THE ORBITAL SEQUENCE IN CYCLIC 1,3-DIKETONES

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Abstract—The He(I) photoelectron (PE) spectra of the cyclic 1,3-diketones 1–5 have been recorded. Based on a comparison between experimental and calculated (MINDO/3) results it is shown, that in all cases the $n_-(A)$ orbital is on top of the $n_+(S)$ orbital. This sequence is confirmed by the comparison between the PE spectra of 1–5 with those of the corresponding vic.triketones 6–10.

Recently the photoelectron (PE) spectra of cyclic β-diketones have been discussed.[3,4] Based on the validity of Koopmans' theorem $(-\epsilon_j = I_{V,j})$[5] and arguments from perturbation theory,[6] the comparison between experimental ionization energies and calculated MO energies (Extended Hückel[7] and CNDO/2[8] model) indicates that the antisymmetric $n_-(A)$ linear combination (see Fig. 1) of the 2p orbitals on oxygen is on top of the symmetric $n_+(S)$ one for the 5-membered ring. For the 6-membered ring the ordering seems less straight forward since some authors[3] favour n_+ on top of n_- while others[4] prefer the reversed ordering. The ordering n_+ on top of n_- in case of the cyclohexane-1,3-dione implies a relatively large change in orbital energies in comparing cyclopentane-1,3-dione with cyclohexane-1,3-dione as indicated in Fig. 1.

In this paper we demonstrate in two independent ways that the sequence in the following five 1,3-diketones (1–5) is $n_-(A)$ on top of $n_+(S)$ ("natural order"). For this purpose the PE spectra of 1–5 have been compared with the PE spectra of the corresponding vicinal triketones 6–10. The PE spectra of 6–9 have already been reported in a previous paper.[9] The first bands of the PE spectra of 1–5 are shown in Fig. 2 and the relevant data are collected in Table 1.

Semiempirical calculations

To interpret the PE spectra of the 1,3-diketones 1–5 we assume the validity of Koopmans' theorem.[5] As a method of calculating the orbital energies we use the MINDO/3[10] method, which has proven to be quite reliable in predicting the orbital energies and the orbital sequence for a large number of 1,2-diketones.[11] During
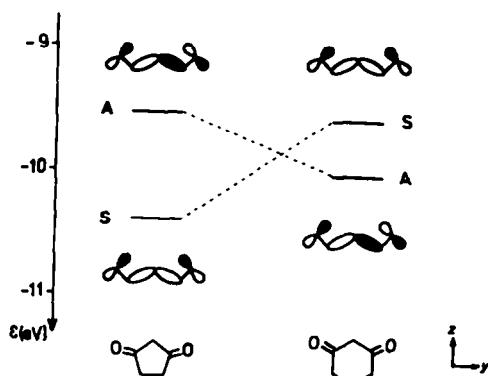

Fig. 1. Correlation between S and A n-levels of cyclopentane-1,3-dione and cyclohexane-1,3-dione as discussed in the literature.[3]
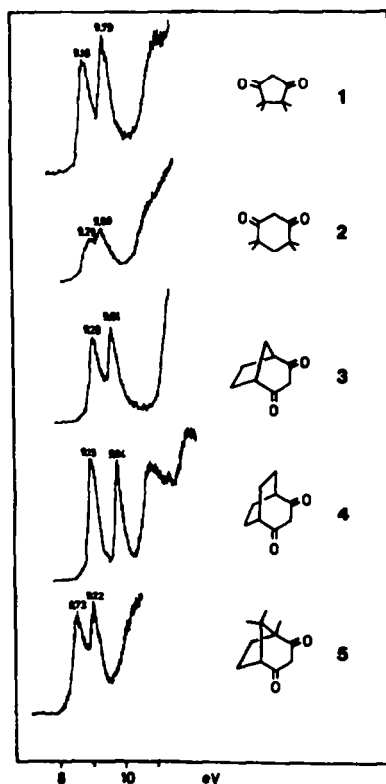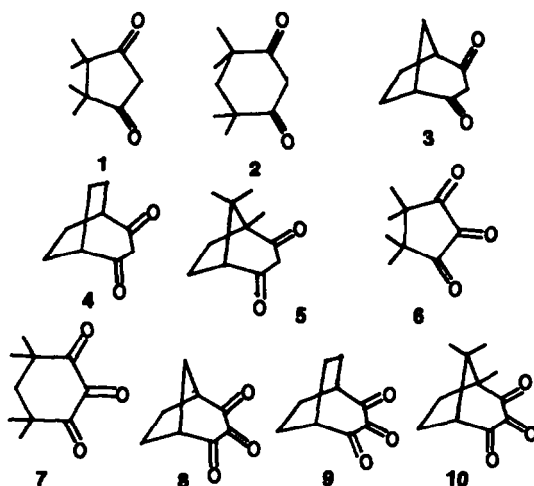
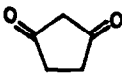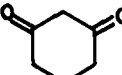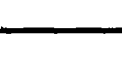Fig. 2. First PE bands of 1 to 5.

