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The energies of cyclobutylene, perfluorocyclobutylene and related compounds have been calculated at levels from MP2/6-31G* through QCISD(T)/6-311+G*, and also at B3LYP and B3PW91/6-311+G*. The relative energies found with the larger basis sets are quite consistent. Cyclobutylene is calculated to be a transition state at most levels of theory, leading to cyclopropylidene carbene. However, the latter does not have C_{2v} symmetry, but rather undergoes a tilt of the carbene carbon toward a ring carbon leading to a distorted C_s structure. Perfluorocyclobutylene is calculated to have a significant activation energy for rearrangement at the MP2 level, but higher levels of theory suggest that it will rearrange spontaneously to perfluorocyclopropylidene carbene, again with a distorted structure. The calculated heats of hydrogenation of the cyclobutylenes are about 70 kcal mol⁻¹ greater than for acetylene. The energy of a process by which perfluorocyclobutylene or perfluorocyclopropylidene carbene might be formed is also calculated.

1. Introduction

Cyclobutylene (**1**) is probably the smallest cycloalkyne that has any possibility of a finite existence. A detailed theoretical study of its rearrangement to butatriene by Carlson, Quelch and Schaefer¹ found the reaction to be exothermic by about 60 kcal mol⁻¹,² and to have an estimated activation energy of 25 kcal mol⁻¹. A subsequent theoretical study of the rearrangement of **1** to cyclopropylidene carbene (**2**) by Johnson and Daoust³ found a small or negligible activation barrier.

It has not been possible to observe cyclobutylene in any experimental study.⁴ On the other hand, it is possible that fluorine substitution might alter the relative energies and lead to a quasi-stable perfluorocyclobutylene. In addition, replacing hydrogens with fluorines has an experimental advantage as indicated below. Therefore, we have carried out a detailed computational study of perfluorocyclobutylene and related compounds.

2. Cyclobutylene

Before examining the reaction of perfluorocyclobutylene, we carried out some additional theoretical studies of cyclobutylene so that we could directly compare the two molecules at the same set of theoretical levels. As noted previously, at MP2/6-31G* it has no imaginary frequencies, and a transition state (**2**) for the rearrangement to cyclopropylidene carbene (**3**) has been located.³ In order to see if this would continue to be the case using a more flexible basis set, the structures of **1**, **2** and **3** were optimized at MP2/6-311+G*. The optimized structures for all of the stationary points are shown in Fig. 1, and the corresponding energies are listed in Table 1.

Although **1** had no imaginary frequencies at this theoretical level, the cyclopropylidene carbene **3** with C_{2v} symmetry was found to have one imaginary frequency⁵ corresponding to the tilt of the carbene carbon toward one of the ring carbons (Fig. 1). Optimization of the distorted structure gave the ground

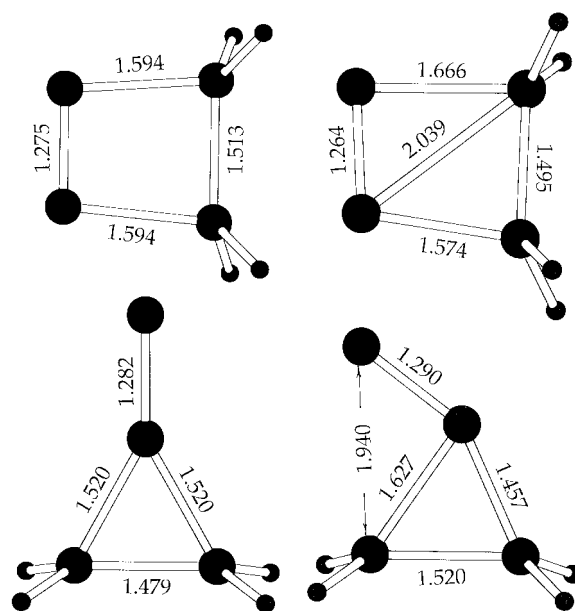


Fig. 1 MP2/6-311+G* optimized structures of cyclobutylene and related compounds.

state of the carbene having C_s symmetry (**3a**) (see Fig. 1), and a significantly lower energy than the C_{2v} carbene (Table 1). The C–C nonbonded distance is only 1.9 Å, suggesting that the distortion leads to weak bonding between these atoms that results in a reduced energy.

