# An ESR and ab−initio MO study of π CH2−n o orbital crossover in cycloalkylketone radical cations

**3 AUTHORS**, INCLUDING:

Kenji Komaguchi
Hiroshima University

**94** PUBLICATIONS **1,522** CITATIONS

SEE PROFILE

Masaru Shiotani
Hiroshima University

**204** PUBLICATIONS **2,459** CITATIONS

SEE PROFILE

# An ESR and ab-initio MO study of $\pi_{\text{CH2}}-n_0$ orbital crossover in cycloalkylketone radical cations

Peng Wang, Kenji Komaguchi, Masaru Shiotani *

*Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi 739-8527, Hiroshima, Japan*

## Abstract

The cyclobutanone and cyclopentanone radical cations were generated in a halocarbon matrix by ionizing radiation at 77 K. The ESR spectrum of a cyclobutanone radical cation consisted of a triple-quintet *hf* structure with ca. 0.9 mT (2H) and 2.4 mT (4H) splittings. Whereas, both cyclopentanone and 2,2,5,5-tetradeuteriocyclopentanone radical cations gave an identical triplet with 1.5 mT (2H) splitting. Based on the [1]H *hf* splittings, it was concluded that the SOMO in cycloalkylketone radical cations was changed from a $\pi_{\text{CH2}}$ oribital to a $n_0$ (and $\sigma_{\text{C-C}}$) orbital (i.e., $\pi_{\text{CH2}}-n_0$ orbital crossover) when the ring size increased from a four-member to a five-member. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

It has been suggested based on both experiments and theoretical calculations that for ketones such as $(CH_3)_2CO$ [1,2], $CH_3COC_2H_5$ [1,2] and $cC_2H_4CO$ [3,4] the $n_0$-type orbital (i.e., oxygen lone pair *p* orbital) can be the HOMO and either the $\pi_{\text{CO}}$ or $\pi_{\text{CH2}}$-type orbital can be the next-HOMO. Their energy sequence, however, may depend on the local structure around the $\rangle C{=}O$ group (i.e., substituted group, bond angle, etc.), especially in radical cations, because of their rather small energy difference of less than ca. 1–2 eV. ESR can provide direct experimental evidence on the SOMO (singly occupied molecular orbital) of radical cations and anions [5–10]. Among ketones, cycloalkylketones ($cC_nH_{2n}CO$)

are attractive to investigate with respect to electronic structure because they have essentially no rotational isomers, which generally make the ESR spectral analysis complicated, and their geometrical structure can be easily changed using different ring sizes. Symons and Boon [5] were the first to report the ESR spectrum of the cyclohexanone radical cation ($cC_5H_{10}CO^+$) with a triplet ^{1}H hyperfine (*hf*) splitting of ca. 2.7 mT in a $CCl_3F$ matrix at 77 K and attributed the triplet to two equatorial protons at the β-carbons (see Scheme 1), the rational being that these protons are held close to the plane containing the singly occupied *p* orbital on oxygen. However, immediately thereafter, their *hf* attribution was found to be erroneous. That is, Snow and Williams [6] have reported that the ESR spectra of the non-deuterated cyclohexanone and 2,2,6,6-tetradeuteriocyclohexanone are identical, and attributed the triplet to the protons at the γ-carbons. Based on these results,

* Corresponding author. Fax: +81-824-24-7736; e-mail: mshiota@ipc.hiroshima-u.ac.jp
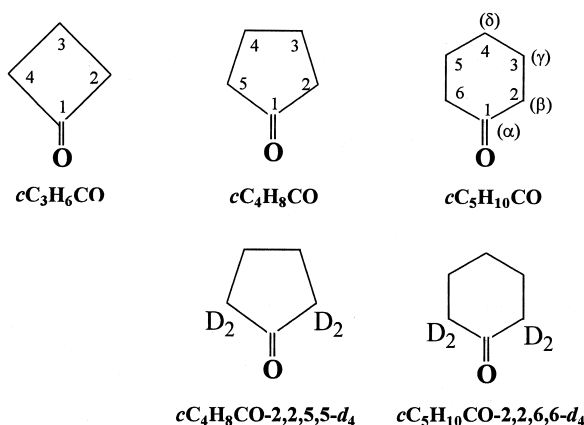
Scheme 1.

