

Semiempirical MNDO Calculations for Halocyclopentynes

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Electronic structures and ethylene addition reaction for halocyclopentynes are investigated using MNDO method. Electronic effects due to the halogen substitution are very small for halocyclopentynes. Fluorocyclopentyne is slightly more stable than cyclopentyne and other halocyclopentynes, but reactivities for cycloaddition reactions are about the same for all halocyclopentynes and cyclopentyne. Stabilization effect is substantial for hexafluorocyclopentyne.

Introduction

Cyclic alkynes are molecules of considerable interest from the academic point of view because of the highly strained ring structure. Theoretical studies using *ab initio* and semiempirical methods indicate that cyclobutyne and cyclopentyne are minima on the energy hypersurfaces¹⁻⁴. From the experimental side, cyclopentyne is the smallest unsubstituted cyclic alkyne for which there is any evidence of even the transient existence^{5,6}. Directly identified cyclopentynes usually have multiple ring structures such as norbornyne⁷ and acenaphthylene⁸. Understanding electronic effects that could stabilize the cyclopentyne without introducing additional rings will be helpful to estimate the probability of directly observing a single five-membered ring compound of cyclopentyne. In this study, electronic structures of the halogen substituted cyclopentynes shown in Figure 1 are investigated by using semiempirical MNDO method⁶.

In cyclopentynes, substitutions are possible only for hydrogen atoms attached to the saturated carbons in the ring, but the reactivity and probably the stability primarily depend on carbons forming the triple bond. As a result, substitution effects of hydrogen atoms are not likely to be large. The trend analysis like substitutions by halogen series is expected to be sufficient to provide most informations necessary to decide on the stability and the reactivity of single ring cyclopentyne when the question of the kinetic stability is not included in the consideration.

Theoretical studies of unsubstituted cyclopentyne by Olivella and coworkers¹⁻³, by using results from *ab initio* calculations as standard, indicate that MNDO calculations yield quite reliable results for this molecule. Therefore, results from MNDO calculations will be reliable enough to draw some qualitative conclusions about the electronic properties of various halocyclopentynes.

From the MNDO and *ab initio* studies of the unsubstituted cyclopentyne, it is known that cyclopentyne has substantial diradical characters which cannot be correctly described by the restricted Hartree-Fock (RHF) method. In order to account for this diradical character which is also expected for all halocyclopentynes, two other methods, unrestricted HF (UHF) and 3×3 configuration interaction (CI) methods,⁹ are used as well as the RHF method in the present study. Computational details and results are given in the next section followed by conclusions and discussion in the final section.

Table 1. Heats of Formation (kcal/mol) and other Properties for Halocyclopentynes from Various MNDO Calculations

| | | C ₅ H ₆ | C ₅ H ₅ I | C ₅ H ₅ Br | C ₅ H ₅ Cl | C ₅ H ₅ F |
|----------------------|-----------------------|-------------------------------|---------------------------------|----------------------------------|----------------------------------|---------------------------------|
| RHF | | | | | | |
| sym ^a | | 137.48 | 156.02 | 142.64 | 130.88 | 92.35 |
| No. Sym ^a | | 137.48 | 156.01 | 142.63 | 130.86 | 92.34 |
| UHF | | | | | | |
| S ₂ = 0 | ΔH_f | 120.4 | 139.0 | 126.0 | 114.5 | 77.1 |
| | $\langle S^2 \rangle$ | 1.002 | 1.029 | 1.022 | 1.018 | 1.000 |
| S ₂ = 1 | ΔH_f | 133.4 | 152.2 | 139.5 | 128.2 | 91.3 |
| | ΔE^b | 13.0 | 13.1 | 13.5 | 13.7 | 14.2 |
| 3×3 CI | | | | | | |
| Singlet | ΔH_f | 121.7 | 140.7 | 127.4 | 115.7 | 78.1 |
| | ν_{CC} | 1925 | 1929 | 1930 | 1944 | 1951 |
| Triplet | ΔH_f | 129.8 | 149.0 | 136.0 | 124.6 | 87.9 |
| | ν_{CC} | 1880 | 1885 | 1886 | 1887 | 1896 |
| | ΔE^b | 8.1 | 8.3 | 8.4 | 8.9 | 9.8 |

^aReferring to optimizations with and without reflection symmetry.