The larger basis set MP2 calculations led to a transition state **2** having almost the same energy as cyclobutylene, and when the zero-point energy was included it had a lower energy than **1**. QCISD generally gives more satisfactory energies than MP2, and a QCISD/6-31G* geometry optimization for **1** led to a structure having two imaginary frequencies. One (700i cm⁻¹) corresponds to the mode leading to the carbene, and the other (165i cm⁻¹) corresponds to a twisting motion. Again, the C_{2v} carbene was found to be a transition state leading to the C_s carbene. QCISD(T) calculations using the QCISD geometries placed **1** at a higher energy than the transition state **2**. Thus, at these levels of theory, **1** would rearrange to **3a** with no activation barrier.

† Tables of calculated energies at different theoretical levels, along with the energies of isodesmic reactions are available as supplementary data. For direct electronic access see <http://www.rsc.org/suppdata/p2/1999/2333>, otherwise available from BLDS (SUPPL. NO. 57630, pp. 6) or the RSC Library. See Instructions for Authors available via the RSC web page (<http://www.rsc.org/authors>).

Table 1 Calculated energies of cyclobutene and its derivatives

Level ^a	Cyclobutene (1)	TS (2)	Carbene (3)	
			C _{2v}	C _s
a. Total energies/H				
MP2/6-31G*	-154.08349 (0)	-154.07926 (1)	-154.11054 (1)	-154.12113 (0)
ZPE ^b	42.0	39.8	39.1	39.9
MP2/6-311+G*	-154.14520 (0)	-154.14285 (1)	-154.16968 (1)	-154.18065 (0)
MP4/6-311+G*	-154.20008	-154.19940	-154.23172	-154.23733
QCISD(T)/6-31G*	-154.13615 (2)	-154.13649 (1)	-154.17234 (1)	-154.17524 (0)
QCISD(T)/6-311+G*	-154.19800	-154.19974	-154.23300	-154.23642
B3LYP/6-311+G*	-154.64411 (1)	^c	-159.68638 (1)	-159.68730 (0)
B3PW91/6-311+G**	-154.62590 (1)	^c	-159.66235 (1)	-154.66506 (0)
b. Relative energies/kcal mol ^{-1d}				
MP2/6-31G*	0.0	0.6	-19.7	-25.6
MP2/6-311+G*	0.0	-0.6	-18.1	-24.3
MP4/6-311+G*	0.0	0.4	-22.6	-23.4
QCISD(T)/6-31G*	0.0	-2.3	-25.5	-26.5
QCISD(T)/6-311+G*	0.0	-3.2	-24.7	-26.1
B3LYP/6-311+G*	0.0		-29.3	-29.1
B3PW91/6-311+G*	0.0		-25.6	-26.6

^a The MP4 energy was calculated at the corresponding MP2 optimized geometry. The QCISD(T) energies were obtained using the QCISD/6-31G* optimized geometries. The number of imaginary frequencies is given in parentheses. ^b Derived from MP2/6-31G* frequencies scaled by 0.96, in kcal mol⁻¹. ^c Optimization to a transition state starting with the MP2/6-31G* geometry led to **1**. ^d The relative energies include the differences in zero-point energies.

Calculations were also carried out at the B3LYP/6-311+G* and B3PW91/6-311+G* levels, and here again **1** was found to be a transition state. Transition state **2** could not be located at these levels of theory; optimization to a transition state starting with the MP2 geometry of **2** resulted in the formation of **1**. The C_{2v} carbene was again found to be a transition state leading to the C_s carbene.

One criticism that could be raised with regard to these calculations is that they may not take into account the possible diradical character of **1**, which has been estimated to be 15%.¹ However, the use of a recently developed diagnostic for the multiconfiguration character in correlated wavefunctions⁶ indicated that the diradical character is well described at the MP2 and QCISD levels. In addition, the relative energies of these compounds are not much affected by the theoretical level used. It seems quite clear that **1** has little possibility for a finite existence.

