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ELECTRONIC STRUCTURE OF CYCLOPROPENONE [1]

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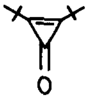
Prompted by a recent paper by Robin et al. [2] dealing with the photoelectron (pe) spectrum of cyclopropenone (1) [3] we present our results on the electronic structure of 1 gained from the pe spectra of 2,3-di-tert-butylcyclopropenone (2) and trans-2,3-di-tert-butylcyclopropanone (3) [4] in conjunction with MINDO/2 [5] calculations. Our interests are (in the framework with studies on the electronic structure of annulenones [6,7]) mainly concerned with the inductive and conjugative interactions between the C=C and C=O moieties.


1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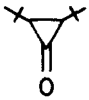
3

The pe spectrum [8] of 2 exhibits bands at 8.23 eV and 9.61 eV (vibrational spacing = 1320 ± 40 cm^{-1}). Table 1 summarizes the observed and calculated vertical ionization of the lone pair (n) MO on the oxygen atom and the second band arises from ionization of the π (b_1) MO which is mainly localized on the C=C bond.

This assignment is supported by two experimental [9] observations: (1) The n-MO (8.45 eV) of 3 is found at nearly the same energy as the n MO of 2 and (2\ the vibrational spacing of the second pe band of 2 lies in a range which is characteristic for the ionization of a π MO.

ionization potenials (eV)

	1			2	
	obs. [2]	ab initio [2]	MINDO/2	obs.	MINDO/2
n	9.57	9.61	9.61	8.23	8.64
π ($2b_1$)	11.19	10.40	10.64	9.61	9.56

Table 1 Measured (obs.) and calculated ionization potentials of 1 and 2

Our results show that both (n and π) MOs are nearly equally raised on the introduction of the two tert-butyl substituents. The observed strong destabilization of the n MO represents an experimental confirmation of the marked delocalization of the lone pair (the n MO appears as a linear combination between the oxygen 2p AO and the e_a MO of cyclopropane) predicted by the ab initio [2] and MINDO/2 calculations which allows significant hyperconjugative interaction with the alkyl substituents.

Now let us turn to the π MO. The carbonyl group may exert three effects on the C=C π MO: (1) a stabilizing inductive effect, (2) a destabilizing conjugative effect (through antibonding interaction between the $\pi_{C=C}$ and $\pi_{C=O}$ MOs) and (3) a stabilizing conjugative effect (through bonding interaction between the $\pi_{C=C}$ and $\pi^*_{C=O}$ MOs). A comparison of the π MO energy of 1 and 2 with the corresponding energies of suitably [10] chosen reference compounds, namely ethylene (10.51 eV [11]) and cis-1,2-di-tert-butylethylene (8.69 eV [12]) suggests that the stabilizing effects (1) and (3) predominate. Experimentally, the three effects (1) to (3) cannot be further separated for the π (b_1) MOs of 1 and 2.

According to MINDO/2 calculations following a method described elsewhere [6] the inductive effects of the carbonyl group on the π (a_2) MOs of cyclopentadienone and tropone are -0.86 eV (the measured effects for derivatives of cyclopentadienone are in good agreement -(0.7 - 0.8) eV[7]) and -0.64 eV, respectively. The same method yields, as expected, an even greater inductive stabilization for the π (b_1) MO of unsubstituted cyclopropenone (1), namely -1.07 eV, and -0.68 eV for 2.

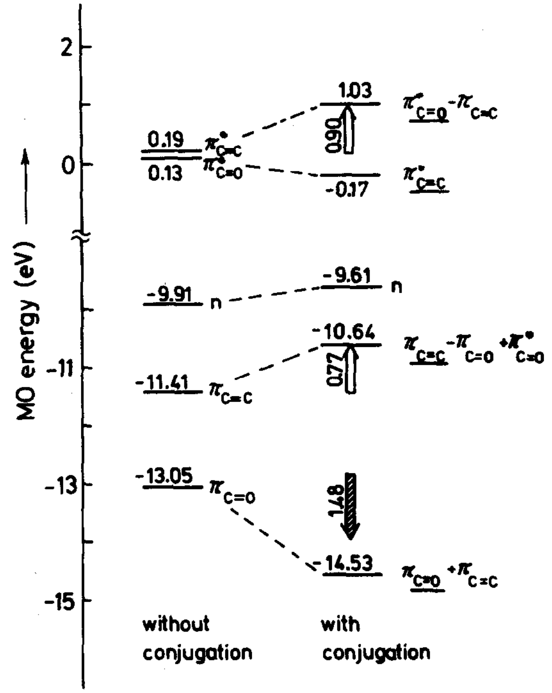

Figure 1

Calculated (MINDO/2 method) relevant occupied and vacant (✱) MO energies with and without (for the method cf. ref. 7) conjugative interaction between the C=C and C=O units.

Based on these values the sum of the conjugative effects (2) and (3) is only about 0.4 eV for 1 and about zero for 2[12]. The corresponding evaluated effects (destabilization of the $\pi_{C=C}$ MO caused by π conjugative interaction between the C=C and C=O fragments) amounts to 0.77 eV for 1 as shown in Figure 1 and to 0.06 eV for 2. Moreover, the obtained (Figure 1) splitting pattern points to the possible existence of $\pi_{C=C}/\pi^*_{C=O}$ mixing[13] (effect (3)). Accordingly, the calculated π charge transfer from the C=C to the C=O unit (mostly to the oxygen atom) amounts to 0.29 e for 1 and 0.24 e for 2. These data suggest that the cyclopropenone system, indeed, bears some resemblance to the aromatic cyclopropenyl cation[14].

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