Photoelectron Spectroscopy of Cyclic β-Diketones and Their Enolone Tautomers

K. N. Houk,[*1] Larry P. Davis, George R. Newkome,
R. E. Duke, Jr., and R. V. Nauman

Contribution from the Department of Chemistry,
Louisiana State University—Baton Rouge, Baton Rouge, Louisiana 70803.
Received June 13, 1973

Abstract: The photoelectron spectra of a series of 1,3-cyclohexanediones and 1,3-cyclopentanediones and of acetylacetone and 3-ethoxy-2-cyclohexenone are reported. The inductive effect of a carbonyl group is estimated. Photoelectron spectra of some of the corresponding trans-enolone tautomers, as well as that of the hydrogen-bonded cis-enolone of acetylacetone, are also reported, and assignments of the structures of the predominant tautomers in the gas phase and observations about the influence of substituents on gas phase tautomeric equilibria are made. Orbital assignments corresponding to each ionization are made by comparison of experimental ionization potentials with semiempirical calculations and by measuring alkyl substituent effects on the ionization potentials of the valence orbitals.

The interactions of formally nonconjugated chromophores have attracted the interest of numerous theoreticians and spectroscopists. Dicarbonyl compounds have these interactions, and numerous theoretical studies of dicarbonyls have been made,[2–5] but experimental verifications of the theoretical conclusions are less abundant.[5,6] We have obtained the photoelectron spectra of a series of 1,3-cyclohexanediones and 1,3-cyclopentanediones and an acyclic analog, acetylacetone. The results of these investigations are relevant to the problem of bonding and interconversions of β-dicarbonyl compounds and their cis- and trans-enolone tautomers, as well as to the problem of the conformation of the cyclohexanedione ring.

The nonbonding (n) orbitals of a 1,3-diketone can interact by direct overlap ("through-space" interaction)[7] or by interactions with connecting σ bonds ("through-bond" interaction).[7] Through-space interaction of the n orbitals will produce a bonding combination which is symmetric (S) with respect to a plane of symmetry passing through the central carbon atom of the molecule and an antibonding combination which is antisymmetric (A) with respect to this plane. If this interaction were dominant, then the "natural" order[8] of n orbitals, S below A, would result. This order is shown on the left side of Figure 1. In cases where the n orbitals overlap very little, the through-space interaction is small, and through-bond interactions will have a dominant effect upon removing the degeneracy of the n orbitals.

S and A combinations of σ orbitals are shown on the right-hand side of Figure 1. The A level is generally of higher energy than the S level due to an antibonding geminal interaction in the former and a bonding geminal interaction in the latter. The result of interaction of the n orbitals with the σ orbitals is shown in the center of Figure 1. The extent of interaction between localized orbitals of the same symmetry is inversely proportional to the difference in energy between the interacting orbitals and directly proportional to the extent of overlap between them. Assuming that overlap is comparable, the A levels will mix to a greater extent than the S levels due to the closer energies of the former. The result is a further split between n orbital energy levels, but the "natural" order still prevails.

Semiempirical calculations indicate that the through-bond interaction generally has a larger magnitude than the through-space interaction.[2–5] Extended Hückel and CNDO calculations indicate that 1,3-cyclobutanedione is an exception and has the n orbitals arranged in the "inverted" order.[3,5] Although magnitudes of the splitting of n orbital levels observed in the photoelectron spectrum agree with those of the calculated splittings,[5] no experimental evidence supporting either the "natural" order or the "inverted" order of orbitals in β-diketones has been obtained. This study of a series of cyclic β-diketones was undertaken in an attempt to seek this experimental support.

Experimental Section

Photoelectron spectra were obtained by means of a Perkin-Elmer, Ltd. PS-18 spectrometer with a resolution of 0.025 eV (Ar half-width) or better. Acetylacetone was admitted to the target chamber as a vapor, while all other compounds were volatilized in the target chamber by means of the heated inlet system in which the sample temperatures varied between 32 and 120°. No noticeable effect of temperature on the spectra was observed. The reported ionization potentials are averages of at least five determinations except in the case of 2-tert-butyl-1,3-cyclohexanedione, for which amounts sufficient for only two determinations were available. The cyclic β-diketones were prepared by literature methods[9] and

(1) Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Recipient, 1972–1977.

(2) J. R. Swenson and R. Hoffmann, Helv. Chim. Acta, 53, 2331 (1970).

(3) W. Hug, J. Kuhn, K. J. Seibold, H. Labhart, and C. Wagniere, Helv. Chim. Acta, 54, 1451 (1971).

(4) E. Haselbach and A. Schmelzer, Helv. Chem. Acta, 55, 1745 (1972).

(5) D. O. Cowan, R. Gleiter, J. A. Hashmall, E. Heilbronner, and V. Hornung, Angew. Chem., Int. Ed. Engl., 10, 401 (1971).

(6) J. Kroner and W. Strack, Angew. Chem., Int. Ed. Engl., 11, 220 (1972).

(7) R. Hoffmann, Accounts Chem. Res., 4, 1 (1971); E. Heilbronner, Israel J. Chem., 10, 143 (1972).

(8) S and A designate symmetry with respect to a plane of symmetry.

(9) (a) 2-Methyl-, 2-ethyl-, and 2-isopropyl-1,3-cyclohexanediones: G. R. Newkome, L. C. Roach, R. C. Montelaro, and R. K. Hill, J. Org. Chem., 37, 2098 (1972); (b) 2-tert-butyl-1,3-cyclohexanedione: G. R. Newkome, R. C. Montelaro, J. D. Sauer, and J. D. Wander, J. Chem. Soc., Chem. Commun., 905 (1972); (c) F. Merényi and M. Nilsson, Acta Chem. Scand., 17, 1801 (1963); 18, 1368 (1964); (d) 2-methyl-1,3-cyclopentanedione: H. Schick, G. Lehmann, and G. Hilgetag, Angew.

