# UV Absorption Spectra of Methyl, Cyclopropyl Ketones

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**The UV absorption spectra of some 1, alkyl, cyclopropyl, methyl ketones are recorded in different solvents. For the 1, methyl, cyclopropyl, methyl ketone (3) a $\Delta-\pi^*$ band is observed in organic solvents. The spectra are discussed in terms of a second order perturbation of both Walsh and MO's of cyclopropane and the carbonyl group. It is found that the hypsochromic shift of the $n-\pi^*$ band in the cyclopropyl ketones is due to a destabilization of the $\pi^*$ MO. The appearance of a $\Delta-\pi^*$ in (3) is due to a rotation of the carbonyl group from the bisected conformation and a stabilization of the $\pi^*$ MO.**

## Introduction

Recently ground state properties of conjugated cyclopropyl derivatives were discussed in terms of second order perturbations using the Walsh orbitals of cyclopropane and the $\pi$-MOs of the conjugated segment as basis functions[1]. The good agreement of the obtained results with the experimental evidences suggested the extension of this method to the excited state properties of similar molecules. Such a treatment should enable the characterization of the molecular electronic absorption bands and the discussion of their photochemical reaction paths[2].

The introduction of a cyclopropyl ring into the ketones should modify their electronic absorption spectra[3]. In fact the $n-\pi^*$ band of the carbonyl group was shown to shift hypsochromically[4], the $\pi-\pi^*$ bathochromically[5] as a result of such an introduction. Theory also predicts the appearance of a novel $\Delta-{}^*\pi$ band representing a charge transfer from $\Delta \rightarrow C=O$[3]. The same theoretical treatment showed that both wave length and oscillator strength should be conformation dependant. The $\Delta-\pi^*$ band was observed in the vapour spectra of several cyclopropyl ketones in the region below 190 nm[6]. However, no observation of such a band has been reported in the solution spectra of the ketones. The photoelectron spectra of cyclopropane[7] and cyclopropyl ketones[8] showed that the highest occupied Walsh orbitals have energies of similar magnitude as those of the carbonyl ($\pi$) and lone pair (n) orbitals.

The present work deals with the influence of the carbonyl group conformation on the UV absorption spectra of methyl, cyclopropyl ketone (1), 2, methyl, cyclopropyl, methyl ketone (2), 1, methyl, cyclopropyl, methyl ketone (3) and 1, isopropyl, cyclopropyl, methyl ketone (4). The unsubstituted cyclopropyl, methyl ketone (1) should favour the bisected conformation (Fig. 1), according to the perturbation treatment[1]. In fact Bartell et al.[9] showed by means of the electron diffraction method that the (bisected) s-cis conformation of this ketone is the most stable one. Less populated was the s-trans conformation; the estimated cis:trans ratio was 80:20. A similar ratio was found by Lee and Schwendeman[10] in their microwave study of the same ketone. MINDO/2 calculations for the same molecule showed that the s-cis conformation is by 3.15 kcal/mol more stable than the s-trans conformation[11].

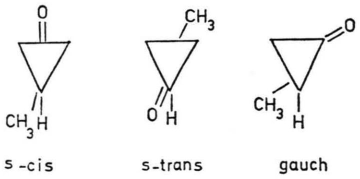
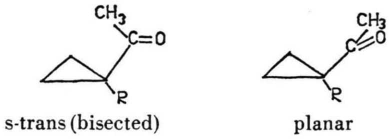


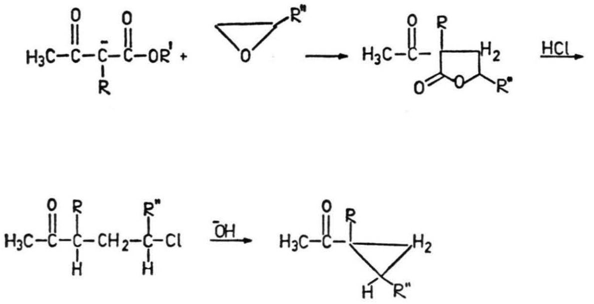
Fig. 1. Possible conformations of cyclopropyl, methyl ketone (1).

Similar conformations are expected for the 2, methyl, cyclopropyl, methl ketone (2). In the case of the 1, alkyl, cyclopropyl, methyl ketones (3) and (4) however, a change in the conformation is expected towards the planar form. This change should after the absorption spectrum of the molecule. To prove this assumption the synthesis of the ketones was undertaken and their UV absorption spectra were recorded.