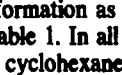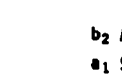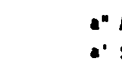Table 1. Comparison between measured vertical ionization potentials of 1-5 and calculated orbital energies. All values in eV

	$I_{v,J}$	assignment	$-\epsilon_J$ (MINDO/3)	ΔH_f [kcal/mol]
1	9.18	b_2 (A)	9.46	
(C_{2v})	9.79	a_1 (S)	9.85	-59.28
2	9.29	a'' (A)	9.64	
(C_s)	9.60	a' (S)	9.74	-65.78
3	9.28	a'' (A)	9.74	
(C_s)	9.81	a' (S)	9.88	-71.85
4	9.15	a'' (A)	9.60	
(C_s)	9.94	a' (S)	10.08	-79.81
5	8.73	A	9.62	
(C_1)	9.22	S	9.72	-40.77
(C_{2v})	9.53 10.40	b_2 A a_1 S	9.72 10.36	-87.55
(C_s)	9.60 10.04	a'' A a' S	9.95 10.17	-70.55

the calculations the geometry of 1-5 has been optimized with respect to minimization of the total energy. The obtained heats of formation as well as the orbital energies are listed in Table 1. In all five cases as well as for cyclopentane- and cyclohexane-1,3-dione $n_-(A)$ is predicted above $n_+(S)$, i.e. there is no indication of an orbital switch in going from the 5- to the 6-membered ring system.

Empirical correlation

To check our conclusions obtained from the comparison between semiempirical SCF-calculations and experiment, we additionally use a correlation procedure outlined below, that relates the observed ionization potentials of diketones 1-5 to those of the corresponding series of vicinal triketones 6-10. The PE spectra of 6-10 are well understood; the two lowest ionization potentials can be unambiguously assigned to the two highest lone pair combinations $2b_2$ and a_1 out of the three possible ones in a 1,2,3-triketo-system.[9]
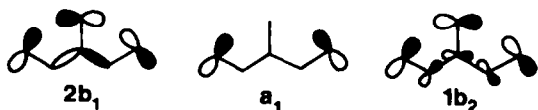
To relate the orbital sequence of 1,3-diketones to the corresponding vicinal triketones, it is reasonable to assume two effects caused by an additional carbonyl group, which replaces the CH_2 fragment in going from

1-5 to 6-10:

(a) an inductive effect δ_{ind}, lowering the energies of both $n_+(S)$ and $n_-(A)$ roughly to the same extent, and

(b) a conjugative or "through bond" effect δ_{con}, caused by the additional p-type lone pair on the central carbonyl group, interacting with the antisymmetric lonepair/σ_{CC}-combination $n_-(A)$ in the diketo-system only,[12] thereby generating the two A-type nonbonding orbitals $2b_2$ and $1b_2$ of the resulting triketones.

