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# PHOTOELECTRON AND ULTRAVIOLET ABSORPTION SPECTRA OF CYCLOPROPYL CONJUGATED 1,2-DIKETONES

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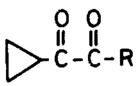
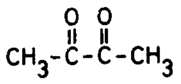
To get more insight into the valence shell structure of cyclopropyl conjugated 1,2-diketones,[2] we have studied both the He I photoelectron spectra and the ultraviolet absorption spectra of dicyclopropylethanedione (I) and 1-cyclopropyl-1,2-propanedione (II). The He I photoelectron spectra (fig.1) were recorded on a Perkin Elmer PS 18, and the UV-spectra on a Cary 14 (fig.3). The synthesis of cyclopropyl conjugated 1,2-diketones has been described by Guillaud, et al.[3] and Kelder, et al.[4]



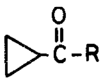
**I R = cyclopropyl**

**II R = methyl**



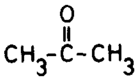
$CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$

**III**



**IV R = cyclopropyl**

**V R = methyl**



$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

**VI**

For a good understanding of the rather complex bands in the photoelectron spectra of the new 1,2-diketones I and II, a comparison with the more simple photoelectron spectra of biacetyl (III), dicyclopropyl ketone (IV), methyl cyclopropyl ketone (V), and acetone (VI) was required (fig.1). The first highest energy bands (lowest I.P.) in the photoelectron spectra of the three monocarbonyl compounds IV-VI are strong sharp peaks lacking an extensive vibrational structure. They are assigned to ionization from the mainly upon oxygen localized "lone pair" orbital. On the contrary the spectra of the 1,2-diketones I-III show rather broad diffuse highest energy bands. Swenson and Hoffmann[5] have calculated that the two "lone pairs" in 1,2-diketones interact substantially by "through bond" coupling with the central carbon-carbon $\sigma$-bond leading to a significant energy difference between the symmetric and antisymmetric lone pair combinations (1.5 - 3.0 eV). Calculations of others[6-8] corroborate this result.

In the He I photoelectron spectrum of glyoxal Turner, et al.[9a] in fact observed a splitting between the two highest energy bands of approximately 1.6 eV. The first band at

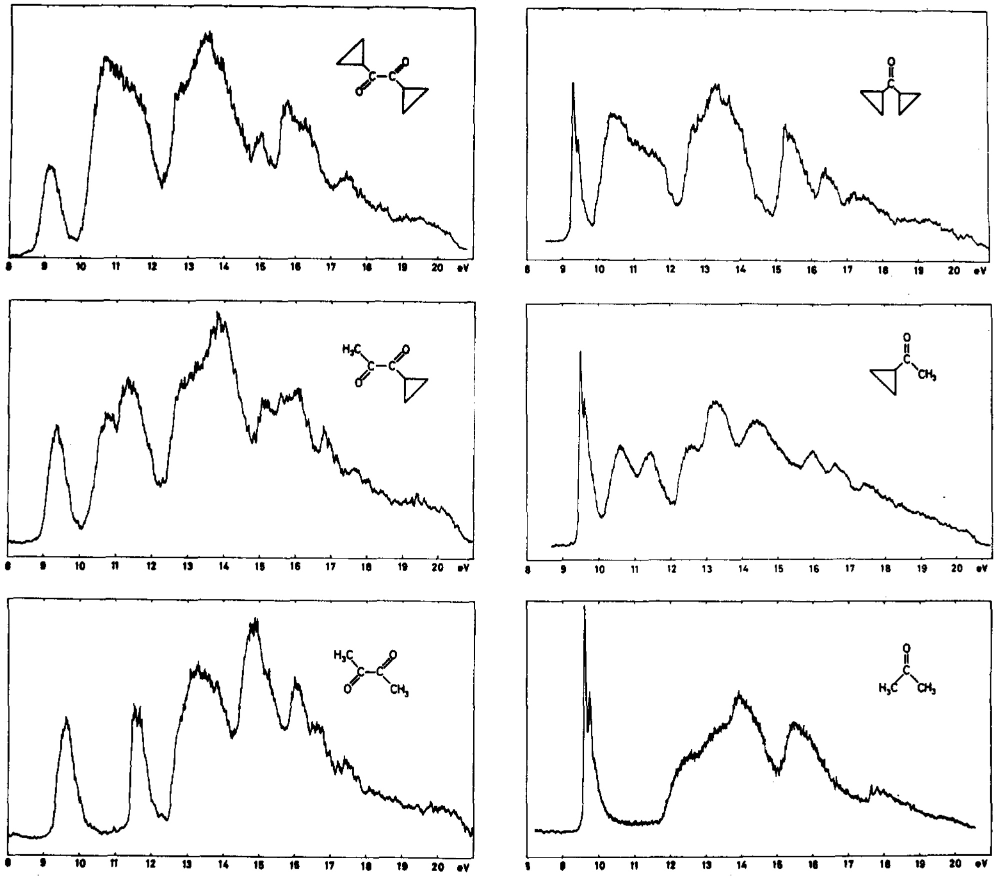
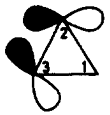