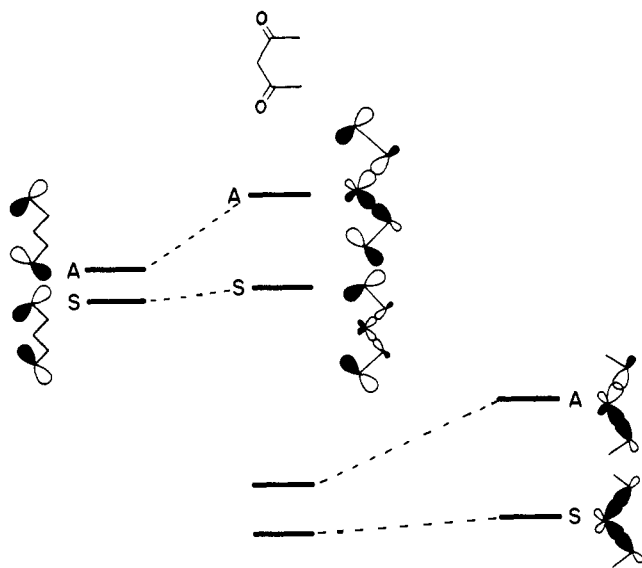Figure 1. Through-bond mixing of n and σ orbitals in a β-dicarbonyl. (See text for explanation.)

Figure 2. Photoelectron spectrum of 2-isopropyl-1,3-cyclohexanedione.

Table I. Ionization Potentials (eV)[a] of 1,3-Cyclohexanediones

Compd	I_v (I_{ad})	I_v (I_{ad})	Δn
1,3-Cyclohexanedione	9.60 (9.52)	10.04 (9.98)	0.4_4
2-Methyl-1,3-cyclohexanedione	9.48 (9.37)	9.81 (9.69)	0.3_3
2-Isopropyl-1,3-cyclohexanedione	9.29 (9.09)	9.61 (9.49)	0.3_2
2-tert-Butyl-1,3-cyclohexanedione[b]	9.15 (9.05)	9.62 (9.41)	~ 0.5
5,5-Dimethyl-1,3-cyclohexanedione	9.46 (9.28)	9.92 (9.83)	0.4_6
2,5,5-Trimethyl-1,3-cyclohexanedione	9.30 (9.10)	9.64 (9.62)	0.3_4
2,2,5,5-Tetramethyl-1,3-cyclohexanedione	9.13 (9.04)	9.52 (9.47)	0.3_9

[a] ± 0.05 eV (standard deviation). [b] ± 0.1 eV (estimated error).

were purified by preparative gas chromatography or by sublimation.

Results

1,3-Cyclohexanediones. The photoelectron spectrum of 2-isopropyl-1,3-cyclohexanedione is shown in Figure 2. The remaining 1,3-cyclohexanedione spectra were very similar to that in Figure 2 except for displacements in vertical ionization potentials. Two ionization potentials were observed in the region where ionization from a carbonyl n orbital is expected. For 2-isopropyl-1,3-cyclohexanedione, the first vertical ionization potential (I_v) is 9.29 eV, and the first broad band has discernible vibrational structure of about 700 cm^{-1}. The second sharper band has an I_v of 9.61 eV, and no fine structure is resolved. The σ onset occurs at 11.0 eV for this molecule. These values and the estimated adiabatic ionization potentials (I_{ad}) are listed in Table I and are shown diagramatically in Figure 3, along with the corresponding values for the remaining 1,3-cyclohexanediones studied.

Since acyclic and cyclic β-diketones are predominantly enolic in solution,[10] it might have been expected

that the observed spectra were those of the enolic forms; however, comparison of the ionization potentials and band shapes for the nonenolizable 2,2,5,5-tetramethyl-1,3-cyclohexanedione and 2-tert-butyl-1,3-cyclohexanedione[9b] with those of the enolizable diketones (Table I and Figure 3) indicates that all of the cyclohexanediones are present in the gas phase predominantly as diketone forms. The vapor phase infrared spectrum of 2-methyl-1,3-cyclohexanedione (1722 cm^{-1} (strong) and 1745 cm^{-1} (medium)) confirms this conclusion because nonenolizable diketones have two bands between 1680 and 1730 cm^{-1} in nonpolar solvents while the trans-enolones have two broad absorptions between 1550 and 1650 cm^{-1}.[10a] The presence of mainly the diketone forms in the gas phase is compatible with the results of solution studies, which have shown that cyclohexanediones exist predominantly as the diketone tautomers in dilute solution in nonpolar solvents,[11] indicating the greater thermodynamic stability of the diketone forms in the absence of hydrogen bonding.

In addition to the strong bands, the spectra of 2-isopropyl-1,3-cyclohexanedione exhibited a shoulder before the first band centered at 8.74 eV (see Figure 2). A similar weak band at 8.90 eV was noted for 2,5,5-trimethyl-1,3-cyclohexanedione, while a stronger band at 9.03 eV was apparent in the spectrum of 2-methyl-1,3-cyclohexanedione. These weak bands can be assigned to the ionization from the enol forms of these molecules in analogy to the identifications made in the cyclopentanedione series (vida infra).

1,3-Cyclopentanediones. Figure 4 shows the 8–11-eV region in the spectra of four 1,3-cyclopentanediones. The spectrum of 2,2-dimethyl-1,3-cyclopentanedione, which cannot form a conjugated enolone, has two bands for which I_v's of 9.34 and 10.05 eV are observed. The spectrum of 1,3-cyclopentanedione is very similar to that of the dimethyl compound, but the first and second