3. Perfluorocyclobutene

The remarkable effect of fluorine substitution on the energies and reactions of organic compounds that has been observed by Lemal and his students^{7,8} led us to examine the possibility that perfluorocyclobutene (**4**) may be more stable than **1**. A suggestion to this effect was noted by Johnson in a footnote to his paper on cyclobutene.³

The perfluoro compound was examined in the same fashion as for **1** giving the results summarized in Table 2. At MP2/6-31G* the structures of **4** and the transition state (**5**) were similar to those in the cyclobutene series (Fig. 2). However, as was found for the above series, the C_{2v} carbene (**6**) has a relatively high energy and exhibits one imaginary frequency. Geometry optimization to the nearest energy minimum found the strongly distorted carbene with only C_s symmetry shown in Fig. 2.

At the MP2 level, the energy for **4** going to the transition state **5** was significantly increased as compared to **1**, but at other theoretical levels (QCISD, DFT) **4** was found to be a transition state. The exothermicity of the conversion of **4** to **6a** was markedly reduced at all theoretical levels with respect to the conversion of **1** to **3a**.

We were particularly interested in the question of whether or not fluorine stabilizes cyclobutene. Therefore we have examined a number of isodesmic reactions that are shown in Table 3. The

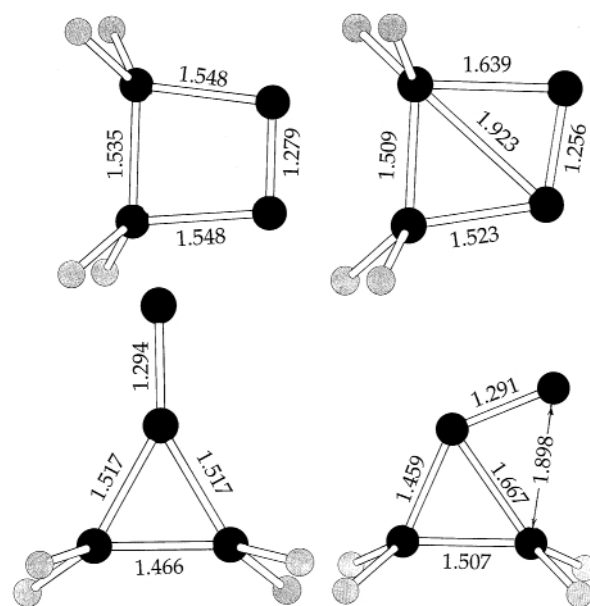


Fig. 2 MP2/6-311+G* optimized structures of perfluorocyclobutene and related compounds.

calculated energies of the compounds are given in Table 4. The first reaction shows that perfluoro substitution destabilizes cyclobutene relative to cyclobutene. The calculated heats of hydrogenation of cyclobutene and perfluorocyclobutene are very large compared to that of acetylene. The experimental heat of hydrogenation of acetylene (298 K) is -41 kcal mol⁻¹,⁹ and it is well reproduced by the calculations. These data do not auger well for the observation of a perfluorocyclobutene, and suggest that any reaction that might form **4** would probably proceed directly to the carbene, **6a**.

One attractive possible reaction that might be used to form **4** or **6a** in the gas phase is shown below.

It is known that desilylation of compounds such as **7**¹⁰ with fluoride ion is a good way in which to form a carbanion.¹¹ Then, there is the question of how much energy would be required for the anion to lose chloride ion and form **4** or **6a**. This could be determined *via* a collisionally induced dissociation (CID) study

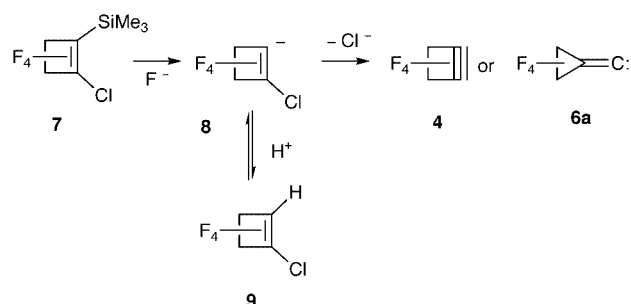
Table 2 Calculated energies of perfluorocyclobutene and its derivatives

