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A Study of the Interactions Between the Double Bonds in Unsaturated Ketones*

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The interactions between C=C and C=O double bonds in several unsaturated ketones have been studied by comparing MINDO/2 calculations with ionisation potentials determined by photoelectron spectroscopy (PES). With one exception (norbornadienone) the direct through-space interactions in conjugated ketones appear to be negligible, the double bonds couple hyperconjugatively *via* the intervening σ bonds. This kind of approach should prove useful for studying other long range interactions.

The MINDO/2 method[1] gives good estimates of the heats of atomisation and geometries for a wide variety of organic molecules. It reproduces the energies of the molecular orbitals quite satisfactorily as revealed by earlier calculations of ionisation potentials[2], employing Koopmans' theorem[3]. The latter implicitly assumes that the orbitals in a molecule and the corresponding cation are the same *i. e.* they remain »*frozen*«. This assumption does not hold exactly since the orbitals adjust themselves to the increase in the positive charge. However, the reorganisation energy is canceled to the large extent by the change in the correlation energy so that Koopmans' theorem is in general fairly well obeyed. It provides invaluable tool for the interpretation of photoelectron spectra in conjuction with the MO model and gives also useful pictorial insight into intramolecular interactions. Namely, the energies of the molecular orbitals describing localised or semilocalised electrons depend on the chemical environment of the electronic group in question, so that the corresponding ionisation potentials exhibit characteristic »*chemical shifts*« in the photoelectron spectrum. The nature and magnitude of such shifts can than provide information concerning the kinds of interaction that take place between the localized group and its environment. Thus the π-electrons of two isolated C=C double bonds can interact with one another either directly across space or hyperconjugatively *via* intermediate σ bonds. Although the physical nature of both interactions is essentially the same, they often lead to different symmetries for higher MO formed by interaction of the CC π MOs[4].

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It is possible to distinguish between them on this basis by comparison of the observed ionisation potentials with those calculated by MINDO/2[4b].

In this paper we examine the magnitude and mode of the interactions between a carbonyl group and one or more C=C double bonds in some five membered cyclic unsaturated ketones and related compounds. The geometries of the molecules were minimized with respect to the parameters determining the molecular skeletons by using the program written by Dr. A. Brown and modified by Dr. J. S. Wasson[5] based on the simplex algorithm[6]. The complete optimization of the molecular geometries was necessary because we found that the orbital energies, in particular the separations between the highest levels, are strongly dependent on the geometry. For instance, the highest molecular orbitals in norbornenone are very sensitive to changes in the angle between the »wings« of the molecule. By optimizing the geometry of each molecule we ensure that the results are compatible and comparable among themselves. The parameters for MINDO/2 method used in this paper were those of ref. (1).

RESULTS AND DISCUSSION

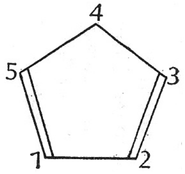
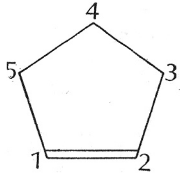
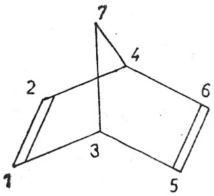
Experimental geometries are available only for cyclopentene, cyclopentadiene and norbornadiene. The calculated bond lengths and bond angles are compared with experiment in Table I. The agreement is only fair, the C—C and C—H bonds being consistently too short and too long respectively. However the qualitative features are very well reproduced, for example the variation in C—C bond lengths with the hybridization of the participating carbon atoms. The C—C single bond lengths in cyclopentene are not known unambiguously[7]. Our calculation supports the suggested assignment[7] in which the shorter C—C bond is adjacent to a double bond, as one would expect in view of the different hybridization of the carbon atoms. Norbornadiene is a very interesting molecule since it has three different kinds of C—C bonds and a somewhat unusual bridge angle. The calculated geometry of norbornadiene is in good overall agreement with experiment although the C_1—C_7 bond length is somewhat too short. The bridge angle in norbornadiene is not uniquely determined by the gas electron diffraction measurements[8] and one has to make a choice between values of 92.2° and 96.0°. Our calculated angle (94.4°) slightly favours the latter value but not significantly since the possible error in bond angles calculated by the MINDO/2 method is about 2°. The calculated dihedral angle of norbornadiene is in good agreement with experiment.

Our calculations lead to a planar arrangement of the heavy atoms in cyclopentene-2-one and cyclopentene-3-one, in full accord with recent micro--wave measurements[9].

The calculated first ionisation potentials are compared with experiment in Table II. The agreement is very good except that the calculated values are uniformly too high. This is not of great significance because the difference is practicaly constant and could be removed by changing the origin of the energy scale. The MOs representing the C=C and C=O π bonds can be quite clearly recognised, being only slightly perturbed by their mutual interaction. The observed and calculated changes in the corresponding ionisation potentials therefore provide a useful guide in studying long range interactions.