Chem., Int. Ed. Engl., 6, 80 (1967); V. J. Grenda, G. W. Lindberg, N. L. Wendler, and S. H. Pines, J. Org. Chem., 32, 1236 (1967); (e) 2-ethyl-1,3-cyclopentanedione was generously supplied by Hoffmann-La Roche, Inc.
(10) (a) S. T. Yoffe, E. M. Popov, K. V. Vatsuro, E. K. Tulikova, and M. I. Kabachnik, Tetrahedron, 18, 923 (1962); (b) J. H. Billman, S. A.
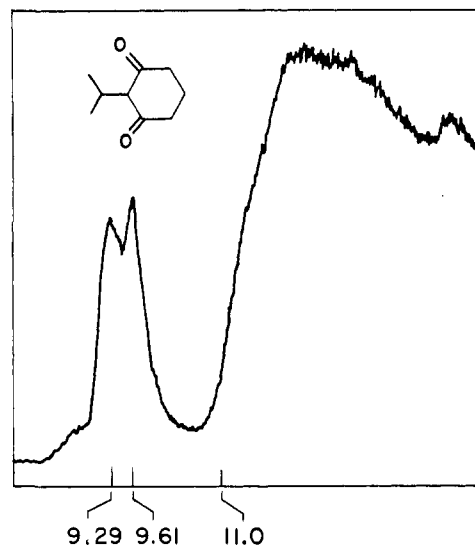
Sojka, and P. R. Taylor, J. Chem Soc., Perkin Trans. 2, 2034 (1972); (c) L.-T. Cheng, Ph.D. Dissertation, Louisiana State University— Baton Rouge, 1968; (d) E. Funck and R. Mecke, "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press, London, 1959, p 433; (e) A. H. Lowrey, C. George, P. D. Antonio, and J. Karle, J. Amer. Chem. Soc., 93, 6399 (1971).
(11) A. Yogev and Y. Mazur, J. Org. Chem., 36, 2162 (1967).
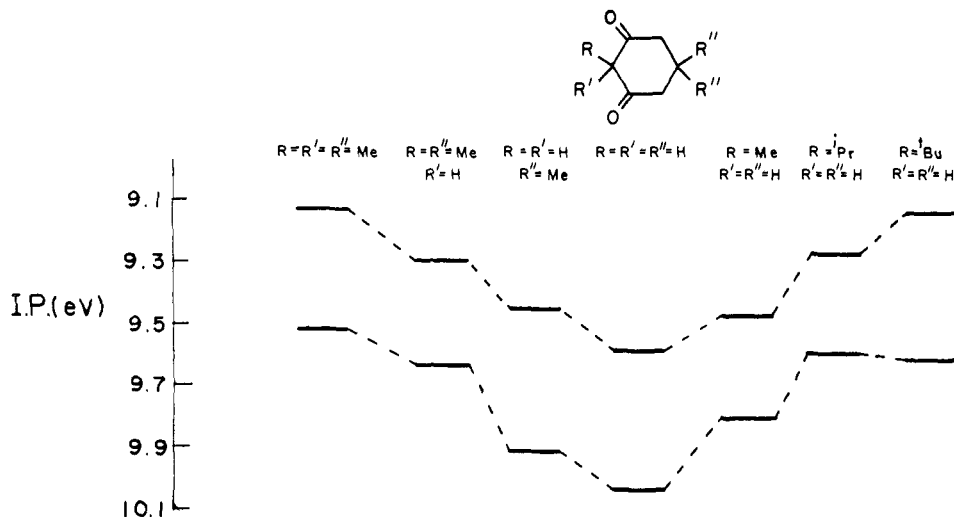
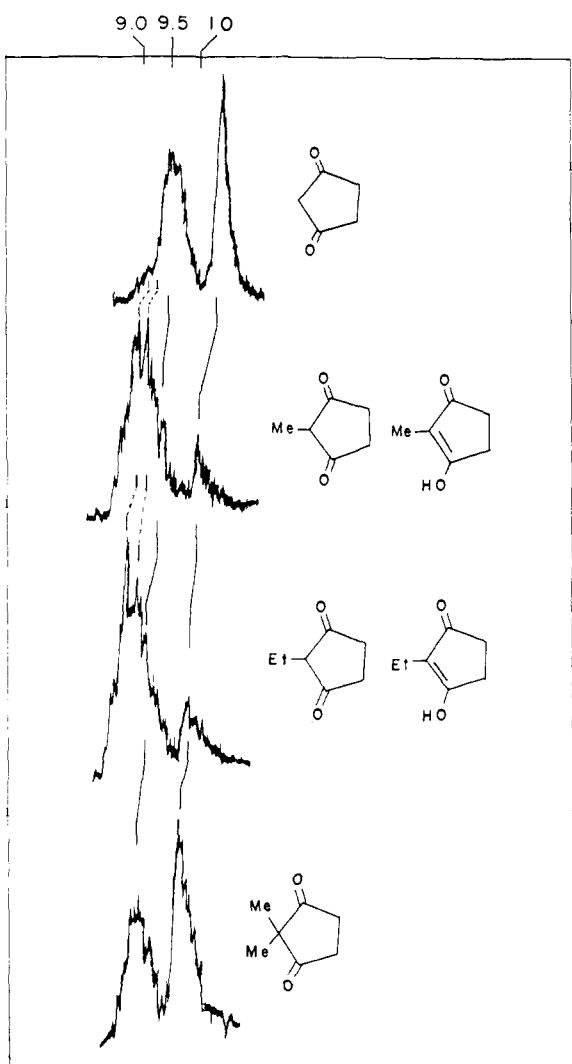Figure 3. Vertical ionization potentials of 1,3-cyclohexanediones.

Figure 4. Photoelectron spectra of: (a) 1,3-cyclopentanedione; (b) 2-methyl-1,3-cyclopentanedione; (c) 3-ethyl-1,3-cyclopentanedione; (d) 2,2-dimethyl-1,3-cyclopentanedione. The stronger peaks in (b) and (c) are due to enolone forms.

Figure 5. Vertical ionization potentials of 1,3-cyclopentanediones (—) and enolones (---) and of the cis-enolone of acetylacetone.

inductive destabilization of the n orbitals is comparable to those found for acyclic ketones.[12] The broad overlapping bands in the spectra of 2-methyl- and 2-ethyl-1,3-cyclopentanedione unexpectedly appear at lower ionization potentials than the corresponding bands of 2,2-dimethyl-1,3-cyclohexanedione. In addition to these strong bands, the spectrum of the 2-methyl compound had a shoulder at 9.40 eV and a weak band at 10.18 eV, while the spectrum of the 2-ethyl compound had a shoulder at 9.35 eV and a weak band at 10.11 eV. These weak bands appear in precisely the positions expected for the bands of diketone tautomers if comparisons with the positions of the corresponding bands of the unsubstituted and dimethyl compounds are made. Since these small bands could not be removed by extensive sample purification, we conclude that the weak bands in the spectra of the methyl and ethyl compounds are due to ionizations from the n orbitals of the diketones tautomers, while the strong bands in these spectra originate from the enolone tautomers. A very weak band is observed in the spectrum of the parent 1,3-cyclopentanedione, and this can also be assigned to the enolone form. Figure 5 shows the