they proposed 'long-range' proton *hf* interactions relayed through a *trans* ('W'-plan) arrangement of $\sigma_{C-C}$ and $\sigma_{C-H}$ bonds in the radical cations of the carbonyl compounds. The hyperconjugation [11] is the most probable mechanism for the unpaired electron in the $n_0$ (and $\sigma_{C-C}$) orbital to be transferred to the 'equatorial' hydrogens at γ-carbons of $cC_5H_{10}CO^+$ with respect to the $C_\beta$–$C_\alpha$, bond, because the hydrogens are located at the position close to the $C_\beta$–$C_\alpha$–O plane having a large spin density, similar to alkane radical cations [12,13]. When the ring size decreases from a six-member to five- and four-members, the dihedral angle between the $C_\alpha$–$C_\beta$ and $C_\gamma$–$H_e$ bonds may increase so as to give less effective hyperconjugation. This might cause a change in the SOMO from a $n_0$ (and $\sigma_{C-C}$)-type orbital to either a $\pi_{CH2}$-type or a $\pi_{CO}$-type orbital, which we call either a '$\pi_{CH2}$–$n_0$' orbital crossover or a '$\pi_{CO}$–$n_0$' orbital crossover. However, no complete ESR study has yet been reported for the cyclobutanone ($cC_3H_6CO$) and cyclopentanone ($cC_4H_8CO$) radical cations. Thus, we investigated the electronic structure of cycloalkylketones, $cC_nH_{2n}CO^+$ ($n$ = 3, 4), using the low-temperature matrix ESR spectroscopy method [12,13]. Based on the [1]H *hf* splittings, it was found that the '$\pi_{CH2}$–$n_0$' orbital crossover took place between the cyclobutanone and cyclopentanone radical cations. This conclusion was theoretically supported by ab-initio MO and density functional theory (DFT) calculations. Furthermore, we observed the ESR spectra of the radical anions of $cC_nH_{2n}CO$ ($n$ = 3–5) radiolytically generated in a

2-methyltetrahydrafuran (2MTHF) matrix at 77 K and confirmed that their SOMO is a $\pi^*_{C=O}$-type orbital, independent of the ring size.

## 2. Experimental

The cycloalkylketones used in this study included cyclobutanone ($cC_3H_6CO$; Aldrich), cyclopentanone ($cC_4H_8CO$; Tokyo Kasei), 2,2,5,5-tetradeuteriocylopentanone ($cC_4H_8CO$-2,2,5,5-$d_4$), cyclohexanone ($cC_5H_{10}CO$; Tokyo Kasei) and 2,2,6,6-tetradeuteriocyclohexanone ($cC_5H_{10}CO$-2,2,6,6-$d_4$). The two partially deuterated ketones were synthesized after F.E. Condon [14]. Their purities were greater than 99% based on the ^{1}H, [2]D and ^{13}C-NMR spectra (Bruker AMX400). Furthermore, 95 atom% deuterium substitution was confirmed by the NMR spectra. Halocarbons such as perfluorocyclohexane ($cC_6F_{12}$; Aldrich), $CCl_3F$ (Tokyo Kasei) and $CFCl_2CF_2Cl$ (Tokyo Kasei) were used without further purification. 2-Methyltetrahydrofuran (2MTHF; Tokyo Kasei) was used after drying with metallic Na.

Solid solutions containing ca. 0.5 mol% cycloalkylketones in either halocarbon or 2MTHF were prepared in a Spectrosil ESR sample tube by several cycles of freezing, degassing and thawing on a vacuum line. They were irradiated with γ-rays from ^{60}Co with a total dose of ca. 10 kGy at 77 K and then subjected to an ESR study. These are well-established methods to generate and stabilize the

solute radical cations or anions in a low-temperature solid matrix [12,13]. The ESR spectra were recorded on a Bruker ESP 300E spectrometer from 4.2 K to ca. 200 K. The temperature was controlled with an Oxford ESR 900 continuous flow cryostat.

The geometrical structure was optimized on a Cray J932/24 computer at the Information Processing Center (IPC), Hiroshima University, at the MP2/6-31G** level using the GAUSSIAN 94 program [15]. The $^1$H–$hf$ splittings were calculated for the optimized structure by the Density Function Theory (DFT) method [16] at the B3LYP/6-31G** level.