## Results and Discussion

For the synthesis of the ketones we followed the general procedure as published by Cannon et al.[12]. Starting with the $\alpha$-substituted acetoaceticesters the $\gamma$, lactones were prepared through a basic condensation with the corresponding epoxides[13]. The $\gamma$, lactones were then converted to the substituted pentanone chlorides through hydrolysis in HCl solution[14]. The chlorides were then cyclized to the ketones in alkaline solutions (Scheme I).



| | R | R'' |
|---|---|---|
| (1) | H | H |
| (2) | H | $CH_3$ |
| (3) | $CH_3$ | H |
| (4) | i-propyl | H |

Scheme I

As has been indicated above the MO diagram of the cyclopropyl ketone may be constructed through a second order perturbation of the carbonyl $\pi$-MOs and the cyclopropyl Walsh orbitals[1]. In this treatment one must distinguish between the two possible conformations of the ketone, as one expects different interaction energies for different conformations. Figures 2 and 3 show the obtained orbital diagrams for the cyclopropyl carbonyl system with both bisected and planar conformations.

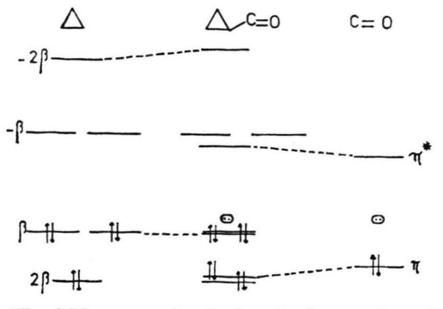


Fig. 2. The MO energy levels for the bisected cyclopropyl, methyl ketone as evaluated using a second order perturbation treatment.

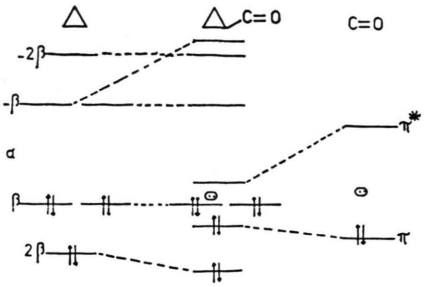


Fig. 3. The MO energy levels for the planar cyclopropyl, methyl ketone as evaluated using a second order perturbation treatment.

The most significant perturbation in the bisected conformation is the stabilization of the carbonyl $\pi$-MO and the destabilization of its $\pi^*$-MO. The occupied Walsh orbitals remain almost unperturbed. The unoccupied external $\sigma$-MO is destabilized by $0.19\,\beta$. As for the discussion of the UV spectrum of such molecule, the energy change of the $\pi^*$-level is of considerable importance. The MO-diagram suggests that excitations from the occupied $\pi$-MO should fall into the vacuum UV region ($\Delta E = 2.68\,\beta$).

In the planar conformation the most signicant perturbation is the stabilization of the $\pi^*$-MO ($\Delta E = +1.16\,\beta$). Less effected is the occupied $\pi$-MO ($\Delta E = -0.18\,\beta$). Within the framework of our present treatment, the energy change of the occupied internal $\sigma$-MO from $2.0\,\beta$ to $2.34\,\beta$ and of the unoccupied internal $\sigma$-MO from $-1.0\,\beta$ to $-2.3\,\beta$ is of no importance for the discussion of the UV spectrum of the ketone. Excitations from the occupied internal $\sigma$-MO are expected to fall in to the vacuum UV region also.

In both diagrams the occupied oxygen nonbonded orbital (n-MO) was placed above the two external $\sigma$-MOs. The assignment is based on a recent photoelectron spectroscopic measurement for different cyclopropyl ketones, which showed that the n-MO is by approximately 1.0 eV less stable than the highest occupied Walsh orbital[7].

According to the diagram in Fig. 2, the bisected conformation should allow the measurement of the carbonyl $n-\pi^*$ absorption band only in the normal UV region. The band should be shifted hypsochromically relative to that of the nonconjugated carbonyl systems. An excitation from the external $\sigma$-Walsh orbitals should fall into the vacuum UV region. The planar conformation however should allow the measurement of the bathochromically shifted $n-\pi^*$ and $\Delta-\pi^*$ (excitation from an external $\sigma$-Walsh orbital) transitions. The bathochromic shift of these bands is caused by the strong stabilization of the $\pi^*$-MO. Thus different absorption spectra, for different conformations, are expected for the cyclopropyl ketones.