TABLE I

Calculated and experimental geometries for cyclopentene, cyclopentadiene, and norbornadiene

Compound	Bond lengths		Bond angles		Dihedral angles
	calcd.	exp.	calcd.	exp.	
	C_1—C_2 = 1.328 C_2—C_3 = 1.454 C_3—C_4 = 1.526 C_1—H = 1.100 C_3—H = 1.105 C_4—H = 1.118	(1.343)[a] (1.519) (1.546)	$C_1C_2H = 123.2^0$ $HC_3H = 104.7^0$ $HC_4H = 102.2^0$ $C_1C_2C_3 = 113.5^0$ $C_2C_3C_4 = 101.9^0$ $C_3C_4C_5 = 109.2^0$	 (111^0)[a] (103^0) (104^0)	$C_1C_2C_3$— —$C_3C_4C_5 = 167.1^0$ (151^0)
	C_1—C_2 = 1.412 C_2—C_3 = 1.344 C_3—C_4 = 1.464 C_1—H = 1.105 C_4—H = 1.108	(1.469)[b] (1.342) (1.509)	$C_1C_2H = 126.9^0$ $C_2C_3H = 127.3^0$ $HC_4H = 95.2^0$ $C_3C_4C_5 = 99.6^0$ $C_1C_2C_3 = 106.5^0$ $C_2C_3C_4 = 113.7^0$	 (102.8^0)[b] (109.4^0) (109.4^0)	
	C_1—C_2 = 1.338 C_1—C_3 = 1.495 C_3—C_7 = 1.546 C_1—H = 1.084 C_3—H = 1.090 C_7—H = 1.093	(1.343)[c] (1.535) (1.573)	$C_1C_2H = 128.3^0$ $C_7C_3H = 119.8^0$ $HC_7H = 97.6^0$ $C_3C_7C_4 = 94.4^0$ (94 ± 3)[c]		$C_1C_2C_3$— —$C_4C_6C_5 = 112.8^0$ $(115.6^0 \pm 2.2^0)$

[a] M. I. Davis and T. W. Muecke, *J. Phys. Chem.*, 14 (1970) 1104.

[b] L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, 43 (1965) 2765.

[c] A. Yokozeki and K. Kuchitsu, *Bull. Chem. Soc.* Jap. 44 (1971) 2356.

TABLE II

Calculated and observed first ionisation potentials

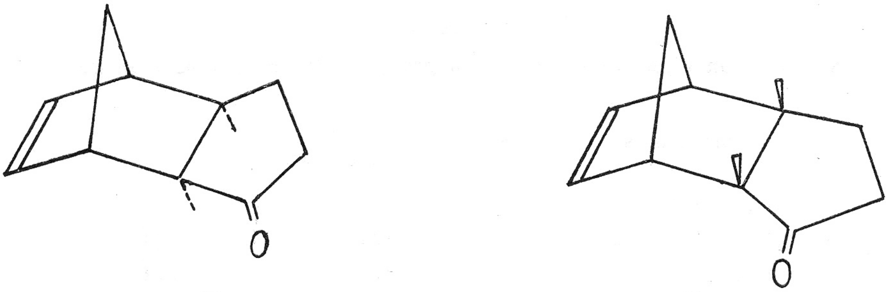
Compound	First Ionisation Potential	
	Calcd.	Observed
cyclopentene	9.30	9.00[a]; 9.18[b]
cyclopentadiene	9.08	8.55[a]
norbornane	9.87	9.74[c,d]
norbornene	9.39	8.97[e] (9.20[c])
norbornadiene	9.26	8.95[c]
cyclopentanone	9.78	9.25[f,g]
cyclopentene-2-one	9.73	9.34[f]
cyclopentene-3-one	9.76	9.44[f]
cyclopentadienone	9.84[h]	—
norbornane-7-one	9.48	9.01[i]
norbornene-7-one	9.47	9.19[i]
norbornadiene-7-one	9.74	—

[a] M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50** (1969) 654.
[b] P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53** (1970) 1677.
[c] D. A. Demeo and A. J. Yencha, *J. Chem. Phys.*, **53** (1970) 4536.
[d] adiabatic I_p given in ref. c)
[e] P. Bischof, J. A. Hashmall, E. Heilbronner and V. Hornung, *Helv. Chim. Acta*, **52** (1969) 1745.
[f] D. Chadwick, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, **93** (1971) 4320.
[g] D. Chadwick, D. C. Frost, and L. Weiler, *Tetrahedron Letters*, (1971) 4543.
[h] assigned to ionisation from *n*-level.
[i] D. Chadwick, D. C. Frost and L. Weiler, *J. Amer. Chem. Soc.*, **93** (1971) 4962.

We first examined the interactions between a carbonyl group and a C=C bond β, γ to it. In order to assess the importance of through-space interactions, we carried out the MINDO/2 calculations omitting the integrals representing these. The results (Table III) show that ommission of these integrals usually has little or no effect on the calculated π_{CC} and π_{CO} ionisation potentials, implying that any π_{CC}—π_{CO} interactions in these compounds must be of hyperconjugative (through—bond) type.