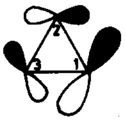
Fig.1. He I photoelectron spectra of some 1,2-diketones and related monoketones.

vertical I.P. 10.59 eV was assigned to the symmetric combination of oxygen lone pair orbitals. The diffuse structure of this band is a strong indication for the delocalization of the "lone pair" electrons in the symmetric combination. The second band with onset at 12.9 eV was ascribed to ionization from the antisymmetric combination of the oxygen lone pair orbitals. Similarly in biacetyl (III) the through bond interaction leads to an energy difference of about 1.9 eV for the two highest energy bands (fig.1).

With methyl cyclopropyl ketone (V) a double maximum is observed at 10.5 - 12 eV, which is considered characteristic for cyclopropyl compounds[9b] (compare the spectrum of acetone (VI)). Using the Walsh model[10-12] for the description of the cyclopropane ring, this double maximum can be ascribed mainly to ionization from the two highest occupied orbitals $e_S$ and $e_A$ (see fig.2) of the carbon skeleton,[11] which are degenerate for cyclopropane itself.[13] The strong band at 10 - 12 eV in the spectrum of dicyclopropyl ketone (IV) can be explained similarly. The spectrum of 1-cyclopropyl-1,2-propanedione (II) also exhibits a double maximum at 10 - 12 eV, but the band at 11.35 eV is enhanced by the band due to ionization from the antisymmetric combination of "lone pair" orbitals (compare with the spectrum of biacetyl).



$e_S$



$e_A$

In the spectrum of dicyclopropylethanedione (I) the band at 10 - 12 eV is further intensified by the introduction of a second cyclopropyl group.

The relevant I.P. data on the outermost orbitals are listed in the table below.

| Compound | Vertical I.P. (eV) | Assignment |
|---|---|---|
| acetone (VI) | 9.71 | $n_O$ |
| methyl cyclopropyl ketone (V) | 9.50 | $n_O$ |
| | 10.62; 11.40 | $e_A$; $e_S$ |
| dicyclopropyl ketone (IV) | 9.28 | $n_O$ |
| | 10.43; 11.5 | $e_A$; $e_S$ |
| biacetyl (III) | 9.57 | $n_S$ |
| | 11.41 | $n_A$ |
| 1-cyclopropyl-1,2-propanedione (II) | 9.33 | $n_S$ |
| | 10.78; 11.35 | $e_A$; $e_S$ and $n_A$ |
| dicyclopropylethanedione (I) | 9.09 | $n_S$ |
| | 10.40; 11-12 | $e_A$; $e_S$ and $n_A$ |

$n_O$ = nonbonding oxygen orbital; $e_S$ and $e_A$ = symmetric and antisymmetric external cyclopropane orbitals; $n_S$ and $n_A$ = symmetric and antisymmetric combination of "nonbonding" orbitals of the diketo system.