Assuming the "natural" level ordering $n_-(A)$ above $n_+(S)$ for the n-orbitals of 1,3-diketones 1-5 as suggested by the MINDO/3 calculations described earlier, the 1,3-dione → vic.trione correlation diagram of Fig. 3 results. The basis orbitals in this figure are the $n_+(S)$ and $n_-(A)$ molecular orbitals of a cyclic 1,3-diketone on one side and a pure p-type in-plane atomic orbital on oxygen on the other. The latter has to be placed at lower energy compared to the $n_+(S)$ and $n_-(A)$ levels, since the destabilization due to antibonding interactions of the intervening C-C-σ-bonds with the symmetry adapted linear combinations of the two oxygen p-AO's of the β-diketone unit has already been taken care of.

The energy difference between the second ionization potentials $I_{v,2}$ of 1-5 and their trione counterparts 6-10 should therefore give us a measure of the inductive effect δ_{ind} of the central CO-group:

$$\delta_{ind} = I_{v,2}(\text{vic.trione}) - I_{v,2}(\text{1,3-dione}).$$

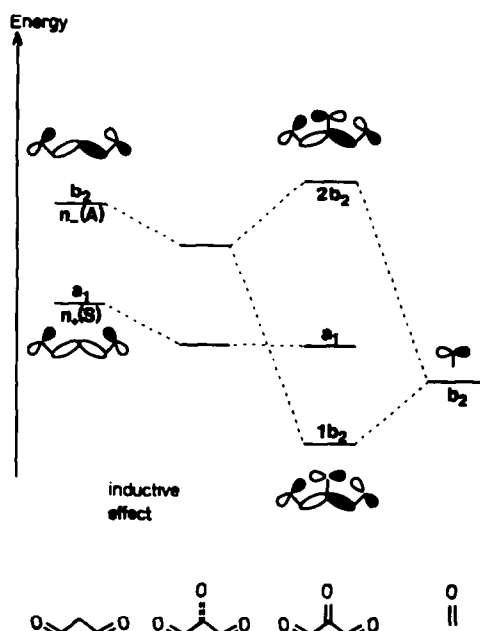If this parameter then is also applied to the 1,3-diketone

Fig. 3. Interaction diagram between a 2p orbital on the oxygen of a CO group and the n_+ and n_- combinations of a 1,3-diketone.

$n_-(A)$ orbital ($I_{V,1}$) a comparison of the resulting values to $I_{V,1}$ of the triketones allows to derive the conjugative

interaction parameter δ_{con}, which describes the destabilization induced by the in-plane oxygen lone pair 2p orbital:

$$\delta_{con} = I_{V,1}(\text{vic.trione}) - \{I_{V,1}(1,3\text{-dione}) + \delta_{ind}\}.$$
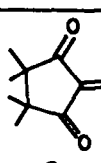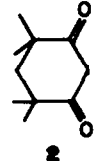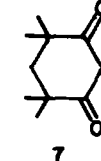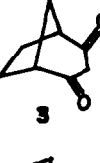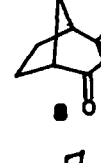
Applying such a correlation scheme to pairs of corresponding compounds in the two series 1–5 and 6–10 yields the results shown in Table 2.

The table also gives the same set of parameters δ_{ind} and δ_{con} which can be calculated under the assumption of a level ordering $n_+(S)$ above $n_-(A)$ in 1–5.