^bHeats of formation difference between two preceding states.

Computational Details and Results

Geometries of halocyclopentynes are optimized in RHF MNDO calculations with and without reflection symmetry and optimized energies are shown in Table 1. When the reflection symmetry is not imposed, heat of formation and thus the total energy of cyclopentyne do not change as shown in Table 1. Heats of formation for halocyclopentynes are lowered by 0.01 kcal/mole by the relaxation of the reflection symmetry. Since these lowerings are rather insignificant and accompanying geometry changes are negligible, the C_s point group symmetry is assumed for halocyclopentynes for all subsequent calculations.

When the UHF method is employed for the S₂ = 0 states, which have equal number of α and β spin electrons, of halocyclopentynes, heats of formation are substantially lowered compared with RHF values as shown in Table 1, indicating that halocyclopentynes are not true closed-shell configurations in their ground states. Heats of formation for the S₂ = 0 states are 15.3, 16.5, 16.6 and 17.0 kcal/mole below for F, Cl, Br, and I substituted cyclopentyne, respectively, when UHF energies are compared with RHF ground state

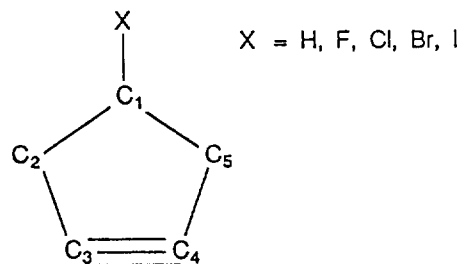
Table 2. Optimized Geometrical Parameters from 3×3 CI MNDO Calculations for Halocyclopentynes, C₅H₅X. Bond Lengths are in Å and Bond Angles in Degrees^a

| | Bond Length | | | | | |
|---------|-------------|-------|-------|-------|-------|-------|
| | C3C4 | C4C5 | C1C5 | C5X | C1H | C5H |
| Singlet | | | | | | |
| X = H | 1.263 | 1.477 | 1.590 | 1.108 | 1.108 | 1.108 |
| F | 1.260 | 1.471 | 1.623 | 1.349 | 1.123 | 1.107 |
| Cl | 1.260 | 1.477 | 1.595 | 1.805 | 1.109 | 1.107 |
| Br | 1.262 | 1.477 | 1.593 | 1.887 | 1.108 | 1.108 |
| I | 1.262 | 1.476 | 1.595 | 2.029 | 1.110 | 1.108 |
| Triplet | | | | | | |
| X = H | 1.313 | 1.484 | 1.571 | 1.109 | 1.109 | 1.109 |
| F | 1.312 | 1.481 | 1.599 | 1.351 | 1.123 | 1.109 |
| Cl | 1.312 | 1.484 | 1.575 | 1.804 | 1.108 | 1.109 |
| Br | 1.311 | 1.483 | 1.573 | 1.889 | 1.108 | 1.109 |
| I | 1.312 | 1.483 | 1.576 | 2.030 | 1.110 | 1.109 |

| | Bond Angle | | | |
|---------|------------|------------|--------|-------------|
| | <C3C4C5 | θ^b | <HC2C3 | φ^c |
| Singlet | | | | |
| X = H | 116.9 | 0.0 | 113.4 | 126.7 |
| F | 117.9 | 1.1 | 113.7 | 131.6 |
| Cl | 117.2 | 1.0 | 113.3 | 130.8 |
| Br | 117.0 | 0.9 | 113.4 | 130.8 |
| I | 116.9 | 0.8 | 113.2 | 134.5 |
| Triplet | | | | |
| X = H | 114.7 | 0.0 | 112.5 | 126.7 |
| F | 115.4 | 1.0 | 112.6 | 131.1 |
| Cl | 114.9 | 0.9 | 112.5 | 130.2 |
| Br | 114.9 | 0.8 | 112.5 | 131.0 |
| I | 114.7 | 0.7 | 112.3 | 134.2 |

