The Charge-transfer Band in the Ultraviolet Spectrum of Cyclopropyl Ketones

By A. Y. MEYER*

(*Department of Organic Chemistry, Hebrew University, Jerusalem, Israel*)

and B. MUEL and M. KASHA

(*Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida*)

Summary The charge-transfer band, predicted to occur in the ultraviolet spectrum of cyclopropyl ketones, is observed at about 180 nm, and has a molar extinction of *ca.* 4000.

AN "Extended-Hückel" analysis[1] indicates that the energy of the degenerate pair of highest-occupied molecular orbitals in cyclopropane (Δ) is comparable with that of the carbonyl π and lone-pair (n) levels. This suggests that the u.v. spectrum of cyclopropyl ketones would contain, somewhere between the $n \rightarrow \pi^*$ (*ca.* 300 nm) and $\pi \rightarrow \pi^*$ (*ca.* 150 nm) absorptions,[2] an additional band, $\Delta \rightarrow \pi^*$, representing charge-transfer from the three-membered ring, to C=O.

To locate the novel transition, we carried out MO calculations of the type used in the study of cyclopropane[3] and phenyl-ketones.[4] $\Delta \rightarrow \pi^*$ is predicted to lie at 176—178 nm, with oscillator strength in the range 0·00—0·08, dependent upon conformation.

We have observed† this transition in the vapour-spectra of several cyclopropyl ketones (*e.g.*, cyclopropylmethyl

† Spectra were recorded on a McPherson vac.-u.v. spectrometer (model 225), a discharge lamp with H_2 continuum serving as source.

ketone and spiro[2,4]heptan-4-one,‡ see Figure). As expected, it is situated at *ca.* 180 nm, in the gap between two bands that characterize all ketones[5] (the band just below 200 nm is the one discerned, in solution spectra, at *ca.* 200 nm).[6] It resembles in intensity [ϵ (mol) *ca.* 4000] the bands that flank it, forming with them a pattern that is quite distinct from that of non-cyclopropyl ketones (*e.g.*, that of 3-methylbutan-2-one, see Figure).

A more detailed analysis of spectra and MO results will be given elsewhere.

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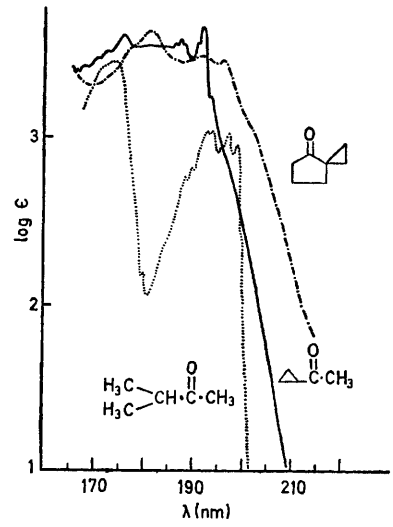

‡ A sample of spiro[2,4]heptan-4-one was kindly supplied by Prof. J.-M. Conia, and used as such. 3-Methylbutan-2-one and cyclopropylmethyl ketone were purified by g.l.c., with a 20 ft × 0·75 in column of 10% carbowax 20 M on acid-washed Chromosorb W (60/80 mesh).

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[6] E. M. Kosower, *J. Amer. Chem. Soc.*, 1958, **80**, 3261.