Level	F4-cyclobutene (4)	F4-TS (5)	F4-carbene (C _{2v})(6)	F4-carbene (C _s)(6a)
a. Total energies ^a				
MP2/6-31G*	-550.16914 (0)	-550.15567 (1)	-550.16081 (1)	-550.17295 (0)
ZPE ^b	22.0	19.1	18.6	19.2
MP2/6-311+G*	-550.49099 (0)	-550.47835	-550.47992 (1)	-550.49282 (0)
MP4/6-311+G*	-550.56104	-550.55312	-550.55953	-550.56642
QCISD(T)/6-31G*	-550.22325	-550.21992	-550.22905 (1)	-550.23191 (0)
QCISD(T)/6-311+G*	-550.54934		-550.55289	-550.55671
B3LYP/6-311+G*	-551.71772 (1)	^c	-551.73260 (1)	-551.73360 (0)
B3PW91/6-311+G*	-551.68095 (1)	^c	-551.69042 (1)	-551.69322 (0)
b. Relative energies/kcal mol ^{-1d}				
MP2/6-31G*	0.0	5.7	2.0	-5.1
MP2/6-311+G*	0.0	5.1	3.9	-3.6
MP4/6-311+G*	0.0	5.0	-2.3	-6.1
QCISD(T)/6-31G*	0.0	-0.7	-6.9	-8.1
QCISD(T)/6-311+G*	0.0		-5.5	-7.3
B3LYP/6-311+G*	0.0	^c	-12.6	-12.7
B3PW91/6-311+G*	0.0	^c	-9.2	-10.4

^a The MP4 energy was calculated at the corresponding MP2 optimized geometry. The QCISD(T) energies were obtained using the QCISD/6-31G* optimized geometries. The number of imaginary frequencies is given in parentheses. ^b Derived from MP2/6-31G* frequencies scaled by 0.96, in kcal mol⁻¹. ^c Optimization to a transition state starting with the MP2/6-31G* geometry led to 4. ^d The relative energies include the differences in zero-point energies.

Table 3 Effect of fluorine substitution on relative energies (kcal mol⁻¹)

	MP4	BPW91	QCISD(T)
	-11	-10	-12
	-112	-114	-114
	-101	-104	-102
	-37	-41	-38



of 8. The acidity of 9 is also of interest since it could be used to calculate the energy for dehydrohalogenation of 9 to form 4 or 6a.

The direct calculation of gas phase acidities often leads to significant errors that result from the use of insufficiently large basis sets, and incomplete correction for the effects of electron correlation. It is frequently more satisfactory to make use of an isodesmic reaction which tends to cancel some of these errors.¹² In the case of the acidity of 9, one might use the following reaction since the acidity of ethylene ($\Delta H_{\text{acid},298}$) has been measured and is 409.4 ± 0.6 kcal mol⁻¹.¹³

The calculated heat of the reaction is 52.9 kcal mol⁻¹ at the MP4 level, 51.8 at B3PW91, and 53.3 using QCISD(T)/6-



311+G* giving an average of 52.7 kcal mol⁻¹. When this is combined with the experimental value for ethylene it gives for 9 $\Delta H_{\text{acid},298} = 356.7$ kcal mol⁻¹. This is in very good agreement with the experimental value of 357.5 ± 2.0 kcal mol⁻¹.¹⁴ The use of a fluorinated derivative simplified this study since 9 has only one proton that could be removed by a base.

The loss of chloride ion from 8 to form 4 is calculated to be endothermic by 83 kcal mol⁻¹. However the loss of chloride ion to form the C_s carbene is calculated to be less endothermic, 75 kcal mol⁻¹. The results of experiments designed to measure the energy change for this reaction will be reported separately.

4. Cyclopropylidenecarbenes

The unusual structures of the cyclopropylidenecarbenes led us to examine the effect of other substitution patterns. The energies of the compounds of interest are given in Table 5, and their structures are shown in Fig. 3. In view of the significant preference for markedly bent structures in the C₄H₄ and C₄F₄ series, it

Table 4 Calculated energies, 6-311+G* basis set^a

Compound	MP4	B3PW91	QCISD(T)	ZPE
Cyclobutene	-155.52856	-155.98125	-155.53015	58.50
F4-cyclobutene	-551.90728	-553.05199	-551.89975	38.31
Acetylene	-77.12505	-77.33460	-77.12490	16.15
Ethylene	-78.35249	-78.58907	-78.35452	32.66
Hydrogen	-1.15265	-1.17366	-1.15350	6.48
F4-1-chlorocyclobutene	-1010.98487	-1012.67977	-1010.97613	28.90
F4-2-chlorocyclobutenyl anion	-1010.41072	-1012.10478	-1010.40170	20.88
Chloride ion	-459.71816	-460.29617	-459.71870	0.0
Vinyl anion	-77.69133	-77.92879	-77.69243	22.89

^a The total energies are given in Hartrees and the zero-point energies are given in kcal mol⁻¹.