vertical ionization potentials of 1,3-cyclopentanedione are 0.19 and 0.35 eV greater than those of 2,2-dimethyl-1,3-cyclopentanedione. The magnitude of the methyl
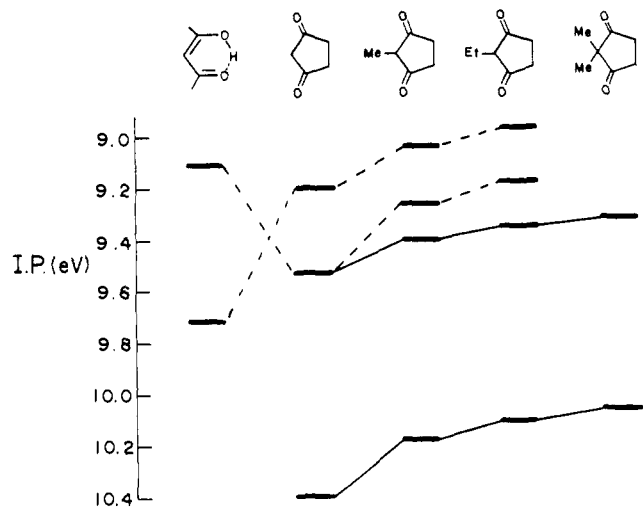
(12) B. J. Cocksey, J. H. D. Eland, and C. J. Danby, *J. Chem. Soc. B*, 790 (1971).

Table II. Ionization Potentials (eV)[a] of β-Diketones and Enolones

	Diketone		Enolone	
	I_v (I_{ad})	I_v (I_{ad})	I_v (I_{ad})	I_v (I_{ad})
3-Ethoxy-2-cyclohexenone			8.99 (8.69)	10.9 (σ onset)
Acetylacetone			9.09 (8.85)	9.70 (9.53)
1,3-Cyclopentanedione	9.53 (9.46)	10.40 (10.39)	9.2$_2$	~9.4
2-Methyl-1,3-cyclopentanedione	9.4$_0$	10.1$_8$	9.04 (8.84)	9.26 (9.22)
2-Ethyl-1,3-cyclopentanedione	9.3$_5$	10.1$_1$	8.97 (8.79)	9.18 (9.02)
2,2-Dimethyl-1,3-cyclopentanedione	9.34 (9.08)	10.05 (10.04)		

[a] ±0.05 eV (standard deviation), except for the diketone forms of the 2-methyl- and 2-ethyl-1,3-cyclopentanediones, which is ±0.1 eV.

correlations which result from this conclusion. The dotted lines indicate correlations between ionization potentials arising from enolone tautomers, while the full lines represent correlations between ionization potentials arising from the diketone tautomers. Table II lists the observed ionization potentials.

Although we cannot be certain that equilibrium has been obtained in the gas phase, particularly where the sample is sublimed directly into the target chamber, it does appear that the tendency for enolization is greater in cyclopentanediones than cyclohexanediones and that primary 2-alkyl substituents favor enolization, whereas bulkier secondary or tertiary 2-alkyl groups discourage enolization. Some solution studies on 3-alkylacetylacetones provide some support for the last contention,[10a] but a direct comparison is not possible, since the solution studies involved acyclic compounds with at least three tautomers in equilibrium.

Acetylacetone and 3-Ethoxy-2-cyclohexenone. In order to facilitate the assignment of the bands in the spectra of the diketones and enolones, the spectra of acetylacetone and 3-ethoxy-2-cyclohexenone were determined. The data for these compounds are recorded in Table II. The position of equilibrium between the diketo and hydrogen-bonded enolone forms of acetylacetone in the gas phase have been studied by ultraviolet spectroscopy (~100% enol at 25°),[10c] infrared spectroscopy (~90% enol at 100°),[10d] and electron diffraction (66 ± 5% enol at ~105°).[10e] Photoelectron spectra were recorded at temperatures from 50 to 150° with no detectable change in band shapes. We have concluded that the two vertical ionization potentials observed are due to the hydrogen-bonded enolone tautomer since all of the studies mentioned above conclude that this is the predominant species present in the gas phase in the temperature range studied.

Calculations

The three limiting planar conformations of the OCCCO skeleton are the "W," "sickle," and "U;" these forms of acetylacetone are 1, 2, and 3, respectively.
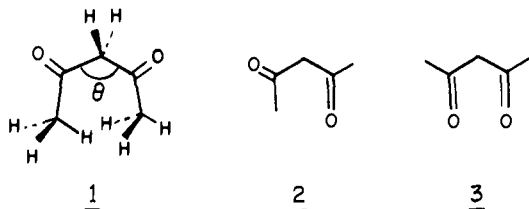
Swenson and Hoffmann calculated the splittings in n levels for an idealized propanedial enolate ion model (θ = 120°). Their EH calculations for the "U" and the "W" conformations gave splittings of 0.81 and 0.60 eV, respectively, and the "natural" order (S below A)

in both cases. For other systems CNDO/2 calculations gave a calculated splitting about twice that obtained from the extended Hückel calculations, but the level ordering was the same.[2]

Heilbronner and coworkers reported the photoelectron spectrum of 1,3-cyclobutanedione and suggest the "inverted" order (A below S) of n orbitals in this system due to the interaction of the nonbonding orbitals with the Walsh orbitals of cyclobutane (vida infra). Calculated splittings (EH) are 0.75 eV for the parent and 0.90 eV for the tetramethyl derivative. The observed splitting of the n orbitals of the latter compound is 0.7 eV.[5]

Hug, et al., reported CNDO (Sichel–Whitehead parameterization) calculations for dicarbonyl compounds.[3] Calculations for propanedial were carried out for three conformations. The calculated splittings for the "U" (C_{2v}), "90°" (C_2), and "W" (C_{2v}) conformations were 1.05, 0.49, and 0.60 eV, respectively. The "90°" conformation of propanedial is obtained from the "U" conformation by 90° rotations about C_1C_2 and C_2C_3 in opposite directions. In each case, the "natural" order (S below A) was found. For 1,3-cyclobutanedione, the "inverted" order (A below S) in which there is a 0.91-eV splitting was calculated.[3]

Further molecular orbital calculations have been carried out in this work by means of the EH,[13] CNDO/2,[14] and CNDO/S[15] methods as an aid to spectral assignments. These calculations will be discussed in turn for the cases of propanedial and its enolones, acetylacetone and its enolones, and the cyclic β-diketones and their enolones.