## 3. Results and discussion

### 3.1. Radical cations

Fig. 1a shows the ESR spectrum of the cyclobutanone radical cation in $cC_6F_{12}$ at 77 K. The spectrum consists of an isotropic triple quintet $hf$ structure with 0.9 mT (2H) and 2.4 mT (4H) splittings with a slight $g$-tensor anisotropy ($g_{\parallel} = 2.0002$ and $g_{\perp} = 2.0035$). The same triple quintet spectrum was observed at 77 K using CFCl$_2$CF$_2$Cl and CFCl$_3$ matrices instead of $cC_6F_{12}$. A possible geometrical structure of $cC_3H_6CO^+$ is either planar $\mathbf{C}_{2v}$ or puckered $\mathbf{C}_s$. Observation of the $hf$ splittings due to two 'equivalent' and four 'equivalent' hydrogens



Fig. 1. ESR spectra of the cyclobutanone radical cation (a) and radical anion (b) generated in $cC_6F_{12}$ and 2MTHF matrices by γ-ray irradiation, respectively, at 77 K, together with the simulated ones, (a') and (b'); the $hf$ splittings are listed in Table 1. Note that (b) was obtained by subtracting the spectrum of the matrix radical (2MTHF radical) from the original one.

strongly suggests that the former can be the case. That is, assuming the $\mathbf{C}_{2v}$ planar structure, the triplet and quintet splittings are straightforwardly attributable to two hydrogens at the γ-carbon and four hydrogens at the β-carbons, respectively. No appreciable change in the spectrum was observed for $cC_3H_6CO^+$ in $cC_6F_{12}$ in the temperature range from 4.2 K to 175 K. This indicates that the $\mathbf{C}_{2v}$ structure is an intrinsic one, not a dynamically averaged one. Based on the large $hf$ splitting due to the four equivalent hydrogens at the β-carbons, a $\pi_{CH2}$-type SOMO is suggested. The possibility of either a $n_0$ (and $\sigma_{C-C}$) or a $\pi_{C=O}$-type SOMO is ruled out. Boon and Symons have reported the same triplet-quintet spectrum as the present one for the irradiated solid solution containing $cC_3H_6CO$ in a CCl$_3$F matrix at 77 K [7]. They have tentatively assigned the spectrum to a ring opening alkyl type of radical, CH$_2$CH$_2$CH$_2$CO$^+$. However, the present study revealed that their assignment of the spectrum was erroneous. It is worthy of note that the $cC_3H_6CO^+$ in CFCl$_2$CF$_2$Cl was irreversibly transformed into the radical with a double triplet splitting of 2.0 mT (1H) and 3.6 mT (2H) when the temperature increased to 115 K. The newly formed radical was attributable to the neutral radical which was formed by a one proton-detachment reaction from $cC_3H_6CO^+$ at the β-carbon.

In order to compare the electronic structure of $cC_3H_6CO^+$ with that of other cycloalkylketone radical cations, the cyclopentanone radical cations were radiolytically generated in $cC_6F_{12}$ at 77 K. Fig. 2a and b show the ESR spectra of $cC_4H_8CO^+$ and $cC_4H_8CO\text{-}2,2,5,5\text{-}d_4^+$, respectively. Both spectra of the non-deuteriated and deuteriated cyclopentanone radical cations consist of an identical triplet with 1.5 mT and $g = 2.0006$, except for the slightly narrower line width for the deuteriated radical cation. If the protons responsible for the $hf$ splitting were replaced by deuterons, the splitting should be reduced by a factor of ca. 6.5, the magnetic moment ratio of $^1$H to $^2$D. However, the observed $hf$ splittings were independent of the deuterium substitution. Thus, that the two interacting protons are not located at C-2 and C-5 (i.e., two β-carbons), is conclusively demonstrated by the present experimental result. Accordingly, the observed triplet must be attributable to two of the four protons at C-3 and C-4 (two γ-carbons).
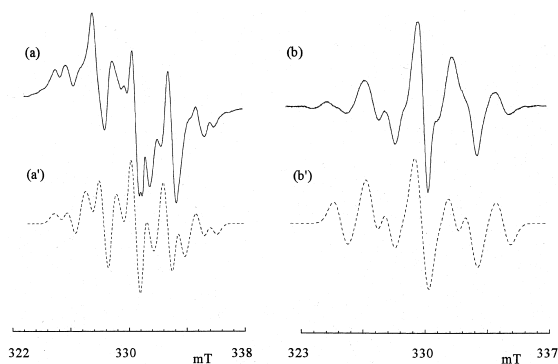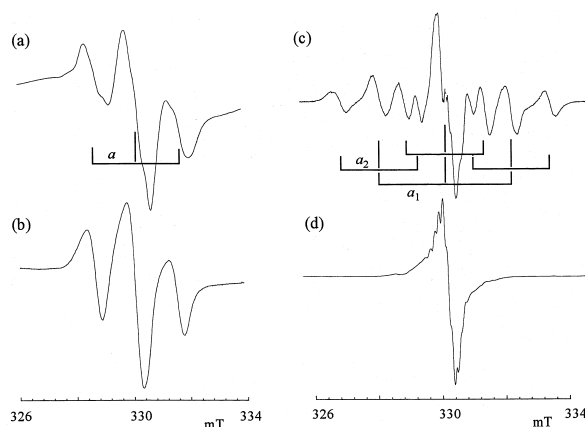
Fig. 2. ESR spectra of the radical cations of cyclopentanone (a) and 2,2,5,5-tetradeuteriocylopentanone (b) generated in $cC_6F_{12}$, together with those of the corresponding radical anions (c) and (d) generated in 2MTHF, by γ-ray irradiation at 77 K. The stick diagrams show the spectral analysis.