We note that for the "natural" assignment in the 1,3-diketones 1–5 ($n_-(A)$ above $n_+(S)$) the attempted correlation to compounds 6–10 yields an average inductive parameter δ_{ind} of 0.79 eV, which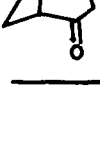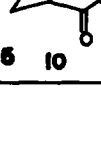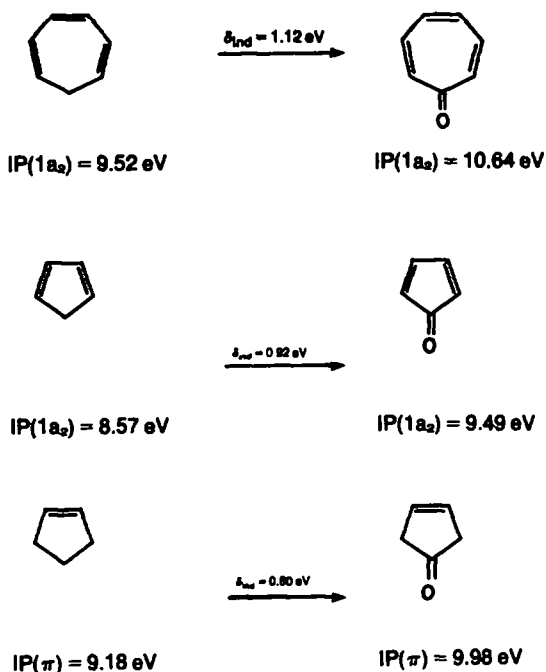 is balanced by a conjugative destabilization δ_{con} of practically equal magnitude (average value −0.76 eV). An orbital sequence $n_+(S)$ above $n_-(A)$ in 1–5 on the other hand would give much larger parameters (mean values: $\delta_{ind} = +1.3$ eV, $\delta_{con} = -1.8$ eV) which, especially for δ_{con}, differ strongly for different diketone/triketone-pairs. Furthermore the latter assignment leads to the conclusion, that δ_{con} should always be larger in magnitude (up to 0.8 eV) than δ_{ind}.

Clearly the data set derived from the correlation which takes the $n_-(A)$ lone pair MO as the HOMO in 1–5 is more consistent, again supporting the level sequence $n_-(A)$ above $n_+(S)$ in cyclic 1,3-diketones. We would like

Table 2. Comparison between experimental ionization potentials of 1–5 and 6–10 assuming the orbital sequence in 1–5 $n_+(S)$ below $n_-(A)$ and $n_-(A)$ below $n_+(S)$. Comparison of δ_{ind} and δ_{con} values. All values in eV

Comparison		Experim. $I_{V,J}$		δ_{ind} δ_{con} (for A above S)		δ_{ind} δ_{con} (for S above A)	
		Dione	Trione				
		$I_{V,1}$ 9.18	9.00	0.76	−0.94	1.37	−2.16
1	**6**	$I_{V,2}$ 9.79	10.55				
		$I_{V,1}$ 9.29	9.10	0.78	−0.97	1.09	−1.59
2	**7**	$I_{V,2}$ 9.60	10.38				
		$I_{V,1}$ 9.28	9.49	0.79	−0.58	1.32	−1.64
3	**8**	$I_{V,2}$ 9.81	10.60				
		$I_{V,1}$ 9.15	9.14	0.66	−0.67	1.45	−2.25
4	**9**	$I_{V,2}$ 9.94	10.60				
		$I_{V,1}$ 8.73	9.06	0.98	−0.65	1.27	−1.43
5	**10**	$I_{V,2}$ 9.22	10.20				

to point out in addition however, that it is possible to estimate the absolute as well as the relative magnitudes of δ_{ind} and δ_{con} independently from some model compounds, and that those data outlined below are in very good agreement with a general orbital sequence $n_-(A)$ above $n_+(S)$ in 1–5 and with the parameter set derived from the correlation to 6–10 on this basis. To get an estimate of the inductive effect (Fig. 3) we compare the orbital energy corresponding to $1a_2$ of cycloheptatriene[13] or $1a_2$ of cyclopentadiene[14] with $1a_2$ of tropone and cyclopentadienone[15] (see below). Another appropriate comparison are the ionization potentials corresponding to the ejection of electrons from the π-orbital of cyclopentene and that of 1-cyclopentene-4-one.[16]


IP($1a_2$) = 9.52 eV   IP($1a_2$) = 10.64 eV

IP($1a_2$) = 8.57 eV   IP($1a_2$) = 9.49 eV

IP(π) = 9.18 eV   IP(π) = 9.98 eV

This comparison shows an inductive effect, δ_{ind}, of a carbonyl group between 0.8 and 1.1 eV.

To obtain an estimate of the conjugative effect we compare the ionization potential of the n orbital in monoketones with the n_+ (destabilized) combination in α-diketones as given below.