Propanedial and Its trans-Enolone. The results of some of our calculations for propanedial and those available in the literature are listed in Table III. An empirical correction factor of 3 eV (cf. 4 eV for hydrocarbons[16]) was subtracted from the results of the calculations performed by means of the EH, CNDO/2, and CNDO (S.W.) methods.

The dependence of the level ordering on θ was examined in the CNDO/2 approximation. As shown in Table III, the "W" conformation has the natural order at θ < 117.5°, but the levels cross at 117.5° and the inverted order obtains at θ > 117.5°. Although the energy of the A level changes only slightly with variations in θ, the S level is progressively destabilized as θ increases. Since the through-space interaction of oxygens is small for all values of θ, the change in energy must arise due to variations in geminal inter-

(13) R. Hoffmann, J. Chem. Phys., **39**, 1397 (1963), QCPE 64.
(14) J. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, QCPE 141.
(15) J. Del Bene and H. H. Jaffé, J. Chem. Phys., **48**, 1807, 4050 (1968); **49**, 1221 (1968); **50**, 563 (1969), QCPE 174.
(16) S. D. Worley, Chem. Rev., **71**, 295 (1971).

Table III. Calculated Ionization Potentials (eV) for the "W" Conformations of 1,3-Propanedial and 3-Hydroxypropenal

Method of calculation	Propanedial			3-Hydroxypropenal (trans)		
	n_A	n_B	$\Delta\epsilon$	π	n	$\Delta\epsilon$
EH ("W," $\theta = 109.5°$, $\xi = 1.0$)[a]	10.52	10.61	0.09	10.20	10.68	0.48
CNDO/S[b] ("W,"$\theta = 109.5°$)	10.63	11.51	0.88	9.90	10.52	0.62
CNDO (S. W.) (ref 3)[a]	9.36	10.41	0.95			
CNDO/2[a] ("W," $\theta = 95°$)	10.77	11.71	0.94			
("W," $\theta = 109.5°$)	10.96	11.30	0.34			
("W," $\theta = 117.5°$)	10.99	10.99	0.00			
("W," $\theta = 122.5°$)[c]	11.01	10.90	−0.11	9.99	10.52	0.53
("W," $\theta = 130°$)[c]	11.04	10.77	−0.27			
("U," $\theta = 115°$)	10.27	11.62	1.36			
("U," $\theta = 122.5°$)	10.50	11.39	0.89			
("U," $\theta = 130°$)	10.63	11.23	0.60			

[a] $-\epsilon - 3$ eV. [b] $-\epsilon$. [c] Note "inverted" order.

action of σ levels as a function of θ, or stated another way, due to either the destabilization of the S σ level through which the n orbitals couple as θ increases or to better overlap of the S σ level and the nσ level as θ increases. Calculations carried out for propanedial distorted somewhat from C_{2v} symmetry resulted in similar behavior, but the electron density became heavily localized on a single carbonyl where near degeneracy occurred, and crossing was avoided.

The "U" conformation does not exhibit this crossing, but the n level separation does decrease steadily as θ increases. In this case, both through-space and angle-dependent geminal interactions can be invoked to explain the increase of the S orbital energy and decrease in A orbital energy as θ increases. Levin, et al., have observed very similar behavior in ab initio calculations on α-amino ketones.[17]

Table III also contains calculations for the enol tautomer of propanedial in the trans "W" (non-hydrogen-bonded) geometry. In each case, the first ionization potential involves ionization from a π orbital, while the second originates from the n orbital.

Acetylacetone. Calculations for the "W" conformation (1) of acetylacetone with standard bond lengths and angles[14] except for variations in θ were performed. Some selected values are shown in Table IV. Although

**Table IV.** CNDO/2 Ionization Potentials[a] for Acetylacetone and 4-Hydroxypent-3-en-2-one

	I_1	I_2	ΔI
Dione 1, "W," $\theta = 121°$	10.18 (A)	10.35 (S)	0.17
"W," $\theta = 123°$	10.25 (S)	10.5 (A)	0.29
"W," $\theta = 135°$	9.9 (S)	10.5 (A)	0.65
Dione, 90°	10.05	10.31	0.26
Dione 2, "Sickle"	10.24	10.44	0.20
Dione 3, "U"	9.96 (A)	10.98 (S)	1.02
trans-Enolone, 4, $\theta = 121°$	8.39 (π)	9.69 (n)	1.30
cis-Enolone, 5 (no H bond)	8.37 (π)	9.08 (n)	0.71
cis-Enolone, 6 (H bond)	8.10 (n)	8.97 (π)	0.87

[a] $-\epsilon - 3$ eV.

this model possesses only C_s symmetry, the pseudo-symmetry of the n orbitals with respect to a plane passing through the methylene at C-3 is preserved. Just as in the case of the "W" propanedial, a crossover from the "natural" order at $\theta < 122°$ to the "inverted" order at $\theta > 122°$ occurs. For a C_{2v} "W" model, this cross-

ing occurred at 115°. Calculations on the "90°," "sickle," and "U" models of acetylacetone are also shown in Table IV. As in the simpler propanedial model calculations of Hug, et al.,[3] splittings decrease in the order "U" > "W" > "90°," with the natural order observed in all cases for θ near tetrahedral.

CNDO/2 calculations for the enolone forms of acetylacetone were also carried out, and these results are shown in Table IV. For the trans-enolone **4**, varia-

4   **5**   **6**
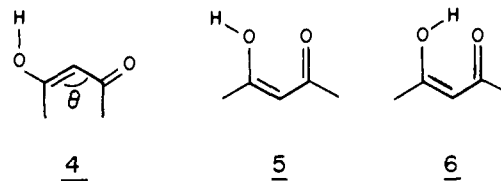
tions in θ resulted in negligible changes in the π orbital energy, while the n orbital energy increased somewhat as θ was increased. The π over n order invariably obtained for a variety of geometrical variations. Calculations on the non-hydrogen-bonded cis-enolone, **5**, indicated little change in π energy level from the trans-enolone but a substantially (0.6 eV) higher n orbital in the cis-enolone than the trans-enolone, causing the π and n levels to be nearly degenerate.