^aNumbering scheme for atoms are given in Figure 1. ^bAngle between the plane formed by C1, C2 and C5 and that by C2, C3, C4 and C5. ^cAngle between C1X and the plane formed by C1, C2 and C5.

energies. Heats of formation for the $S_z = 1$ states from UHF calculations, also shown in Table 1, are larger than those for the $S_z = 0$ states. Energy differences between the $S_z = 0$ and the $S_z = 1$ states also decrease as the halogen changes from F to I. Based upon RHF and UHF calculations, halocyclopentynes have the singlet ground states that have some diradical characters.⁹ The same is true for cyclopentyne, which can be seen in Table 1 and was also the conclusion of other studies¹. UHF calculations usually do not yield pure spin states and this spin contamination is especially problematic when a singlet state has large open-shell characteristics as the present case. The degree of spin contamination can be estimated from the expectation value of total spin angular momentum operator S^2 , $\langle S^2 \rangle$. The values of $\langle S^2 \rangle$ for halocyclopentynes are about 1 for the $S_z = 0$ states for all the species as shown in Table 1, indicating that the $S_z = 0$ states are about 50-50 mixture of pure singlet and pure triplet states. In a situation like this, 3×3 CI method is probably the simplest method that can correctly describe the singlet diradical states. The $S_z = 1$ states are very close to the pure triplet

**Figure 1.** Numbering scheme of atoms for cyclopentyne and halocyclopentynes.

states, but the triplet states are also better described by 3×3 CI method which corresponds to open-shell RHF method for the two open-shell triplet states.

MNDO heats of formation for open shell states from 3×3 CI calculations are also summarized in Table 1. Compared with UHF energy differences between the $S_z = 0$ and the $S_z = 1$ states, energy separations between the singlet and the triplet states are smaller by about 5 kcal/mole, mainly because energies for triplet states are lowered in 3×3 CI calculations. On the contrary, singlet energies are slightly higher for 3×3 CI calculations probably because all high spin components are eliminated. The trend in the energy separations is the same as that in the UHF values. Halogen substitution increases the energy separation between singlet and triplet states according to the electron withdrawing ability of the halogen atom. The effect is largest for the F and smallest for I. It is noted that this trend is observed for almost all the properties discussed in this paper.

Diradical characters can be estimated from the 3×3 CI calculations by examining mixing coefficients for the closed shell ground state configuration and those for doubly excited configurations. Diradical characters are reduced by halogen substitution by a small amount. The weights for the excited configuration in MNDO 3×3 CI calculations are 17% for cyclopentyne and 15.6% for fluorocyclopentyne and in between for other halocyclopentynes. It is possible to expect this trend also from energy separations shown in Table 1. The larger the singlet triplet separations, the less the diradical character for the singlet state.

Geometrical parameters optimized in MNDO 3×3 CI calculations are shown in Table 2 and corresponding numbering scheme is shown in Figure 1. The multiply bonded carbon-carbon bond lengths, C3C4 in Table 2, are about 1.26 Å for all the singlet states and 1.31 Å for all the triplet states. Comparing these bond lengths with those of ethylene (1.329 Å) and acetylene (1.203 Å), we may assume that singlet states contain some triple bond characters. Differences in CC bond lengths among halides are small, but triple bond characteristics increase as $I < Br < Cl < F$ since the bond length is the shortest for fluorocyclopentyne. Calculated bond orders and electron densities are in the same order. Effects of halogen substitutions are smaller for the triplet states than for the singlet states. In the MNDO calculations, cyclopentynes have planar structures as indicated by θ values in Table 2 which is the angle between two planes, one defined by C1, C2 and C5 and the other by C2, C3, C4 and C5. The largest deviation from the planarity is found for fluoride, but even there deviation is only about 1°, implying that interactions between pi electrons and halogen electrons are insignificant.