### *Absorption Spectrum of Cyclopropyl, Methyl Ketone (1)*

For this ketone the well known and already reported $n-\pi^*$ band could be reproduced[15]. In accordance with the results of the perturbation treatment, it showed a hypsochromic shift relative to the $n-\pi^*$ band of acetone [$\lambda_{max} = 265$ nm ($H_2O$)][16]. In the light of the same treatment, the single band suggests a bisected conformation for the ketone, in agreement with the electron diffraction[9] and microwave studies[10]. MINDO/2 calculations for the same ketone yielded an increased stability of the bisected cis-conformation over the planar (by 5.81 kcal/mol) and over the bisected transconformation (by 4.12 kcal/mol)[11]. The $n-\pi^*$ band showed the expected bathochromic shift on transition to a nonpolar solvent (Table I and Figure 4).

### *Absorption Spectrum of 2, Methyl, Cyclopropyl, Methyl Ketone (2)*

The UV absorption spectrum of this ketone is composed of a single $n-\pi^*$ band appearing at 275 nm in n-hexane solution (Figure 5). No $\Delta-\pi^*$ transition band was detected, a fact that suggests a bisected conformation for this ketone also. MINDO/2 calculations[11] showed that the bisected-cis is the most stable conformation of this ketone. The calculated energy difference between the bisected-cis and the planar conformation is approximately 7.0 kcal/mol. The $n-\pi^*$ band was shifted bathochromically on transition to nonpolar solvents (Table 1 and Figure 5).

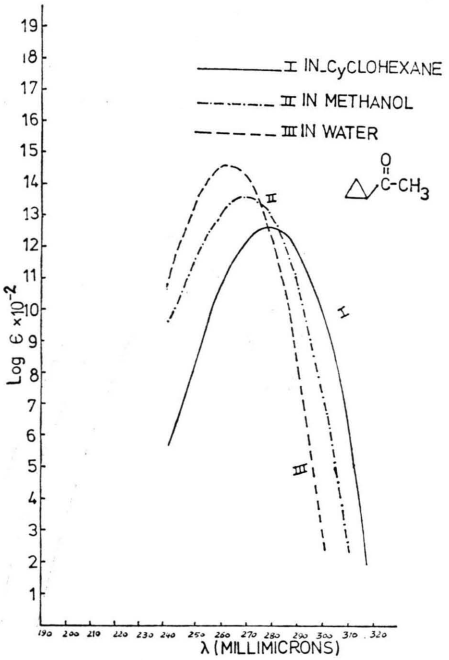


Fig. 4. Absorption Spectrum of methyl, methyl, cyclopropyl, methyl ketone (2).

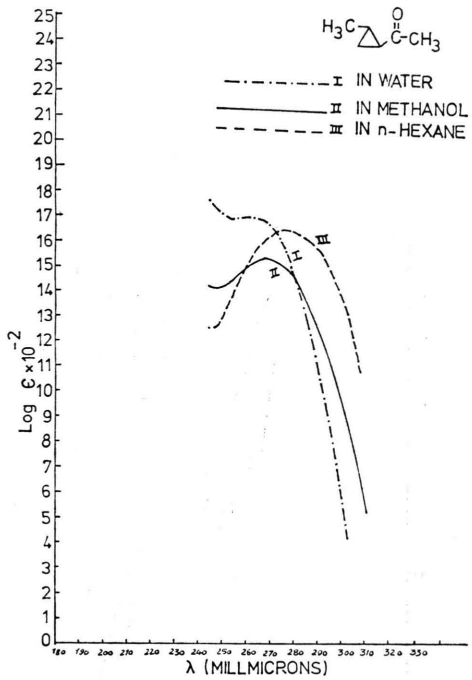


Fig. 5. Absorption spectrum of 2, methyl, cyclopropyl, methyl ketone (3).

| | n → π* (mu) | | | Δ → π* (mu) | |
|---|---|---|---|---|---|
| | water | methanol | n-hexane | methanol | n-hexane |
| Ketone (1) | 262.5 (28.2) | 270.0 (22.9) | 277.5 (18.1) | | |
| Ketone (2) | 259.5 (48.6) | 267.5 (45.2) | 275.3 (43.6) | | |
| Ketone (3) | — — | 274.8 (21.9) | 282.5 (13.2) | 273.8 (25.3) | 272. (16.1) |
| Ketone (4) | 257.1 (27.0) | 265.9 (20.1) | 274.0 (15.4) | | |

Table 1. The recorded UV-absorption maxima for the cyclopropyl, methyl ketones in different solvents.

