of 30°. Oxetane ring also undergoes ring inversion easily through the low barrier of planarity. Easy deformation including ring inversion makes various experimentalists and theoreticians to predict different conformers as the minimum of the potential energy surface. Our theoretical results using MP2/6-31G* level of theory ap-

pear to describe the PPEF of oxetane accurately. Previous Hartree-Fock results with the modest basis sets inadequately characterized the shape of PPEF to be relatively steep with the minimum at 0°. This study demonstrates that the inclusion of electron correlation effect is important to describe the exact nature of potential energy surface of oxetane derivatives, especially the PPEF.

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- All the vibrational frequencies for oxetane have not been assigned experimentally yet.¹⁰ By comparing 21 (out of 24) vibrational frequencies, our MP2/6-31G* calculated frequencies are in excellent agreement with those observed empirically by multiplying the scaling factor, 0.94. Thus, we also have scaled down ZPVE by using the same scaling factor. Vibrational frequencies calculated by MP2/6-31G* along with those measured experimentally are summarized as follows (unit: cm⁻¹).

Measured frequencies¹⁰

53.5	703.0	784.5	842	908.7
937.3	1008.3	1032.7	(839.9) ^c	—
1137.3	1183	1230	1289.0	1343.1
1452.0	1480	1505.0	2887.1	2893.9
2979.0	2938.2	—	3006.0	—

MP2/6-31G* calculated frequencies (at the puckered conformation)

122.3 ^b	682.2	814.0	821.8	895.0
(130.1) ^c	(725.7)	(866.0)	(874.2)	(952.1)
928.8	990.8	1017.4	1110.5	1112.5
(988.1)	(1054.0)	(1082.3)	(1181.4)	(1183.5)
1163.5	1183.5	1227.6	1263.1	1329.1
(1237.7)	(1259.0)	(1305.9)	(1343.7)	(1413.9)
1458.2	1483.2	1510.8	2903.7	2910.2
(1551.3)	(1577.9)	(1607.3)	(3089.1)	(3095.9)
2961.2	2973.4	2973.4	3016.0	—
(3150.2)	(3163.2)	(3163.2)	(3118.5)	—
ZPVE: 56.059 kcal/mol				

MP2/6-31G* calculated frequencies (at the planar conformation)

—85.7 ^d	746.0	760.5	816.4	987.4
(-91.2) ^d	(793.6)	(809.0)	(868.5)	(954.7)
929.3	1005.4	1015.1	1100.9	1118.2
(988.6)	(1069.5)	(1079.9)	(1171.1)	(1189.6)
1155.6	1196.2	1222.3	1262.7	1332.9
(1229.3)	(1272.6)	(1300.3)	(1343.3)	(1418.0)
1460.5	1486.7	1513.9	2972.4	2917.4
(1553.7)	(1581.6)	(1610.6)	(3096.3)	(3103.7)
2963.7	2964.7	2965.6	3024.9	—
(3152.9)	(3154.0)	(3154.8)	(3218.0)	—
ZPVE: 55.915 kcal/mol				

^aThis value has a large error. Measured as 1142 cm⁻¹ by Zürcher and Günthard (reference, *Helv. Chim. Acta*, **1955**, *38*, 849). ^bScaled down by multiplying 0.94 (*vide supra*). ^cRaw data in parentheses. ^dImaginary frequency.

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