Then, assuming the $n_0$ (and $\sigma_{C-C}$)-type SOMO, the observed triplet is attributed to the two 'equatorial' protons at the γ-carbons, one at each γ-carbon, which are located at the 'trans' position with respect to the $C_\alpha$–$C_\beta$ bond, having a large unpaired electron density. The assumption is supported by the theoretical calculations, as described below.

Similar to $cC_4H_8CO^+$, both spectra of $cC_5H_{10}CO^+$ and $cC_5H_{10}CO$-2,2,6,6-$d_4^+$ generated in $cC_6F_{12}$ consisted of an identical triplet, but with a larger $^1$H $hf$ splitting of 2.6 mT (2H), at 77 K. The splitting is in good agreement with the previously reported one for the normal and partially deuterated cyclohexanone radical cations (2.75 mT for $cC_5H_{10}CO^+$) in CFCl$_3$ [6,7]. Thus, it was reconfirmed that the cyclohexanone radical cation also takes the $n_0$, $\sigma_{C-C}$-type SOMO.

### 3.2. Radical anions

It was demonstrated in the above section that when the ring size of $cC_nH_{2n}CO^+$ increases from four-member to five- and six-members, the SOMO is changed from the $\pi_{CH2}$ type to the $n_0$ (and $\sigma_{C-C}$) type. It is of interest to see if such orbital crossover can be observed for the corresponding radical anions. Then, we have radiolytically generated the cycloalkylketone radical anions, $[cC_nH_{2n}CO]^-$ ($n = 3$–5), in a 2MTHF rigid glass matrix at 77 K. The

ESR spectrum of $cC_3H_6CO^-$ consisted of a triple triplet with 2.7 mT (2H) and 1.8 mT (2H) splittings. Almost the same $hf$ splittings were previously reported for the $cC_3H_6CO^-$ generated by chemical reduction with an Na atom in the Ar matrix at 4 K: ca. 2.7 mT (2H) and ca. 1.7 mT (2H) splittings [9]. Assuming the $\pi^*_{C=O}$-type SOMO and hyperconjugation mechanism [11], the larger and smaller triplets are attributable to two pairs of 'axial' and 'equatorial' hydrogens at the β-carbons with respect to the C=O bond having a large spin density. The nonequivalent two hydrogens at the one β-carbon suggest that $cC_3H_6CO^-$ has a puckered $C_s$ structure, contrary to the planar $C_{2v}$ structure of $cC_3H_6CO^+$.

The spectrum of $cC_4H_8CO^-$ in 2MTHF gave a triple triplet $hf$ structure with 3.2 mT (2H) and 1.7 mT (2H) splittings at 77 K (Fig. 2c); these values being in good agreement with the previously reported ones for $cC_4H_8CO^-$ generated with an alkali metal in tetrahydrofuran (THF).[10] Whereas, $cC_4H_8CO$-2,2,5,5-$d_4^-$ in 2MTHF gave a singlet which is further poorly resolved with many $hf$ lines (Fig. 2d). This indicates that the $hf$ splittings of the non-deuteriated radical cation were reduced by a factor of ca. 6.5, the magnetic moment ratio of $^1$H to $^2$D, in the spectrum of the partially deuterated radical cation. Thus, the triple triplet splittings must be attributable to four hydrogens at the β-carbons. The result is fully consistent with the $\pi^*_{C=O}$-type SOMO,

similar to $cC_3H_6CO^+$. Furthermore, we confirmed that $cC_5H_{10}CO^-$ in 2MTHF gave a triple triplet with 2.5 mT (2H) and 0.6 mT (2H) splittings at 77 K, whereas $cC_5H_{10}CO\text{-}2,2,6,6\text{-}d_4^-$ gave a singlet. These results are consistent with the $\pi_{C=O}^*$ SOMO. Note that the triple triplet splittings of the non-deuteriated radical anion were almost the same as the previously reported ones, 3.1 mT (2H) and 0.7 mT (2H), in THF with Na at 77 K [10]. Thus, it was experimentally concluded that the $cC_nH_{2n}CO^-$ ($n$ = 3–5) radicals take the $\pi_{C=O}^*$-type SOMO, independent of the ring size. The ab-initio MO calculations support this conclusion as, described below.