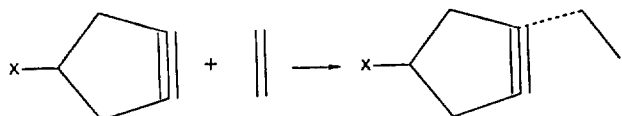


Figure 2. Schematic representation of the first step for the cycloaddition reaction of halocyclopentynes with ethylene. Structure on the right hand side is the first transition state in MNDO calculations.

Nonplanar molecule is the stable structure in *ab initio* calculations, but energy difference between the planar and nonplanar structure is very small even in those calculations.

The harmonic vibrational frequencies corresponding to C3C4 stretching, ν_{cc} in Table 1, are calculated as 1951, 1944, 1930, 1929 and 1925 cm^{-1} for F-, Cl-, Br-, I- and H- substituted cyclopentynes, respectively, as shown in Table 1. The trend here is in accordance with the amount of the triple bond characters. The same harmonic frequency from the *ab initio* 3-21G basis set calculations³ is 2054 cm^{-1} and tentative experimental value for acenaphthene⁵ is 1930 cm^{-1} . Usually harmonic vibrational frequencies from HF calculations are about 10% larger than the experimental values¹⁰. Therefore, it is reasonable to guess that triple bond characters are larger for acenaphthene than for any of the molecules considered here. In cyclopentynes, CC stretching frequency is probably in the neighborhood of 1850 cm^{-1} . The CC stretching frequencies for the triplet states are about 50 cm^{-1} smaller than those for the singlet states as shown in Table 1.

Results summarized in Table 1 and 2 imply that cyclopentynes are slightly stabilized by the halogen substitution and the largest effect is for the fluoride.

In the experiments where cyclopentyne is established as an intermediate, cyclopentyne undergoes cycloaddition with olefins⁶. In the subsequent model studies of cycloaddition reaction of cyclopentyne with ethylene, Olivella *et al.*² suggest that this cycloaddition is stepwise and not concerted, *i.e.* the first transition state has the structure shown in Figure 2. Similar transition states are calculated for all halocyclopentynes and activation barriers for these transition states are all about 22 kcal/mol, which is the same as the activation barrier for cyclopentyne. It appears that 1.5% change in diradical characters has negligible effect for the reactivity of this molecule at least for this particular reaction pathway. Optimized geometrical parameters at the transition state do not differ very much from the above fluoride and the iodide. The main modification from the equilibrium structure of Table 2 is the increase in bond length of 0.01 Å for carbon carbon multiple bond implying that triple bond characters are further weakened upon formation of the bond with ethylene.

Since the largest substitution effect is found for the fluoride, we also performed series of MNDO calculations for hexafluorocyclopentyne. For this molecule, the ground state is also a singlet with diradical characters of 10% which is about 5% less than fluorocyclopentyne. Energy separation between the singlet and the triplet states increases to 16.4 kcal/mol. The CC bond length for the carbon multiple bond becomes 1.245 Å, displaying substantially more triple bond characters than mono substituted species. Therefore, stabilization effect is fairly large for hexafluorocyclopentyne. The activation barrier for the cycloaddition reaction with ethylene, however, is still 21 kcal/mol which is about the

same as that for other species.

Conclusions and Discussion

Halogen substitutions in cyclopentyne only slightly modify the electronic properties of carbon-carbon multiple bond. Electron withdrawing properties of halogens increase the triple bond characters and reduce the diradical characters. The trend among different halides is the usual one expected for this series, monotonic increase or decrease as one goes from F to I. It is expected that fluorides, especially hexafluorocyclopentyne, are more stable than cyclopentyne, which may be used as a guideline in an effort to isolate cyclopentyne with single ring. However, the reactivity of the cycloaddition reaction is little affected by the substitution.