Calculations for the hydrogen-bonded cis-enolone, **6**, were carried out for an unsymmetrical skeleton with alternating double and single bonds and for a symmetrical skeleton with C_{2v} symmetry. Conversion of **5** to unsymmetrical **6** results in a 0.10-eV stabilization on the π level and 0.58-eV destabilization of the n level. Conversion of this hydrogen-bonded form to a symmetrical geometry resulted in further destabilization of both the n and π levels, but the n over π order is clearly favored. Experimental support for the destabilization of an n orbital upon involvement in hydrogen bonding arises from Thomas' studies of the photoelectron spectra of carboxylic acids and their chelated dimers.[18] In the latter, the carbonyl n orbital ionization potential is 0.2 to 0.3 eV lower than in the monomer.[18] The symmetrical model is calculated to be more stable than the unsymmetrical, compatible with the electron-diffraction structure of acetylacetone enol.[10e,18a]

1,3-Cycloalkanediones. Finally, calculations were performed for 1,3-cyclopentanedione, 1,3-cyclohexane-

(17) C. C. Levin, R. Hoffmann, W. J. Hehre, and J. Hudec, *J. Chem. Soc., Perkin Trans. 2*, 210 (1972).

(18) R. K. Thomas, *Proc. Roy. Soc., Ser. A*, **331**, 249 (1972).
(18a) NOTE ADDED IN PROOF. An INDO geometry optimization has been reported for acetylacetone enol: M. S. Gordon and R. D. Koob, *J. Amer. Chem. Soc.*, **95**, 5863 (1973). The optimum geometries reported therein and found here by CNDO/2 are nearly identical.

Table V. Calculated Vertical Ionization Potentials

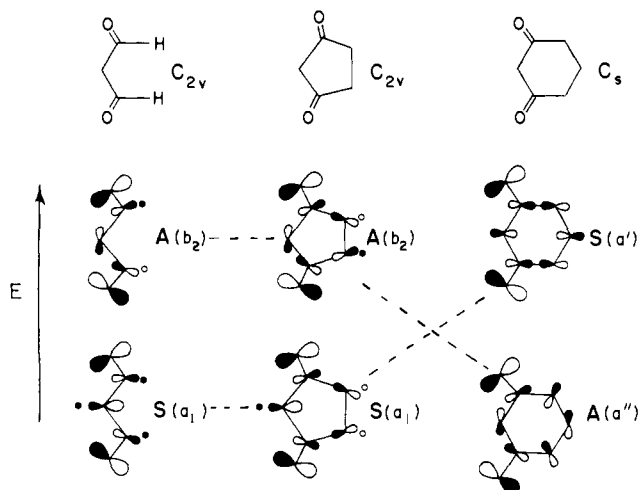|	CNDO/2, eV[a]	EH, eV[a]	CNDO/S	Exptl
1,3-Cyclohexanedione	9.78 (S), 10.18 (A)	9.68 (S), 10.18 (A)	10.23 (A), 10.54 (S)	9.60, 10.04
2(e)-Methyl-1,3-cyclohexanedione	9.29 (S), 9.76 (A)	9.32 (S), 9.83 (A)		9.48, 9.81
1,3-Cyclopentanedione	10.02 (A), 10.62 (S)	9.87 (A), 10.08 (S)	10.20 (A), 10.81 (S)	9.53, 10.40
2-Methyl-1,3-cyclopentanedione	9.64 (A), 10.19 (S)	9.65 (A), 9.71 (S)	10.10 (A), 10.54 (S)	9.40, 10.18

[a] IP(calcd) $= -\epsilon - 3$ eV.

Figure 6. Computed "nonbonding orbitals" of propanedial, 1,3-cyclopentanedione, and 1,3-cyclohexanedione.

dione, and their 2-methyl derivatives in several conformations. Table V gives the results of calculations by three different semiempirical methods, along with the observed ionization potentials for the diketone forms of these molecules. The eigenvectors obtained by the CNDO/2 method are shown schematically in Figure 6, along with those obtained for the 109.5° propanedial model. EH calculations produced the same ordering of levels and qualitatively similar eigenvectors. The geometries chosen for these calculations were based on a planar model for 1,3-cyclopentanedione and its 2-methyl derivative and a chair model for 1,3-cyclohexanedione and its 2-methyl derivative (see Discussion). These calculations used standard bond angles and lengths,[14] and strain was equally distributed to all CCC angles. In a qualitative sense, 2-alkylation might be expected to have a considerably greater destabilizing influence on the S orbital than on the A orbital. However, the node through C-2 in the A orbital requires only that the $2p_A$ orbital have a nonzero coefficient, and coefficients at C_2 are similar in magnitude for both S and A orbitals. The calculations do indicate greater destabilization by 2-methyl of the S orbital than the A orbital in both compounds; the difference in destabilization varied from 0.01 to 0.17 eV. All three methods of calculation predict the "natural" order of n orbitals (S below A) in the cyclopentanediones. However, the "inverted" order is predicted for the cyclohexanediones by CNDO/2 and EH but not by CNDO/S. The $C_1C_2C_3$ angles in the five-membered ring and the six-membered ring models for which calculations were performed were 106 and 109.5°, respectively, while the O–O distances were 4.75 and 4.45 Å, respectively. The variation in $C_1C_2C_3$ angle by itself is too small to cause the reversal of level ordering, and similarly, the O–O distance is too great in both cases to allow significant
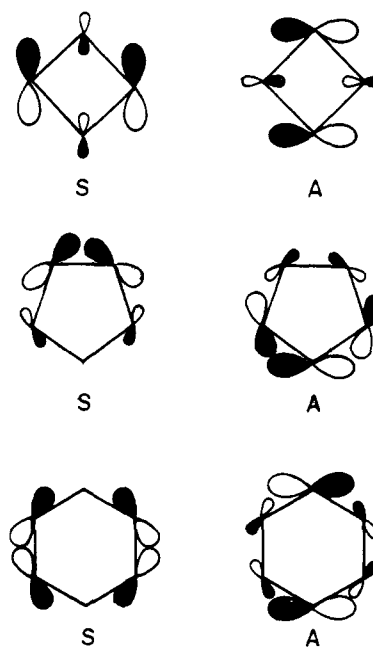

Figure 7. Highest occupied "outside" Walsh orbitals for cyclobutane, cyclopentane, and cyclohexane.[18,19]

"through-space" interaction.[2] However, the two models do significantly differ in one respect; while the S orbital is bonding at C_4C_5 in the five-membered ring, ring expansion to a six-membered ring eliminates this bonding interaction, and further destabilization of the S level can occur by hyperconjugative interaction with a low-lying C–H σ level; conversely, the antibonding C_4C_5 interaction in the A orbital of the five-membered ring is diminished in the six-membered ring.