### 3.3. MO calculations

In order to obtain theoretical supports for the $\pi_{CH2}-n_0$ orbital crossover in the cycloalkylketone radical cations, ab-initio MO calculations were performed. The calculations of the cyclobutanone radi-

cal cation resulted in a geometric structure very close to the planar $C_{2v}$ one with a dihedral angle of 179.8° between the C2–C1–C4 and C2–C3–C4 planes (see the geometric parameters in Fig. 3). The $^1H$ $hf$ splitting calculated for the two paired hydrogens at the β-carbons was 2.21 mT (4H), which was in good agreement with the experimental value of 2.4 mT. The calculated splitting for two hydrogens at γ-carbon (C3) was 0.2 mT, this value being also rather close to the experimental one (0.9 mT). Thus, the $C_{2v}$ structure was supported for $cC_3H_6CO^+$ by the theoretical calculations. These calculations are fully consistent with the $\pi_{CH2}$-type SOMO (Fig. 3), which was proposed based on the experimental result. Furthermore, the calculations for the corresponding radical anion ($cC_3H_6CO^-$) resulted in a puckered $C_s$ structure which has a dihedral angle of 171.6°; the calculations were found to be consistent with the experimental results based on the agreement between the experimental and calculated $^1H$ $hf$ splittings (Fig. 3).
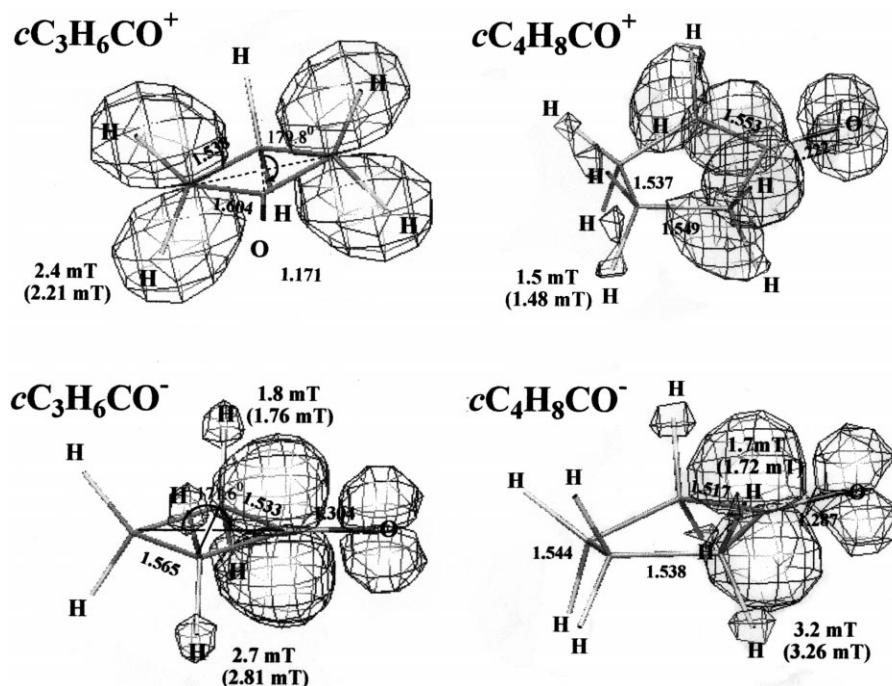


Fig. 3. Geometrical structures (bond length in Å and angle in degree) of $cC_3H_6CO^+$, $cC_3H_6CO^-$, $cC_4H_8CO^+$ and $cC_4H_8CO^-$ optimized by ab-initio MO calculations using Gaussian 94/MP2/6-31G**, together with the illustration of SOMOs. The experimental $^1H$ $hf$ splittings are compared with the theoretical ones (in parentheses) calculated at DFT B3LYP/6-31G** level for the optimized structures.

