Ground-state Interactions between a Carbonyl Group and Double Bond(s) in γδ-Unsaturated Ketones

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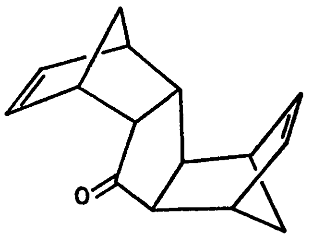
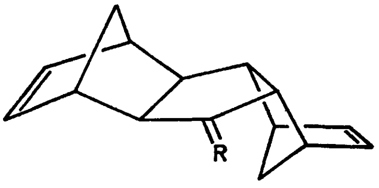
Summary A ground-state interaction, which shows a dependence on conformation leads to the splitting of the degenerate $\pi_{C=C}$ orbitals in the ketone (2).

DURING our synthetic work[1] designed to prove the stereochemistry of the $C_{15}H_{16}O$ ketone obtained from the reaction between iron pentacarbonyl and norbornadiene,[2] we were able to synthesize and measure the u.v. spectra of the three *trans*-isomers and their dihydro- and tetrahydro-derivatives. Whilst the *endo–trans–endo*-isomer (1) and its dihydro-derivative (1a) exhibited only a normal $n \rightarrow \pi^*$ transition the *exo–trans–exo*-isomer (2) and its dihydro-derivative (2a) showed enhanced $n \rightarrow \pi^*$ transitions with $\epsilon = 137$, and $\epsilon = 84$, respectively, and a "σ-coupled transition"[3] at shorter wavelength with λ_{max} 225 nm and $\epsilon = 2540$ and $\epsilon = 1310$, respectively.

We have examined the photoelectron spectra of these compounds to establish whether the ground states in these compounds show interactions that might account for the u.v. spectra. The ionisation potentials (I.P.) of the compounds are reported in the Table and presented graphically



(1)
(1a) dihydro ketone
(1b) tetrahydro ketone



(2) R=O
(2a) R=O; dihydro
(2b) R=O; tetrahydro
(2c) R=H$_2$

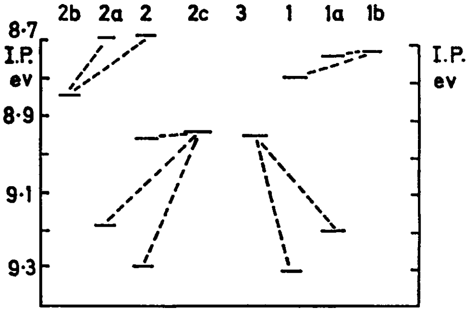
TABLE

Vertical ionisation potentials

Compound	I.P. of n_{CO} in eV	I.P. of $\pi_{C=C}$ in eV
Norbornene (3)	—	8·97[a]
(2c)	—	8·94
(1)	8·78	9·31
(1a)[b]	8·75	9·20
(1b)	8·73	—
(2)	8·68	8·96 and 9·30
(2a)	8·69	9·19
(2b)	8·84	—

[a] Ref. 5. [b] As (1a) was not available to us, we have recorded the I.P. of the *endo–trans–exo*-isomer (saturated in the *exo* part of the molecule), which has a very similar u.v. spectrum to (1a) and is likely to have very similar I.P. values.

in the Figure. The assignment of the I.P. to the n_{CO} orbital was simplified by the fact that the band showed vibrational fine structure in most cases. Significantly the I.P. of the n_{CO} orbital in the ketones (2) and (2a) is lowered by comparison with the tetrahydro-derivative (2b) but in the *endo–trans–endo*-series there is a small increase in the I.P. of the n_{CO} orbital in the unsaturated ketones (1) and (1a) relative to the tetrahydro-derivative (1b). Further, the I.P. associated with the π-orbital of the double bond is increased in all the unsaturated ketones relative to the diene (2c) and to norbornene (3). In the *exo–trans–exo*-dieneone (2) an extra band is observed at low I.P., but not in the *exo–trans–exo*-enone (2a).



FIGURE

The following conclusions are derived from the I.P. and u.v. data: (i) in both the *endo–trans–endo-* and the *exo–trans–exo*-series there is a ground-state inductive interaction between the donor $\gamma\delta$-double bond and the acceptor ketone. This results in an increase in the I.P. of $\pi_{C=C}$ in all the unsaturated ketones and a decrease in the n_{CO} level in (2) and (2a) relative to (2b) and (2c). The slight increase of the n_{CO} level in the *endo–trans–endo*-ketones (1) and (1a) relative to (1b) suggests that interactions of donation and back-donation have a conformational dependence. (ii) In the *exo–trans–exo*-ketone (2) where the σ-framework has a favourable geometry for interaction,[4] there is a splitting of the $\pi_{C=C}$ levels. This interaction is absent in the diene (2c) and in the enone (2a). (iii) There is a red-shift in the $n \rightarrow \pi^*$ transition when the π-orbital of the double bond is suitably oriented in the σ-framework, as in (2) and (2a). The observed lowering in the I.P. of the n_{CO} orbital, a ground-state interaction, implies that there is also a perturbation of the π^* energy level. This effect in the excited state is a shift to lower energy but is slightly less than that observed in the n_{CO} level.

These results further demonstrate the interaction of "remote" substituents[4] and show that photoelectron spectroscopy uniquely distinguishes between effects in the ground state and effects in the excited state.

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