An alternative, but related, explanation for this reversal may be made on qualitative grounds. The Walsh orbitals of planar cycloalkanes consist of a set of orbitals that overlap inside the ring constructed from sp^2 orbitals on each carbon and a second set of orbitals that overlap outside the ring and are constructed from p orbitals in the molecular plane. Peterson has shown that the highest occupied orbitals of the latter set consist of a degenerate pair of S and A orbitals.[19] These are shown in Figure 7. Mixing of the Walsh orbitals of cyclobutane[19,20a] with the S and A combinations of 2p orbitals on oxygen will lead to efficient mixing of the S Walsh level with the S nonbonding orbitals but no mixing of the corresponding A orbital pair. The "inverted" order results from the resulting destabilization of the S level in 1,3-cyclobutanedione.[3,5]

For 1,3-cyclopentanedione, the A orbital will be destabilized more than the S due to the larger coefficients

(19) P. E. Peterson, J. Org. Chem., 37, 4180 (1972).

(20) (a) R. Hoffmann and R. B. Davidson, J. Amer. Chem. Soc., 93, 5699 (1971); (b) R. Hoffmann, P. D. Mollére, and E. Heilbronner, ibid., 95, 4860 (1973).

at the site of union in the A Walsh orbital than in the S Walsh orbital; the natural order results. In the case of 1,3-cyclohexanedione, the S level will be destabilized more than the A, leading to the "inverted" order, while 1,4-cyclohexanedione should have the "natural" order.

Although the Walsh model assumes planar rings, Hoffmann, Mollére, and Heilbronner[20b] have shown that Walsh-like "ribbon" orbitals persist as a degenerate pair in chair cyclohexane but are split (S below A) in boat cyclohexane. In the four-, five-, and six-membered rings, strict adherence to the Walsh model would require methyl substitution to destabilize the A orbital more than the S orbital.

Discussion

The average of the two n orbital vertical ionization potentials of 1,3-cyclohexanedione (9.82 eV) is 0.09 eV higher than the average of the n ionization potentials of 1,4-cyclohexanedione (9.73 eV),[5] while the splitting in the former (0.44 eV) is much larger than in the latter (~0.15 eV).[5] If the average ionization potential of the diketones is taken to be the value for n orbital ionization of a cyclohexanone inductively stabilized by a second carbonyl group in the ring, the inductive effect of a second carbonyl is calculated to be 0.68 eV for 1,3- and 0.59 eV for 1,4-cyclohexanedione, if the vertical ionization potential of cyclohexanone (9.14 eV)[21] is used for comparison. Similarly, the average ionization potential of 1,3-cyclopentanedione (9.96 eV) is 0.71 eV higher than that of cyclopentanone (9.25 eV).[21] Thus, the mutual inductive effects of two carbonyl groups in a ring are similar for at least two different ring sizes. If these values and that of the α-diketone biacetyl are used, an empirical relationship, $\Delta\epsilon = \Sigma_i(0.90 \pm 0.05 \text{ eV}/n_i)$ can be derived; $\Delta\epsilon$ is the inductive stabilization of an n orbital by substitution of a carbonyl group for a methylene group in a ketone, the summation is over all pathways connecting the two carbonyls, and n_i is the number of bonds separating the carbonyls for connective pathway i.

A second way of viewing the inductive effect of a second carbonyl group, suggested by Professor Weiler, is to compare the ionization potential of the cyclic diketone with an acyclic monoketone formed by dissection of one carbonyl group. Thus, conversion of 3-pentanone (IP = 9.31 eV)[12] to 1,4-cyclohexanedione causes an 0.42-eV stabilization, as does conversion of 2-pentanone (IP = 9.40 eV)[12] to 1,3-cyclohexanedione or of 2-butanone to 1,3-cyclopentanedione.

Although the previous discussion describes the mutual lowering of the basis n orbital energies as an inductive effect, the word "inductive" is used here only as a convenient way to describe mixing with vacant orbitals, hybridization changes which alter effective atom electronegativities, and similar effects of this type.

Alternatively, further dissection of the "inductive" effect may be attempted. Thus, Weiler and coworkers estimate that conversion of a ring sp^3 carbon to an sp^2 carbon results in an 0.24-eV stabilization of a carbonyl n orbital elsewhere in the ring.[22,23] Assuming that

differential interaction of S and A σ orbitals with the n orbitals does not greatly affect the average ionization potential and that interactions with vacant orbitals are unimportant, the inductive effect of oxygen is 0.33 eV for 1,4-cyclohexanedione, 0.42 eV for 1,3-cyclohexanedione, and 0.44 eV for 1,3-cyclopentanedione. An equation similar to that above but counting bonds separating oxygens and allowing different parameters for separation by an odd or even number of bonds accounts nearly perfectly for the inductive effects in these three compounds.

$$\Delta\epsilon = \sum_i^{\text{odd}} \frac{0.825 \text{ eV}}{i} + \sum_i^{\text{even}} \frac{1.008 \text{ eV}}{i}$$

An alternation of inductive effects has been suggested by Pople.[14]

The splitting of n levels in the 1,3-cyclopentanediones decreases from 0.87 eV in the parent compound to 0.69 eV in the dimethyl derivative. This decrease is larger than experimental error and agrees with all three types of calculations (but not the Walsh model) which indicate that the lower (S) level should be destabilized to a greater extent than the upper (A) level of 1,3-cyclopentanedione. The experimental separations in n levels of the cyclopentanediones are larger than those calculated by any of the methods for the cyclopentanedione model, but they are similar to those calculated by Hug, et al. (CNDO/CI),[3] and here by CNDO/S for propanedial. The magnitudes of the lowering of n orbital ionization potentials by alkyl groups have the same order of magnitude as those found for acyclic ketones.[12] In the cases of the 1,3-cyclopentanediones all of the evidence and the calculations are consistent with the "natural" order for the n orbitals.