The calculations of the cyclopentanone radical cation ($cC_4H_8CO^+$) resulted in the $\mathbf{C}_2$ structure with a twist angle of 11.9° between the C2–C1–C5 plane and the C3–C4 bond (see the bond distances in Fig. 3). The $\mathbf{C}_s$ structure was calculated to be 243 kJ/mol higher than the $\mathbf{C}_2$ one. The $\mathbf{C}_2$ structure is fully consistent with the experimental results. That is, the $^1H$ $hf$ splitting calculated for two equatorial hydrogens at the γ-carbons was 1.48 mT, which is in excellent agreement with the experimental value of 1.5 mT. Thus, as expected, the SOMO of $cC_4H_8CO^+$ was concluded to consist of the 'in-plane' $n_0$ (and $\sigma_{C-C}$) orbital as depicted in Fig. 3. Furthermore, the experimental triplet $hf$ splitting of the cyclohexanone radical cation ($cC_5H_{10}CO^+$) was very well reproduced by the calculations: 2.6 mT (exp.) vs. 2.86 mT (calc.) for the two equatorial hydrogens at the γ-carbons. The dihedral angle between the $C_\alpha$–$C_\beta$ and $C_\gamma$–$H_e$ bonds was calculated to be 1.5° for $cC_5H_{10}CO^+$, this angle being much smaller than that for $cC_4H_8CO^+$ (46.3°). This could be the reason why the experimental $^1H$ $hf$ splitting is

larger for $cC_5H_{10}CO^+$ (2.6 mT) than for $cC_4H_8CO^+$ (1.5 mT), because of more effective hyperconjugation in the former radical cation. Thus, the calculations supported the $n_0$ (and $\sigma_{C-C}$) SOMO of both $cC_4H_8CO^+$ and $cC_5H_{10}CO^+$.

The calculated $^1H$ $hf$ splittings for cyclopentanone and cyclohexanone radical anions were also nicely compared with the experimental ones, as shown in Table 1. Thus, the $\pi^*_{C=O}$-type SOMO was both experimentally and theoretically confirmed for $cC_nH_{2n}CO^-$ ($n = 3$–$5$).

In order to demonstrate the $\pi_{CH2}$–$n_0$ orbital crossover more clearly, ab-initio calculations were carried out at the ROHF/6-31G** level. The results for cyclobutanone and cyclopentanone are schematically shown in Fig. 4. It can be seen from the figure, that the energy level sequence of the higher three occupied molecular orbitals is the $n_0$, $\sigma_{C-C}$–$\pi_{CH2}$–$\pi_{C=O}$ for neutral $cC_3H_6CO$, but is changed to the $n_0$, $\sigma_{C-C}$–$\pi_{C=O}$–$\pi_{CH2}$ for neutral $cC_4H_8CO$. When the one-electron oxidation reaction takes place to form $cC_3H_6CO^+$, the energy level of the original