Table 5 QCISD/6-31G* energies for cyclopropylidene carbenes^a

Compound	Energy	ZPE	<i>E</i> _{rel} /kcal mol ⁻¹
Parent (3a)	-154.15205	39.44	
F4- (6a)	-550.19370	19.24	
<i>cis</i> -2,3-diF (10)	-352.16706	29.78	7.2
<i>trans</i> -2,3-diF (11)	-352.16850	29.66	6.2
2,2-diF (12)	-352.17692	29.01	0.2
2,2-diF (13)	-352.17797	29.43	0.0

^a The total energies are given in Hartrees and the zero-point energies and relative energies are given in kcal mol⁻¹.

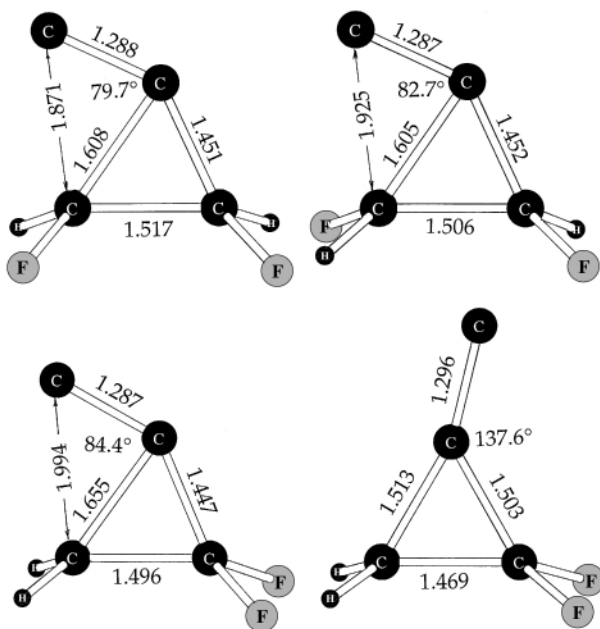


Fig. 3 QCISD/6-31G* optimized structures of difluoro substituted cyclopropylidene carbenes.

is surprising that the lowest energy C₄H₂F₂ structure (**13**) is only slightly bent. Its counterpart with the carbene center bent toward the CF₂ group (**12**) is only 0.2 kcal mol⁻¹ higher in energy. The vicinal difluorides, **10** and **11**, are 6–7 kcal mol⁻¹ higher in energy. It is known that fluorine substitution on a cyclopropane ring usually leads to destabilization,⁷ but the relative effects of *gem* vs. *vicinal* substitution do not appear to have been explored.

The isodesmic reaction in which **3a** + **6a** form two **13** is calculated to be exothermic by 6 kcal mol⁻¹. Thus, the C₄F₄ carbene is relatively destabilized, as is perfluorocyclobutene itself.

The factors that control the structures of the cyclopropylidene carbenes are not well understood, and will be the subject of further studies.

Conclusions

At the highest level of theory used in this study, QCISD, both cyclobutene and perfluorocyclobutene are predicted to be transition states for rearrangement to the corresponding cyclopropylidene carbene. The calculated energies of reaction of the cyclobutenes are relatively independent of the theoretical level that was used. The differences in energy between the cyclobutenes and the corresponding cyclobutenes are about 70 kcal mol⁻¹ greater than the difference between acetylene and ethylene. The carbenes do not have C_{2v} symmetry, but rather distort to a C_s structure.

Calculations

The *ab initio* calculations were carried out using GAUSSIAN95^{15,16} using standard basis sets. Complete lists of calculated energies and energies of isodesmic reactions are available as supporting information.[†]

Acknowledgements

This investigation was prompted by the remarkable success of Robert Squires and his students in gaining thermochemical information for transitory species such as benzyne *via* the CID technique. The present report represents the computational part of a collaborative study. The investigation was supported by a grant from the National Science Foundation.

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