The present study is limited to a few cases of halides, but it should be enough to shed some light to the range of electronic effect caused by the substitution for cyclopentyne. Any relative change substantially greater than those of the present cases is expected only when one or more ring carbon atoms are replaced by larger atoms¹¹ such as Si or S. Of course, increasing kinetic stability by introducing bulky groups is still an open question not addressed in the present study.

It is noted that the results of the present study should not be taken seriously as the quantitative predictions. Semiempirical MNDO calculations have many limitations. Two of them particularly relevant to the present results are that triplet states are usually described as too stable and that parameters for halogen atoms are probably not of the same quality as those for C and H atoms¹².

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A Theoretical and Experimental Study of Physical Adsorption of Gases on Uniform Flat Solid Surface

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In this work we have experimentally observed the physisorption isotherms for nitrogen, TMS, cyclohexane, benzene, and *n*-hexane adsorbed on flat aluminum foil surface and have analyzed them theoretically on the basis of the theory proposed by Chang *et al.* The results show that the theory by Chang *et al.* can provide a useful means to describe the physisorption of gases on uniform flat solid surface which is essentially important for analysis of the pore volume distribution in porous solid surface. We have also discussed the application of the results obtained in this work to the analysis of pore volume distribution in porous alumina we reported previously.

Introduction

In the process of analysis of pore volume distribution in porous solids the knowledge of statistical thickness of adsorbed gas on the uniform flat solid surface is required and this thickness plotted against the relative gas pressure forms the so-called "*t*-curve".¹ In other words one may say that the knowledge of *t*-curve is essential for analysis of pore volume distribution in porous solids by the gas adsorption method. Gaseous nitrogen has been the most popular adsorbate used for this purpose and its *t*-curves have been reported by several authors.² De Boer *et al.*³ have noted that the shape of nitrogen *t*-curve is nearly independent of the adsorbent used and have suggested that such a universal feature of the nitrogen *t*-curve should be used for the study of pore volume distribution. Since then the universal *t*-curve for gaseous nitrogen has become the major tool with which one can investigate into the mesopore distribution problems.

In a previous paper⁴ (hereafter, referred to as Paper I), however, the authors have demonstrated that the use of non-polar and spherical molecules with relatively large molecular weight as adsorbates is more advantageous and gives more reliable and consistent results in the analysis of pore volume distribution by the gas adsorption method. Unfortunately, for such molecules as TMS, CCl₄, and cyclohexane, which are recommended as more suitable than nitrogen as adsorbate, little is known about their flat-surface adsorption isotherms. Therefore, in Paper I we have used their adsorption-desorption isotherms measured for the porous alumina sample to estimate their flat-surface isotherms by fitting the former into the theoretical isotherms derived from the theory

due to Chang *et al.*⁵ over the relative pressure range of 0.0-0.3 and thereby have obtained very encouraging results. Thus we have decided that it is worth following this route for further investigation of the aforementioned problems. Ultimate justification of the validity of this method requires the experimental measurement of the flat-surface isotherm for each adsorbate and its comparison with the corresponding theoretical isotherm. Thus the objective of this paper is to observe the experimental flat-surface isotherms for adsorbates such as TMS, CCl₄, and cyclohexane and compare them with those calculated from the Chang's theory.

The theoretical isotherm derived by Chang *et al.* contains four adjustable parameters that can be fixed in such a way that it gives the best fit into the experimental data over a wide range of relative pressure. Among these four parameters, *a* is the one that has the largest influence on the shape of isotherm over the relative pressure range of 0.8-1.0 which is the most crucial region for the analysis of pore volume distribution. In Paper I we have simply assumed *a* = 0.95 because from the adsorption-desorption isotherms observed for the porous alumina system the value of this parameter could not be determined directly. By observing the experimental flat-surface isotherm one may find a better way to determine the value of this parameter via direct comparison with the theoretical isotherm. In this work we have measured the flat-surface physisorption isotherms for nitrogen, TMS, cyclohexane, benzene, and *n*-hexane adsorbed on the uniform aluminum foil and the results have successfully been compared with the calculated ones. We have also recalculated the pore volume distribution curves for the porous alumina system we discussed in Paper I using the results ob-