Table 1
ESR parameters of cyclo-alkylketone radical cations and anions

| Radical | Matrix | Temp. (K) | $^1H$ $hf$ splitting (mT) | | $g$-value | SOMO | Ref. |
|---|---|---|---|---|---|---|---|
| | | | Exp. | Cal.[a] | | | |
| $cC_3H_6CO^+$ | $cC_6F_{12}$ | 4.2, 77 | 2.4 (4H) 0.9 (2H) | 2.21 (4H at $C_\beta$) 0.20 (2H at $C_\gamma$) | 2.0024[c] | $\pi_{CH2}$ | This letter |
| $cC_4H_8CO^+$ | $cC_6F_{12}$ | 4.2, 77 | 1.5 (2H) | 1.48 (2H$_e$ at $C_\gamma$)[b] | 2.0006 | $n_0, \sigma_{C-C}$ | This letter |
| $cC_4H_8CO^+$ | $CCl_3F$ | 77 | 1.95 (2H) | | 2.0035 | | [7] |
| $cC_4H_8CO$-2,2,5,5-$d_4^+$ | $cC_6F_{12}$ | 4.2, 77 | 1.5 (2H) | | 2.0006 | $n_0, \sigma_{C-C}$ | This letter |
| $cC_5H_{10}CO^+$ | $CCl_3F$ | 77 | 2.75 (2H) | | 2.0035 | | [6,7] |
| $cC_5H_{10}CO$-2,2,6,6-$d_4^+$ | $cC_6F_{12}$ | 4.2, 77 | 2.6 (2H) | 2.86 (2H$_e$ at $C_\gamma$)[b] | 2.0004 | $n_0, \sigma_{C-C}$ | This letter |
| $cC_3H_6CO^-$ | 2MTHF[b] | 77 | 2.7 (2H) 1.8 (2H) | 2.81 (2H$_a$ at $C_\beta$)[b] 1.76 (2H$_e$ at $C_\beta$)[b] | 2.0027[d] | $\pi^*_{C=O}$ | This letter |
| | Ar (with Na) | 4.2 | 2.7 (2H) 1.9 (2H) | | | | [9] |
| $cC_4H_8CO^-$ | 2MTHF[b] | 77 | 3.2 (2H) 1.7 (2H) | 3.26 (2H$_a$ at $C_\beta$)[b] 1.72 (2H$_e$ at $C_\beta$)[b] | 2.0021 | $\pi^*_{C=O}$ | This letter |
| | THF (with Na)[b] | 77 | 3.3 (2H) 2.3 (2H) | | | | [10] |
| $cC_4H_8CO$-2,2,5,5-$d_4^-$ | 2MTHF[b] | 77 | $< \Delta H_{pp} = 0.5$[b] | | 2.0021 | $\pi^*_{C=O}$ | This letter |
| $cC_5H_{10}CO^-$ | 2MTHF[b] | 77 | 2.5 (2H) 0.6 (2H) | 2.42 (2H$_a$ at $C_\beta$)[b] 0.29 (2H$_e$ at $C_\beta$)[b] | 2.0020 | $\pi^*_{C=O}$ | This letter |
| | THF (with Na)[b] | 77 | 3.1 (2H) 0.7 (2H) | | | | [10] |
| $cC_5H_{10}CO$-2,2,6,6-$d_4^-$ | 2MTHF[b] | 77 | $< \Delta H_{pp} = 0.5$[b] | | 2.0020 | $\pi^*_{C=O}$ | This letter |

[a]Theoretical $^1H$ $hf$ splittings were calculated at B3LYP/6-31G**∥MP2/6-31G**.

[b]2MTHF: 2-methyltetrahydrofuran; THF; tetrahydrofuran; $\Delta H_{pp}$: peak to peak line width in the 1st derivative spectrum; $H_e$ and $H_a$ stand for equatorial and axial hydrogens, respectively.

[c]Averaged $g$-value of $g_\parallel = 2.0002$ and $g_\perp = 2.0035$.

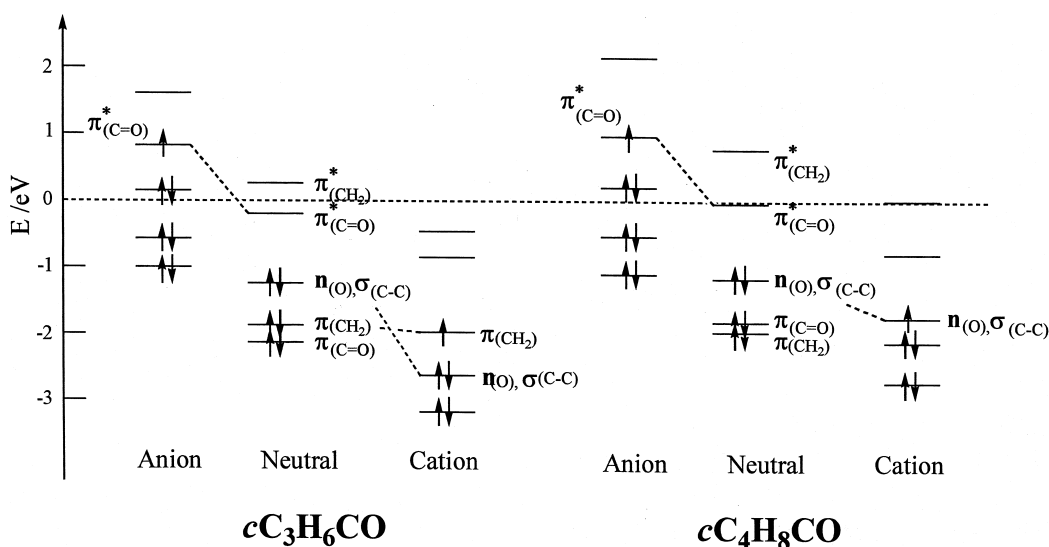[d]Averaged $g$-value of $g_\parallel = 2.0021$ and $g_\perp = 2.0030$.