CH$_3$—CH$_2$—CO—CH$_3$ CH$_3$—CO—CO—CH$_3$

IP(n) = 9.5 eV[25]   IP(n_+) = 9.55 eV[25]

CH$_3$—CHO   CHO—CHO
IP(n) = 10.2 eV[25]   IP(n_+) = 10.59 eV[26]

IP(n_+) = 9.55 eV[25]   IP(n_+) = 9.61 eV[11]
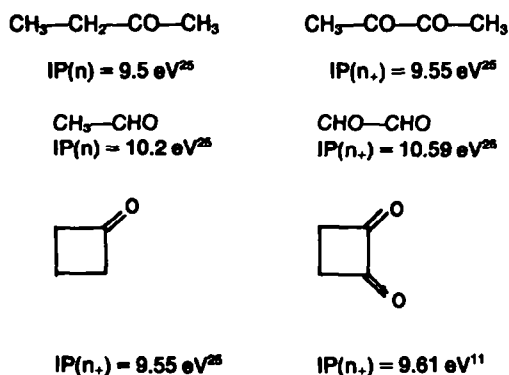
Knowing the inductive effect, this comparison should give a fairly good estimate of the conjugative effect of an

additional CO group since in both cases, the α-diketone and the vic.triketone, the main interaction takes place between the 2p orbital on oxygen and the σ-frame as sketched below. Assuming an average inductive effect of 0.92 eV as discussed before, we conclude that the conjugative effect (interaction with σ-frame) has about the same magnitude but the opposite sign.

$n_+(S)$ $2b_2(A)$
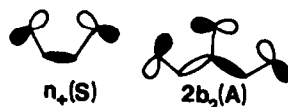
The parameters derived by this comparison are therefore:

$$\delta_{ind} = +0.9\,eV$$
$$\delta_{con} = -0.9\,eV.$$

Thus our conclusions based on a qualitative correlation of 1–5 and 6–10 and resulting in practically identical numbers for δ_{ind} and δ_{con} find strong support and *the only possible assignment with respect to the n level ordering in 1,3-diketones is clearly $n_-(A)$ above $n_+(S)$*. As can be seen from an inspection of Table 2, the application of values of 0.9 eV to 1,3-diketones 1–5 would have yielded quite a good approximation of the actually observed PE bands in 6–10, the prerequisite again being that the sequence of the symmetry adapted linear combinations of the lone pairs in 1–5 is $n_-(A)$ above $n_+(S)$, as obtained with the MINDO/3 method.

Having discussed the orbital sequence in our series of 1,3-diketones, it is interesting to compare the first two bands in the PE spectra of 1 and 2 with those of cyclopentane-1,3-dione and cyclohexane-1,3-dione. We notice, that the shift of the first band (corresponding to the antisymmetric orbital) is less than for the second band (corresponding to the symmetric orbital) (see Fig. 4). This difference is accounted for by considering the relevant wave functions as shown in Fig. 4. In both types of ring systems we notice, that the coefficients of the atomic orbitals next to the carbonyl groups are larger in the symmetrical molecular orbitals than in the antisymmetrical ones. Thus, methyl groups should affect $n_+(S)$ more than $n_-(A)$, consistent with the observed trend.
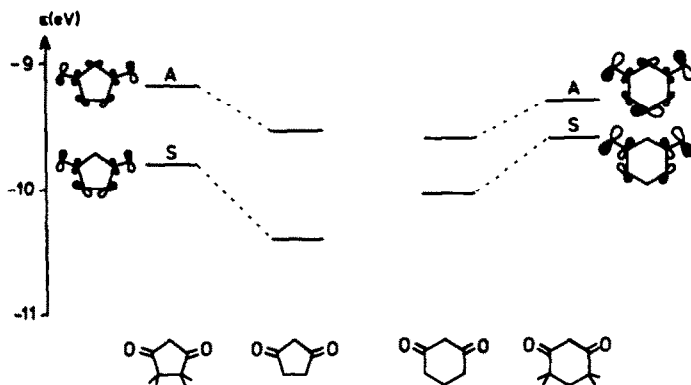
Fig. 4. Correlation of the first two bands in the PE spectra of 1 and 2 with those of cyclopentane-1,3-dione and cyclohexane-1,3-dione respectively.

REFERENCES

[1]Darmstadt.