This conclusion is supported by the comparisons in Table IV. Introduction of a carbonyl group into an olefine raises the π_{CC} ionisation potential, implying a lowering of the energy of the π_{CC} MO. If the π_{CC}/π_{CO} interaction were of through-space type the opposite would be the case; for the π_{CO} MO lies below π_{CC} in energy and a direct interaction between them should therefore raise π_{CC} and lower π_{CO}. Furthermore, since through-space interactions depend on overlap of the interacting orbitals, they should die away very rapidly with distance. This is not the case for the π_{CC}/π_{CO} interactions in Table IV, the interactions remainig large in the $\gamma\,\delta$ unsaturated ketones I and II, which are shematically shown in Figure 1.

Norbornadienone is particularly interesting in this connection being the only case studied in which the first ionisation potential is predicted to correspond to ionisation from π_{CC} rather than n_o. This is because it was the only compound for which the direct through-space π_{CC}/π_{CO} interaction was predicted

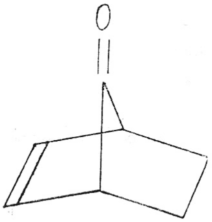
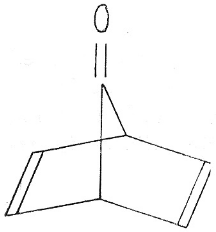
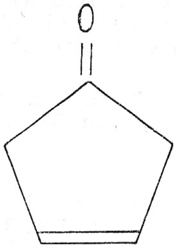


I II

Figure 1.

TABLE III

Comparison of ionisation potentials (eV) *obtained by the full MINDO/2 method with those calculated when integrals corresponding to through-space interactions were set equal to zero*

Compound	full MINDO/2	through space interaction excluded	
		$\pi_{C=C}$ *vs.* lone pair	$\pi_{C=C}$ *vs.* $\pi_{C=O}$
	I_p 9.47 (n_o) 9.93 ($\pi_{C=C}$)	9.48 (n_o) 9.93 ($\pi_{C=C}$)	9.48 (n_o) 9.97 ($\pi_{C=C}$)
	I_p 9.74 ($\pi_{C=C}$) 9.76 (n_o)	9.74 ($\pi_{C=C}$) 9.77 (n_o)	9.82 (n_o) 10.03 ($\pi_{C=C}$)
	I_p 9.76 (n_o) 9.84 ($\pi_{C=C}$)	9.76 (n_o) 9.84 ($\pi_{C=C}$)	9.73 (n_o) 9.81 ($\pi_{C=C}$)

to be appreaciable. The direct interaction is large (~ 0.3 eV) and, as expected, raises the energy of the π_{CC} MO. As a result, for this compound alone π_{CC} lies above n_o. This difference is very small indeed (0.02 eV) and consequently may

TABLE IV

Stabilization effect of the carbonyl group on the $\pi_{C=C}$ levels (in eV)

Compounds	$\pi_{C=C}$	$\Delta\pi$[a] calc. (obs.)	n_o
cyclopentene	9.30	0	—
cyclopentene-3-one	9.84	0.54 (0.80)[b]	9.76
cyclopentene-2-one	10.26	0.96 (0.92)[b]	9.73
cyclopentadiene	9.08	0	—
cyclopentadienone	10.12	1.04	9.84
norbornene	9.53	0	—
norbornene-7-one	9.93	0.40 (0.65)[c]	9.47
exo-ketone (I)	9.67	0.14[d] (0.22)[e]	9.44
endo-ketone (II)	9.73	0.20[d] (0.23)[e]	9.42
norbornadiene	9.26	0	—
norbornadiene-7-one	9.74	0.48	9.76
cyclopentanone	—	—	9.78
norbornane-7-one	—	—	9.48

[a] the difference $\Delta\pi$ is calculated relative to the parent cycloalkene if it is not stated otherwise.
[b] Reference i) Table II.
[c] Reference f) Table II.
[d] Relative to the norbornene.
[e] M. D. Brown, J. Hudec, and J. M. Mellor, *Chem. Comm.*, (1971) 1640.

not be significant at all in view of the large number of approximations involved in the theoretical model. In any case, one can expect that π_{CC} and n_o levels are very close. It is curious that the direct π_{CC}/π_{CO} interaction in 7-norbornenone (~ 0.4 eV) is so much smaller. This again shows how sensitive direct interactions are to small changes in geometry.

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SAŽETAK

Studij interakcija dvostrukih veza u nekim nezasićenim ketonima

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Studirana je interakcija između dvostrukih C=C i C=O veza u nekim konjugiranim ketonima usporedbom izračunatih ionizacijskih potencijala s eksperimentalnim vrijednostima. Pri tome je korištena MINDO/2 semiempirijska metoda. Ustanovljeno je da je direktna interakcija »kroz prostor« vrlo mala. Izuzetak je jedino 7-norbornadienon. Kod ostalih molekula se interakcija dvostrukih veza prenosi preko kemijskih veza. Izračunani ionizacijski potencijali su u dobrom slaganju s eksperimentalnim vrijednostima.

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