Fig. 4. Energy level diagrams of $c\mathrm{C_3H_6CO}$ and $c\mathrm{C_4H_8CO}$ showing how each MO level of the neutral molecules is shifted when they suffered one electron loss or addition to form their radical cations or anions, respectively. The energy levels were calculated by the ab-initio ROHF/6-31G** method.

HOMO ($n_0$, $\sigma_{\mathrm{C-C}}$) sharply drops, but the next HOMO ($\pi_{\mathrm{CH2}}$) remains at almost the same level so that the latter orbital becomes the SOMO. For $c\mathrm{C_4H_8CO}$, the energy level sequence is maintained even after a one-electron oxidation so as to give the $n_0$ (and $\sigma_{\mathrm{C-C}}$) SOMO. The energy separation between $\pi_{\mathrm{CH2}}^*$ and $\pi_{\mathrm{C=O}}^*$ orbitals is so large that no orbital crossover takes place for the cyclobutanone and cyclopentanone radical anions.

## 4. Conclusion

The present ESR study of the cycloalkylketone radical cations, $c\mathrm{C_nH_{2n}CO^+}$, revealed that the SOMO was changed from the $\pi_{\mathrm{CH2}}$ orbital to the $n_0$ (and $\sigma_{\mathrm{C-C}}$) orbital when the ring size increased from four ($n = 3$) to five and six ($n = 4, 5$). The $c\mathrm{C_4H_8CO^+}$ and $c\mathrm{C_5H_{10}CO^+}$ radicals have the 'twist' $\mathbf{C}_2$ structure and the '*chair-like*' $\mathbf{C}_s$ structure, respectively. The unpaired electron in these radical cations can be effectively transferred to the '*trans*' $\mathrm{C_\gamma-H}$ hydrogen from the $\sigma(\mathrm{C_\alpha-C_\beta})$ orbital which is conjugated with the $n_0$ orbital having a large spin density. Whereas, the $c\mathrm{C_3H_6CO^+}$ radical has the $\mathbf{C}_{2v}$ planar with the smaller $\mathrm{C_\beta-C_\alpha-C_\beta}$ (and $\mathrm{C_\beta-}$

$\mathrm{C_\gamma-C_\beta}$) bond angles close to 90°. In this structure the unpaired electron in $c\mathrm{C_nH_{2n}CO^+}$ is less effectively transferred to the '*trans*' $\mathrm{C_\gamma-H}$ hydrogens and the SOMO turned out to be the $\pi_{\mathrm{CH2}}$ orbital.

## Acknowledgements

## References

[1] K. Kimura, S. Katsumata, T. Yamazaki, H. Wakabayashi, J. Electron Spectrosc. 6 (1975) 41.
[2] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, S. Iwata, Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules, Japan Scientific Societies Press, Tokyo/Halsted Press, New York, 1980, p. 156.
[3] R. Hoffmann, R.B. Davidson, J. Am. Chem. Soc. 93 (1971) 5699.
[4] W.L. Jorgensen, L. Salem, The Organic Chemist's Book of Orbitals, Academic Press, New York/London, 1973, p. 197.
[5] M.C.R. Symons, P.J. Boon, Chem. Phys. Lett. 89 (1982) 516.
[6] L.D. Snow, F. Williams, J. Chem. Soc. Chem. Commun. (1983) 1090.

[7] P.J. Boon, M.C.R. Symons, K. Ushida, T. Shida, J. Chem. Soc. Perkin Trans. II (1984) 1213.

[8] L.B. Knight Jr., B.W. Gregory, S.T. Cobranchi, F. Williams, X.Z. Qin, J. Am. Chem. Soc. 110 (1988) 327.

[9] R. Koppe, P.H. Kasai, J. Phys. Chem. 98 (1994) 12904.

[10] J.E. Bennett, B. Milee, A. Thomas, J. Chem. Soc. A (1968) 298.

[11] N.M. Atherton, Electron Spin Resonance, New York/London/Sydney/Toronto, 1973, p. 103.

[12] M. Shiotani, ESR studies of radical cations in solid matrices, Magn. Res. Rev. 12 (1987) 333.

[13] A. Lund, M. Shiotani (Eds.), Radical Ionic System, Kluwer, Dordrecht, 1991, p. 99, p. 127.

[14] F.E. Condon, J. Am. Chem. Soc. 73 (1951) 4675.

[15] M.J. Frisch et al., Gaussian 94, Gaussian, Pittsburgh, PA, 1995.

[16] A.D. Becke, Phys. Rev. A 38 (1988) 3098.