Comparisons of the experimental ionization potentials for the cyclopentanediones and cyclohexanediones show that the most striking differences are the much smaller splittings in the cases of the cyclohexanediones (0.32–0.47 eV) than in those of the cyclopentanediones (0.69–0.87 eV). The two CNDO methods predict a larger splitting in the five- than in the six-membered rings, whereas the EH calculations do not make that prediction. These calculations were carried out for the chair conformation of 1,3-cyclohexanedione, whereas some doubt about the preferred conformation of the 1,3-cyclohexanedione ring exists. Some of the experimental evidence used to argue for one or another conformation is summarized in the following paragraph.

Equilibrium studies with 2-alkyl-4-*tert*-butylcyclohexanones indicate that eclipsing of 2-equatorial substituents with the carbonyl group decreases the usual energetic preference for substituents to assume the equatorial conformation.[24] Variable temperature nmr studies indicate that the barrier to chair–chair interconversion in cyclohexanone is less than 5 kcal/mol.[25] Kwart, et al., have concluded from the chemical shifts and temperature independence of the nmr spectrum of 2,2-dibenzyl-5,5-dimethyl-1,3-cyclohexanedione that this compound exists in the flexible boat conformation.[26] Similar studies on 2,2,5,5-tetramethyl-1,3-cyclohexane-

(21) D. Chadwick, D. C. Frost, and L. Weiler, *Tetrahedron Lett.*, 4543 (1971).
(22) D. Chadwock, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, 93, 4320 (1971).
(23) D. Chadwick, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, 93, 4962 (1971).

(24) N. L. Allinger and H. M. Blatter, *J. Amer. Chem. Soc.*, 83, 994 (1961).
(25) F. R. Jensen and B. H. Beck, *J. Amer. Chem. Soc.*, 90, 1066 (1968).
(26) H. Kwart, M. C. Rock, R. Sánchez-Obergón, and F. Walls, *J. Amer. Chem. Soc.*, 94, 1759 (1972).

dione show no temperature dependence in the nmr spectrum down to $-160°$.[27] However, the closely related 2,2,5,5-tetramethyl-3-methylenecyclohexanone and 2,2,5,5-tetramethyl-1,3-dimethylenecyclohexane do have barriers of 5.9 and 7.6 kcal/mol, respectively, and analyses of the low temperature spectra indicate these two compounds are predominantly chair conformers.[27] The implication of the last work is that the tetramethylcyclohexanedione is predominantly in the chair conformation and that there is a low barrier to inversion.

Our results do not provide unequivocal evidence for either the conformation or the n level order of the 1,3-cyclohexanediones. From Figure 3, a slight bias for greater destabilization of the lower n orbital level by alkyl substitution can be seen, but the effect is too small and irregular to provide definitive evidence for the natural order. Calculations on 1,3-cyclohexanedione models other than those in Table V show that the magnitude of the splitting of n levels decreases in the order: chair $(C_s) \approx$ boat $(C_s) >$ twist boat (C_2). These results are consistent with the small splittings calculated for 90° acetylacetone or propanedial models, which resemble the twist boat conformation. If the effect of σ orbitals other than those of the $C_1C_2C_3$ bond system could be neglected, the small splitting observed in the cyclohexanediones as compared to the cyclopentanediones could be construed as evidence for the twist boat conformation. However, we cannot confidently make the necessary assumption in the absence of suitable rigid model compounds.

Finally, the enolone spectra will be considered. The two lowest ionization potentials for the enolone forms of the cyclopentanediones are separated by only about 0.2 eV. The n and π ionization potentials of 2-cyclopentenone have been assigned to the bands at 9.34 and 10.10 eV, respectively.[23] A β-hydroxy or -alkoxy substituent should lower the ionization potential of the π orbital to a large extent and should inductively raise the n orbital ionization potential to a small extent. For example, the π ionization potential of ethylene (10.52 eV) is lowered by 1.43 eV upon substitution to form n-butyl vinyl ether (9.08 eV),[28] while the n orbital ionization potential of acetaldehyde (10.22 eV)[12] is raised by 0.37 eV upon substitution to form methyl acetate (10.59 eV).[29] The ionization potentials observed for the parent 3-hydroxycyclopentenone at 9.2 and 9.4 eV can be assigned to π (lowered by 0.9 eV $vs.$ 2-cyclo-

pentenone) and n (raised by 0.1 eV $vs.$ 2-cyclopentenone) orbital ionizations, respectively. The only ionization potential for 3-ethoxy-2-cyclohexenone at less than 10 eV is a relatively broad band at 9.0 eV. The carbonyl n and the π orbitals of this compound must be of approximately the same energy. The ionization potentials of the cyclopentenolones should be, and indeed are, very nearly the same. Calculations on non-hydrogen-bonded $trans$-enolene models invariable predict that the π ionization potential is lower than the n ionization potential (Tables III and IV). Thus, the lowest ionization potentials are assigned to ionization from the π levels in the cyclopentenolones.

Finally, the 0.61-eV splitting between the n and π levels in acetylacetone is significantly larger than the splittings found for the cyclic $trans$-enolones. The model calculations indicate that hydrogen bonding reverses the order of the n and π levels. In the case of simple ketones, a linear correlation of the ir stretching frequency with n orbital ionization has been observed.[21,30] If this relationship and the solution ir frequencies are used,[10a] n orbital ionization potentials of $\sim$8.5 eV for hydrogen-bonded cis-enolones, $\sim$9.1 eV for $trans$-enolones, and $\sim$9.2 eV for the β-diketones are estimated; these estimates qualitatively agree with the experimental results. Thus, the reversal of level order upon hydrogen bonding seems conclusive.

Conclusions

This study has provided evidence for the "natural" order of n orbital levels of 1,3-cyclopentanediones; the results agree with those of numerous model calculations. However, model calculations more extensive than those that had previously been performed revealed the possibility of a reversal of the "natural" order in the cases of some geometries. In the case of 1,3-cyclohexanediones, definitive assignments could not be made. Photoelectron spectra of enolones were measured for the first time, and evidence for the order π over n for non-hydrogen-bonded and for the order n over π for hydrogen-bonded enolones was shown.

(27) M. Bernard, F. Sauriol, and M. St.-Jacques, *J. Amer. Chem. Soc.*, **94**, 8624 (1972).

(28) R. Sustmann and H. Trill, *Angew. Chem., Int. Ed. Engl.*, **11**, 838 (1972).

(29) R. Sustmann and H. Trill, *Tetrahedron Lett.*, 4271 (1972).

(30) D. Cook, *Can. J. Chem.*, **39**, 31 (1961), and references therein.