

The Electronic Structure of Saturated Cyclic Ketones

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A theoretical investigation of the electronic structure and spectra of the saturated cyclic ketones, cyclobutanone, cyclopentanone, and cyclohexanone, has been made using the semi-empirical zero-differential overlap method within the SCF-CI scheme. In all, three types of calculation were performed: (1) CNDO/2 using the original parameterization of Pople and Segal, (2) INDO as formulated by Pople, Beveridge, and Dobosh, and (3) CNDO/s with the parameterization of Dél Bené and Jaffé. Configuration interaction with up to forty singly excited states was included in each of these calculations. It was found that only the CNDO/s scheme gave results in fairly good agreement with experiment. In all three ketones the first and second bands are calculated to be $n\pi^*$ and $\sigma\pi^*$ transitions. The third and fourth bands are found to be composite bands, that is composed of near-lying transitions of different origin.

Although the electronic structure and spectrum of formaldehyde has been much studied, and is now fairly well understood, the electronic properties of the cyclic ketones, cyclobutanone (CB), cyclopentanone (CP), and cyclohexanone (CH) of which formaldehyde can be considered the parent molecule, have been relatively neglected. In 1942 Benson and Kistiakowsky¹ reported the hexane solution spectrum of the lowest energy transition (now known to be $n\pi^*$) in CB, CP, and CH. Later, Horwood and Williams² determined the vapor spectra of the second transition in CP and CH. Udvarhazi and El-Sayed³ corroborated Horwood and Williams' work and extended their measurements to include the second and third bands of vapor phase CB, CP, and CH, and noted an intensity interdependence of these two bands. Chandler and Goodman⁴ have studied the allowed and forbidden character in the $n\pi^*$ transition in CB, CP, and CH. Moule⁵ has recently published a report on the high resolution ultraviolet spectrum of the $n\pi^*$ band of vapor phase CB and indicated the presence of a double minimum in the excited state. In the most complete work on CB to date, Whitlock and Duncan⁶ have measured the electronic spectrum in the vapor phase up to $78\,000\text{ cm}^{-1}$. Nine transitions

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were observed, five of which were assigned to Rydberg transitions. Assignments for the remaining four bands were presented, the first and fourth bands being denoted, with relative certainty, $n\pi^*$ and $\pi\pi^*$ transitions, respectively. With less certainty, the second and third bands were assigned to $\sigma(n')\rightarrow\pi^*$ and $n\rightarrow\sigma_{\text{co}}^*$ transitions, respectively. These latter two assignments are identical with previous work on simple non-cyclic ketones.⁷ Other authors have, however, assigned the second band to an $n\rightarrow\sigma^*$ ⁸ and to a Rydberg transition⁹ and the third band to a transition involving the $\sigma(\text{c}-\text{c})$ bond.¹⁰

Heretofore, there has been no theoretical investigation of these molecules reported. With the presently available semiempirical LCAO-MO-SCF methods (CNDO/2 and INDO) which include all valence electrons, it was felt that an investigation of the electronic structures of these molecules was both feasible and needed. The primary goal of this work was to provide theoretical justification for the experimental band assignments in the CB, CP, CH series. Since the original CNDO/2 parameterization scheme developed by Segal and Pople¹¹ was shown by Dél Bené and Jaffé¹² to be less than optimum for the description of electronic transitions and since the parameterization scheme proposed by the latter authors has not been tested on simple ketones (except for formaldehyde), it was also decided to study the relative merits of the two CNDO schemes as applied to the present cyclic ketones.

GEOMETRICAL PARAMETERS

Microwave studies have been reported for both CB¹³ and CP,¹⁴ and an electron diffraction study carried out on CH.¹⁵ In Table 1 the bond angles and bond lengths taken from these reports are listed. Unfortunately, only the ring geometry was given for CB,¹³ the R_{CH} and the R_{CO} values given in Table 1 are reasonable estimates. The geometries contain two interesting features. First, the carbon-carbon bonds adjacent to the carbonyl group in CB and CP are shorter than the other bonds. (No such difference was detected in the electron diffraction work on CH.) And, secondly, the angle at the carbonyl

Table 1. Geometrical parameters for cyclic ketones.

Parameters Symmetry group	CB[P] C_{2v}	CP[P] C_{2v}	CP[NP] C_2	CH[P] C_{2v}	CH[NP] C_s
$R(\text{CO})$	1.21 Å	1.215 Å	1.215 Å	1.24 Å	1.24 Å
$R(\text{C}_1\text{C}_2)$	1.527	1.504	1.504	1.54	1.54
$R(\text{C}_2\text{C}_3)$	1.556	1.557	1.557	1.54	1.54
$R(\text{C}_3\text{C}_4)$	—	1.557	1.557	1.54	1.54
$R(\text{C}_2\text{H})$	1.10	0.950	0.950	1.09	1.09
$(\text{C}_2\text{C}_1\text{C}_i)^a$	93.1°	110.5°	110.5°	117°	117°
Special angle	—	0° ^b	23.6° ^b	0° ^c	60.9° ^c

^a i = Number of carbon atoms in ring.