There is a regular decline of the I.P.'s of the highest energy bands in the monoketone and diketone series with increasing cyclopropyl substitution. (Plotting the lowest vertical I.P.'s of the three ketones versus the lowest vertical I.P.'s of the corresponding diketones gives a straight line.)

Unfortunately the photoelectron spectra of the cyclopropyl ketones and diketones are too complex to identify the $\pi$-levels of the carbonyls. Therefore it is not justified to embark upon a discussion about the degree of conjugation between the cyclopropane ring and the (di)keto system from our photoelectron spectra. For that reason we also compared the UV absorption spectra of dicyclopropylethanedione (I), 1-cyclopropyl-1,2-propanedione (II), and biacetyl (III) (fig.3). The UV spectrum of biacetyl shows two bands of low intensity, corresponding with two $n\pi^*$ transitions. Introduction of a cyclopropyl group leads to a third band of strong intensity at 220 nm. This band corresponds to a charge-transfer from the cyclopropyl group ($e_A$) to the antibonding $\pi$-MO's of the diketo chromophore. The molar extinctions of these charge-transfer bands are 6000 and 3000 for I and II respectively. Recently Meyer, et al.[15] observed such a charge-transfer band for two cyclopropyl monoketones at 180 nm ( $\epsilon_{max} \sim 4000$). It is well-known that cyclopropyl conjugated carbonyl systems prefer a conformation in which the nodal plane of the $\pi$-system bisects the cyclopropane ring.

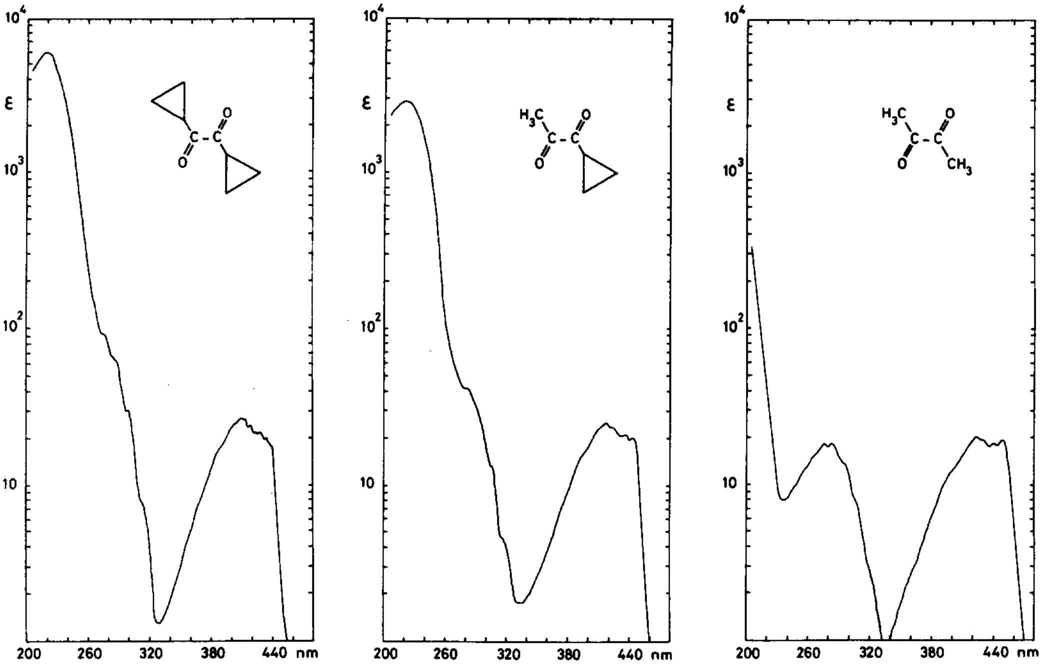


Fig.3. UV absorption spectra of some 1,2-diketones in cyclohexane at room temperature.

In that case the $e_A$ Walsh orbital is ideally suited for conjugation with the $\pi$-system. This direct conjugative effect seems to be rather small. Relative to biacetyl only a small blue shift is observed for the long wavelength $n\pi^*$ transitions of the cyclopropyl diketones I and II (fig.3).

Acknowledgement:

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