### *Absorption Spectrum of 1, Methyl, Cyclopropyl, Methyl Ketone (3)*

The absorption spectrum of this ketone differs from that of ketone (1) by the appearance of a new band progression that starts with 225 nm. The progression can be viewed as composed from two different excitation bands; a) an $n-\pi^*$ transition band with an extrapolated wave length 282.5 nm in n-hexane, obviously overlaping with the second band; b) a $\Delta-\pi^*$ transition band, caused by the excitation from an external $\sigma$-Walsh orbital to the $\pi^*$-M Oof the carbonyl group in the planar conformation. The second band can be traced up to 272 nm (Figure 6).

The vibronic structure of the second band shows frequency differences of $1270\ \text{cm}^{-1}$ or $750\ \text{cm}^{-1}$ between each two successive vibronic peaks. These values show a close agreement with the well known C – C symmetric and asymmetric stretching frequencies in cyclopropane ($\tilde{\nu}_s = 1188\ \text{cm}^{-1}$ and $\tilde{\nu}_{as} = 866\ \text{cm}^{-1}$)[17] and may be attributed to similar vibrations in cyclopropyl, methyl ketone.

The appearance of the $\Delta-\pi^*$ band in the UV region suggests that the planar conformation is at least as stable as the bisected conformation.

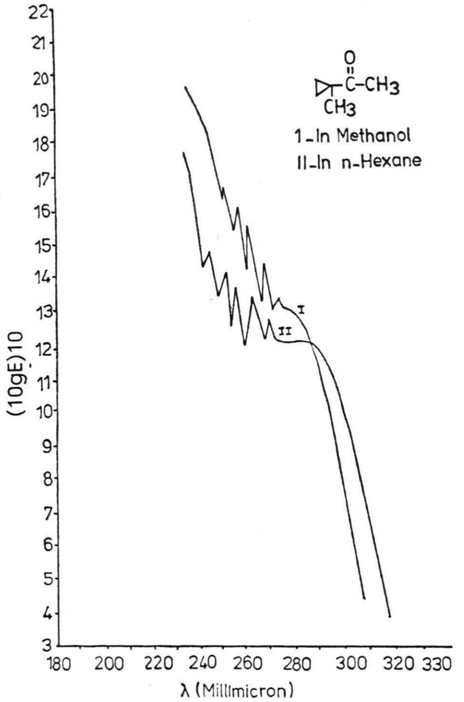


Fig. 6. Absorption spectrum of 1, methyl, isopropyl, cyclopropyl, methyl ketone (4).

MINDO/2 calculations[11] yielded an energy difference of 0.29 kcal/mol between both conformations. It also suggests that both conformations should exist at room temperature.

The $n-\pi^*$ band of the ketone undergoes bathochromic shifts when measured in nonpolar solvent. The $\Delta-\pi^*$ band is shifted hypsochromically as a result of a similar solvent change (Fig. 6 and Table I).

### *Absorption Spectrum of 1, Isopropyl, Cyclopropyl, Methyl Ketone (4)*

The absorption spectrum of this ketone includes a single $n-\pi^*$ band at 274 nm in n-hexane (Figure 7). The spectrum suggests a bisected conforma-