^b Angle of twist of carbon No. 3 above and carbon No. 4 below the plane of the molecule (*i.e.*, plane of $\text{OC}_1\text{C}_2\text{C}_5$).

^c Angle by which the plane defined by $\text{OC}_1\text{C}_2\text{C}_6$ is rotated out of the plane defined by $\text{C}_2\text{C}_6\text{C}_3\text{C}_5$. The $\text{C}_3\text{C}_4\text{C}_5$ plane is rotated the same amount in the opposite sense.

carbon increases as the ring enlarges, reflecting the decreased ring strain and change in hybridization. The planar conformations of all three molecules belong to the C_{2v} point group, whereas non-planar CP (formed by rotation of bond 3–4 23.6° around an axis collinear with CO) belongs to C_2 , and the non-planar boat form of CH belongs to the C_s symmetry group.

CALCULATION PROCEDURE

All the calculations were performed within the SCF-CI scheme, and based upon the semi-empirical zero-differential overlap method. Specifically, three types of calculation were done. (1) A CNDO/2 computation in which the original parameterization given by Pople and Segal¹⁰ was retained. (2) An INDO calculation identical with that formulated by Pople, Beveridge, and Dobosh¹⁰ was carried out. Both of these methods have been most successfully applied to the ground state-properties of small molecules. Determinations of spectroscopic excited state energies using the original parameterization of the CNDO/2 scheme have, by and large, been unsuccessful.^{11,12} An attempt to modify this method by using a different parameterization scheme has been made by Dél Bené and Jaffé.¹² (3) In this improved version (called CNDO/s) the electron repulsion integrals are replaced by new semi-empirical parameters, and a parameter K introduced to distinguish the resonance integrals due to σ -type orbital interactions from those for π -type interactions.

In all three of the above calculations, configuration interaction was included among singly excited states in the following way. The one-electron excitations were sorted according to symmetry type, the full C. I. matrix blocked off and each block diagonalized. If the number of transitions belonging to one symmetry class was less than 40, they were all included in the full C. I. calculation. If the number was less than 63, the transitions were ordered according to their triplet diagonal elements with only the lowest 40 included in the C. I. computation, all others being ignored. Although this procedure discriminates against some low energy transitions, their number is kept to a minimum by the order in which they are determined.

Table 2. Electronic transitions in cyclobutanone (planar). (All energies in eV.)

Band	Energy (exp.)	CNDO/2 and INDO			CNDO/s		
		Excited state	Orbital type	Energy (CNDO/2)	Energy (INDO)	Energy (CNDO/s)	Excited state
1.	3.76 ⁵	1A_2	$n\pi^*$	4.32	4.24	3.23	1A_2 ($n\pi^*$)
2.	6.11 ⁵	1B_1	$\sigma\pi^*$	8.32	8.04	5.52	1B_1 ($\sigma\pi^*$)
3.	6.89 ⁵	1B_2	$n\sigma^*$	10.24	9.74	7.31	1A_1 ($n\sigma^*$)
						7.57	1A_2 ($\sigma\pi^*$)
						7.89	1B_2 ($\sigma\sigma^*$ and $n\sigma^*$)
4.	7.75 ⁵	1A_1	$\pi\pi^*$	10.55	10.74	8.29	1B_2 ($\sigma\sigma^*$ and $n\sigma^*$)
						8.35	1A_2 ($\pi\pi^*$ and $n\sigma^*$)

Table 3. Electronic transitions in cyclopentanone. (Planar [P] and non-planar [NP]; all energies in eV.)

Band	Energy (exp.)	CND0/2 and INDO						CND0/s				
		Excited state		Orbital type	Energy (CND0/2)		Energy (INDO)	Energy [P]	Excited state	Energy [NP]	Excited state	
		P	NP		P	NP						P
1.	4.13 ¹	¹ A ₂	¹ A	nπ*	4.62	4.72	4.45	4.51	3.24	¹ A ₂ (nπ*)	3.19	¹ A(nπ*)
2.	6.22 ³	¹ B ₁	¹ B	σπ*	8.93	10.12	8.63	8.67	6.05	¹ B ₁ (σπ*)	5.83	¹ B(σπ*)
									8.20	¹ A ₁ (ππ*)	8.04	¹ B(nσ*)
										¹ A ₁ (nσ*)		¹ B(σσ*)
										¹ A ₁ (nσ _{CO} *)		
3.	7.08 ³	A ₁	¹ A	ππ*	10.58	11.70	10.84	11.57	8.34	¹ B ₂ (nσ*)	8.10	¹ A(σπ*)
										¹ B ₂ (σσ*)		¹ A(nσ*)
										¹ A ₂ (σπ*)		¹ A(ππ*)
									8.52	¹ A ₂ (nπ*)	8.36	¹ B(σπ*)
4.		¹ B ₂	¹ B	nσ*	11.15	11.75	10.33	10.75	8.72	¹ A ₁ (ππ*)		¹ A(ππ*)
										¹ A ₁ (nσ*)	8.67	¹ A(σπ*)
												¹ A(nσ*)