[2]Erlangen.

[3]K. N. Houk, L. P. Davis, G. R. Newkome, R. E. Duke Jr. and R. V. Naumann, *J. Am. Chem. Soc.* 95, 8364 (1973).

[4]D. Dougherty, P. Brint and S. P. McGlynn, *Ibid.* 100, 5597 (1978).

[5]T. Koopmans, *Physica* 1, 104 (1934).

[6]E. Heilbronner und H. Bock, *Das HMO.Modell und seine Anwendung*, Verlag Chemie, Weinheim/Bergstr., W. Germany (1968).

[7]R. Hoffmann, *J. Chem. Phys.* 39, 1397 (1963); R. Hoffmann and W. N. Lipscomb, *Ibid.* 36, 2179, 3489 (1962); 37, 2872 (1962).

[8]J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw Hill, New York (1970) and refs therein.

[9]P. Bischof, R. Gleiter and P. Hofmann, *Helv. Chim. Acta* 58, 2130 (1975).

[10]R. C. Bingham, M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.* 97, 1285 (1975).

[11]R. Gleiter, R. Bartetzko, P. Hofmann and H.-D. Scharf, *Angew. Chem.* 89, 414 (1977); *Int. Ed. Engl.* 16, 400 (1977); R. Gleiter, P. Schang and G. Seitz, *Chem. Phys. Letters* 55, 144 (1978); P. Schang, R. Gleiter and A. Rieker, *Ber. Bunsenges. Phys. Chem.* 82, 629 (1978); H.-D. Martin, H. J. Schiwek, J. Spanget-Larsen and R. Gleiter, *Chem. Ber.* 111, 2557 (1978); R. Bartetzko, R. Gleiter, J. L. Muthard and L. A. Paquette, *J. Am. Chem. Soc.*

100, 5589 (1978).

[12]E. Heilbronner, *Israel J. Chem.* 10, 143 (1972); E. Heilbronner and H.-D. Martin, *Helv. Chim. Acta* 55, 1490 (1972).

[13]C. Batich, P. Bischof and E. Heilbronner, *J. Electron Spectrosc.* 1, 333 (1972/73).

[14]P. J. Derrick, L. Åsbrink, O. Edquist, B. O. Jonsson and E. Lindholm, *J. Mass Spectrom. Ion Phys.* 6, 161 (1971).

[15]T. Koenig, M. Smith and W. Snell, *J. Am. Chem. Soc.* 99, 6663 (1977).

[16]D. Chadwick, D. C. Frost and L. Weiler, *Ibid.* 93, 4320, 4962 (1971).

[17]G. Hesse, in *Houben–Weyl–Müller: Methoden der organischen Chemie*, 4. Aufig., Thieme, Stuttgart (1978), Bd. VI/1d, S. 84.

[18]J. G. Durocher and H. Favre, *Can. J. Chem.* 42, 260 (1964).

[19]Diplomarbeit A. Sieber, Universität Erlangen–Nürnberg (1978).

[20]B. Eistert, D. Greiber and J. Caspari, *Liebigs Ann. Chem.* 659, 64 (1962).

[21]The precursors of 3 and 4, e.g. bicyclo[2.2.1]heptane-2,3-dione and bicyclo[2.2.2]octane-2,3-dione can be made more easily than reported in the literature by acyloin condensation of cis-cyclopentane - 1,3 - dicarboxylic - acid - dimethyl - ester and of cis - cyclohexane - 1,4 - dicarboxylic - acid - dimethyl - ester in the presence of chlorotrimethylsilane and subsequent reaction of the resulting bis-trimethylsiloxy-olefins with bromine. For the general method see also Ref. [22].

[22]J. P. Barnier and J. M. Conia, *Bull. Soc. Chim. France* 281 (1976).

[23]Dissertation A. Sieber, Universität Erlangen, in Vorbereitung.

[24]M. Regitz and H.-G. Adolph, *Z. Naturforsch.* 23b, 1269 (1968).

[25]*Handbook of Spectroscopy* (Edited by J. W. Robinson), Vol. I. CRC Press (1974) and refs cited therein.