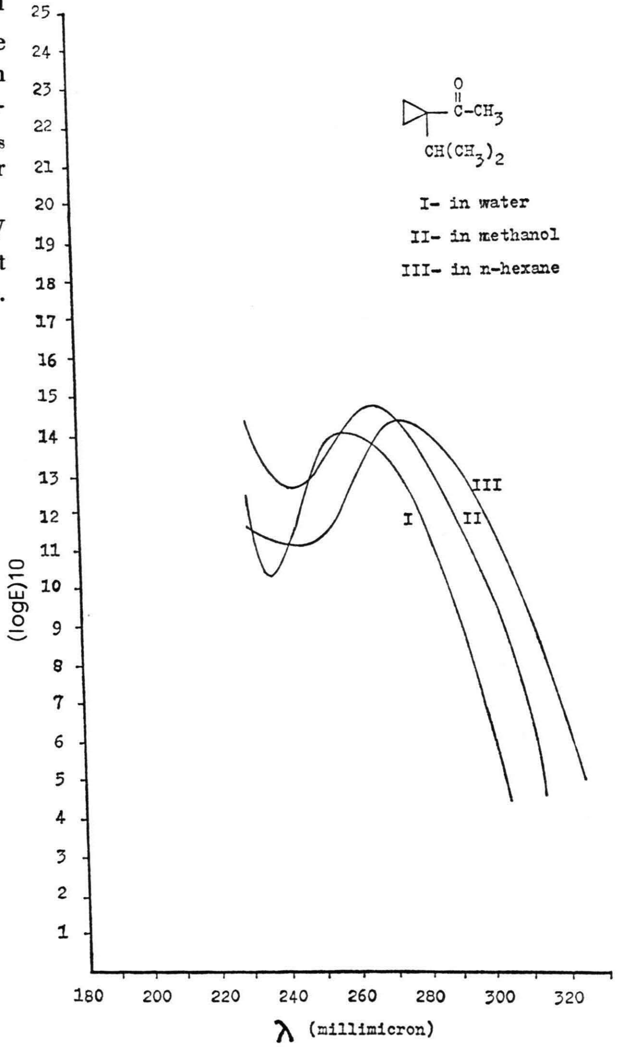
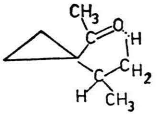


Fig. 7. Absorption spectrum of 1, isopropyl, cyclopropyl, methyl ketone (4).

tion for the molecule. Since there has been no theoretical calculation for its conformation nor any experimental studies, no definite description for its geometry can be provided. The bisected conformation might be stabilized due to a weak hydrogen bridge formation between the oxygen of the carbonyl group and a hydrogen of the isopropyl moiety;



## Experimental Section

All the UV absorption spectra were recorded on a Beckman DG spectrophotometer over the range of interest. The proton magnetic resonance spectra were recorded on a Varian A 60-A NMR spectrometer at the Department of Chemistry, University of Mosul, Iraq. $CCl_4$ was used as a solvent. The C, H analyses were performed by the Alfred Bernhardt Microanalytisches Laboratorium in West Germany.

The cyclopropylketones were synthesized through the basic cyclization of the $\gamma$-pentanone chlorides according to the general method of Cannon et al.[12]. The C, H value of the four ketones were as follows. The pentanone chlorides were prepared from the corresponding $\alpha$, acetyl, $\alpha$, alkyl lactones through HCl hydrolysis according to the same reference[12]. They were used directly for the synthesis of the ketones. The $\gamma$, lactones were prepared through the basic reaction of the epoxide with the $\alpha$, substituted acetoacetic esters (in alcoholate[13, 14]). The C, H analysis values of the $\gamma$, lactones were as follows;

| | | C | H |
|---|---|---|---|
| Ketone (1) | Calc. | 71.39 | 9.59 |
| | Found | 70.95 | 9.73 |
| Ketone (2) | Calc | 73.33 | 10.27 |
| | Found | 72.92 | 10.41 |
| Ketone (3) | Calc. | 73.33 | 10.27 |
| | Found | 72.55 | 9.77 |
| Ketone (4) | Calc. | 76.18 | 11.11 |
| | Found | 75.31 | 10.34 |

| | | C | H |
|---|---|---|---|
| 1, acetyl, $\gamma$, lactone | Calc. | 56.25 | 6.25 |
| | Found | 55.84 | 6.83 |
| 1, acetyl, 1, methyl, $\gamma$, lactone | Calc. | 59.16 | 7.04 |
| | Found | 58.35 | 7.39 |
| 1, acetyl, 3, methyl, $\gamma$, lactone | Calc. | 59.16 | 7.04 |
| | Found | 58.39 | 7.14 |
| 1, acetyl, 1, isopropyl, $\gamma$, lactone | Calc. | 63.52 | 9.41 |
| | Found | 62.71 | 9.20 |

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