Table 4. Electronic transitions in cyclohexanone (Planar [P] and non-planar [NP]; all energies in eV.)

Band	Energies (exp.)	CNDO/2 and INDO						CNDO/s				
		Excited state		Orbital type	Energy (CNDO/2)		Energy (INDO)		Energy [P]	Excited state	Energy [NP]	Excited state
		P	NP		P	NP	P	NP				
1.	4.28 ¹	¹ A ₂	¹ A''	nπ*	4.46	5.11	4.27	4.80	3.19	3.25	¹ A ₂ (nπ*) ¹ A ₂ (σ(n')π*)	¹ A''(nπ*)
2.	6.30 ³	¹ B ₁	¹ A'	σπ*	9.03	10.45	8.59	9.58	5.94	6.04	¹ B ₁ (σπ*) ¹ B ₁ (σ _{CO} π*)	¹ A'(σπ*)
3.	6.99 ³	¹ B ₂	¹ A''	nσ*	11.01	11.97	10.08	10.68	7.62	7.83	¹ A ₂ (nπ*) ¹ A ₂ (σ _{CO} π*) ¹ A ₂ (σπ*)	¹ A'(ππ*) ¹ A'(σπ*) ¹ A'(ππ*) ¹ A'(nπ*) ¹ A'(nσ _{CO} *)
4.		¹ A ₁	¹ A'	ππ*	11.06	11.99	10.62	11.60	8.05	8.24	¹ A ₁ (ππ*) ¹ A ₁ (nσ _{CO} *)	¹ A''(nσ _{CO} *) ¹ A''(nσ*) ¹ A''(σσ _{CO} *)
									8.21	8.38	¹ B ₂ (nσ*) ¹ B ₂ (σσ*)	¹ A''(σ _{CO} π*)

The CNDO/2 and INDO calculations were performed with QCPE program 141 as reprogrammed for the IBM 7094 computer by A.D.C. Towl. The CNDO/s calculations were performed by modifying the former program; the modified program was tested against a calculation on formaldehyde.¹⁷

RESULTS AND DISCUSSION

Dél Bené and Jaffé have demonstrated¹² that the CNDO/s parameterization scheme reproduces the charge densities of ground state molecules calculated by *ab initio* and more extensive semi-empirical LCAO-SCF methods. This finding also holds true in the present work, a measure of which can be gotten from the good agreement between calculated and experimental dipole moments: for CB, $\mu_{\text{exp}} = 2.89$ D,¹³ $\mu_{\text{calc}} = 3.02$ D; for CP_{exp}, $\mu = 3.25$ D,¹⁴ $\mu_{\text{calc}} = 3.59$ D; for CH, $\mu_{\text{exp}} = 3.08$ D,¹⁹ $\mu_{\text{calc}} = 3.76$ D.

A. Cyclobutanone. The results of our calculations on planar CB together with the energies of the observed (non-Rydberg) transitions are given in Table 2. It can be seen that both the CNDO/2 and INDO calculations using the original Pople-Segal parameterization give energies which are generally too large compared to experimental. The agreement using the Dél Bené-Jaffé CNDO/s scheme is, however, much better. The first two bands at 3.76 eV and 6.11 eV are calculated to be simple $n\pi^*$ and $\sigma\pi^*$ type transitions in corroboration with Whitlock and Duncan's assignment.⁶ These authors found the third band, assigned by them to an $n\sigma_{\text{co}}^*$ transition, to be very broad and continuous. Our calculations indicate the presence of three close-lying bands in this region: 1A_1 ($n\sigma^*$) at 7.31 eV, 1A_2 ($\sigma(n)\pi^*$) at 7.57 eV, and 1B_2 ($\sigma\sigma^*$ and $n\sigma^*$) at 7.89 eV. These bands could possibly overlap each other and thus account for the broadness of the observed band. The fourth band at 7.75 eV has been assigned by Whitlock and Duncan to a $\pi\pi^*$ transition; like the third band our computations indicate a composite band of several near-lying transitions: 1B_2 ($\sigma\sigma^*$ and $n\sigma^*$) at 8.29 eV and 1A_1 ($\pi\pi^*$ and $n\sigma^*$) at 8.35 eV. The $\pi\pi^*$ component will probably predominate intensitywise in this band.

We consider the overall agreement using the CNDO/s method to be quite good and the experimental assignments of Whitlock and Duncan to be sound, particularly with respect to the first and second bands. The third and fourth bands appear to be composite in character and difficult to describe simply.

B. Cyclopentanone. The calculations for cyclopentanone were performed on both a hypothetical planar molecular and the actual non-planar form. Again, the results of the CNDO/2 and INDO computations, given in Table 3, give transition energies substantially higher than the observed, whereas the CNDO/s results agree fairly well with the experimental values. It can be seen from Table 3 that the first and second bands can be assigned to $n\pi^*$ and $\sigma\pi^*$ transitions, respectively, in analogy with the similar bands in cyclobutanone. Theoretically, no clear distinction between or assignments for the third and fourth bands can be made in the CNDO/s scheme since a total of four composite transitions fall in the range 8.0 eV to 8.7 eV. Furthermore, the ordering of these transitions is very dependent on the ground state geometry. Note that the group of 1A_1 transitions at 8.20 eV and the group of 1B_2 transitions at 8.34 in the planar molecule invert (and decrease in energy) in the non-planar molecule.

C. Cyclohexanone. The results on this molecule largely mimic those of cyclopentanone. The CNDO/2 and INDO energies are too large, while the CNDO/s results give much better agreement. Here, however, only the first transition in the non-planar conformation can be simply described as $n\pi^*$. The second band is now predicted to contain some $\pi\pi^*$ character along with the predominant $\sigma\pi^*$ type transition. And, as before, several composite bands fall in the region expected for the third and fourth bands.

It is striking that although the CNDO/2 and INDO techniques over-estimate the spectroscopic transition energies, they do provide a simple description of the higher energy bands. This is in contrast to the CNDO/s scheme which mixes a large number of one-electron transitions to arrive at the final description of the band.

D. Intensity considerations. Our calculations confirm Chandler and Goodman's ⁴ finding that the $n\pi^*$ transitions in CP and CH are formally allowed. In planar CP and CH (and CB) the $n\pi^*$ transition is, of course, rigorously (electric dipole) forbidden. Upon twisting and bending, the n orbital (in CP) and the π^* orbital (in CP and CH) change character. For example, upon twisting planar to non-planar CP, the oxygen p_y and p_z orbitals mix in both the n and π^* orbitals leading to a non-zero $n\pi^*$ transition moment.

Because of this allowed character one might expect that an intensity prediction could be used to corroborate our energy predictions, at least in CP and CH. However, Chandler and Goodman ⁴ have shown that, although formally allowed, vibronic coupling is responsible for part of the intensity of the CP and CH $n\pi^*$ bands and all of the intensity in the corresponding CB band. Thus direct comparison of calculated allowed intensities is meaningless until the two contributions (electronic and vibronic) can be separated.

Udvarhazi and El-Sayed have noted ³ that the intensity of the second band increases in the order $CH < CB < CP$. From our calculations, this band is assigned to a ${}^1B_1(\sigma\pi^*) \leftarrow {}^1A_1$ type transition in all three ketones. If one analyzes the transition dipole moment for a transition of this type,¹⁸ one needs only to consider the one center integral $\langle 2s|z|2p_z \rangle$, where the z direction is out-of-plane and perpendicular to the CO group. The only significant contributions to the total transition moment integral come from the carbon and oxygen atoms of the carbonyl group. The predicted intensity pattern is $CH < CB \approx CP$. As noted previously for the $n\pi^*$ transition, vibronic mixing could be responsible for part of the observed intensity in these bands also.

Any intensity comparison of the third or fourth bands within the series is seriously hampered by the composite nature of the transitions. Indeed, it is difficult to even correlate the individual components of these bands from compound to compound.

CONCLUSIONS

Calculations on the present saturated cyclic ketones have shown that the CNDO/2 and INDO schemes with the original parametrization of Pople and Segal greatly overestimate the energies of the non-Rydberg transitions. On the other hand, results using the Dél Bené-Jaffé parameters in the CNDO/s method give energies in fairly good agreement with experiment.

The first and second bands in all three ketones are assigned to $n\pi^*$ and $\sigma\pi^*$ transitions, respectively, as suggested by Whitlock and Duncan among others. The third and fourth bands are calculated as composite bands, that is, bands composed of a number of different types of transitions. For example, in cyclobutanone, three transitions, an $n\sigma^*$, a $\sigma\pi^*$, and a combined $\sigma\sigma^* - n\sigma^*$, are predicted in the region of the third observed band, while two transitions, a combined $\sigma\sigma^* - n\sigma^*$ and a combined $\pi\pi^* - n\sigma^*$, are predicted in the region of the fourth band.

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