

Transcription of the results of quantum chemical calculations in terms of the classical notion of molecular structures: The cases of some small carbonyls in the ground and excited states

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Abstract. Quantum chemical valence parameters of several carbonyl molecules in the ground and excited states are calculated by invoking the INDO-orthogonal gradient method in an MC-SCF framework. These parameters are then used to construct state-specific structural descriptions of these molecules in terms of superposition of several canonical structures. Photochemical reactivities of some of these molecules are sought to be explained on the basis of the picture that emerges.

Keywords. INDO-orthogonal gradient method; MC-SCF framework; specific structural description.

1. Introduction

Chemists have not paid much attention to structural modelling of molecules in the excited state primarily because of the scarcity of structural data. Apart from changes in reactivity, a molecule in the excited electronic state often shows significant structural changes as well as changes in acidity, basicity etc. These changes occur because the distribution of electron density in the molecule changes on excitation. Sometimes, a molecule may display very significant differences in structure or other observable properties in excited states arising from the same orbital configuration but with different spin coupling. Systematic generation and analysis of quantum chemical valence parameters of molecules in the ground and excited states can therefore be useful in establishing a connection between classical structural models for different molecules in various electronic states and their quantum chemical descriptions in terms of wavefunctions. In this paper we will show that the computed net charges on different atoms and bond orders provide parameters which can be very useful in this analysis.

2. Method

For a single determinant LCAO-MO-SCF wave function ψ made up of n occupied molecular spin orbitals (ϕ_i), which are linear combinations of N ($N \geq n$) atom centred

*For correspondence

non-orthogonal functions (χ_i), we have

$$\begin{aligned}\psi(1, 2, \dots, n) &= A(\phi_1 \cdots \phi_n), \\ \phi(\phi_1 \phi_2 \cdots \phi_n) &= \chi(\chi_1 \cdots \chi_n)T, \quad \langle \chi/\chi \rangle = S, \quad T^+ ST = 1, \\ \bar{P} &= TT^+, \quad P = \sum_{i=1}^{\text{occ}} n_i T_i T_i^+ \equiv 2P.\end{aligned}$$

Considering all the m -occupied spin orbitals to be paired, P is the one-electron density matrix and one can define the atomic charge q_A on an atom A in the molecule as the expectation value of an LCAO-atomic charge density operator $\langle Z_A - \hat{q} \rangle$ such that (Armstrong *et al* 1973; Wiberg 1973),

$$q_A = Z_A - \langle q_A \rangle = Z_A - \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu} S_{\nu\mu},$$

Z_A being the nuclear charge of the atom A. $\langle q_A \rangle$ is clearly the Mulliken gross charge density. From the partial charges, bond order between a pair of atoms in a molecule has been defined as

$$B_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} (PS)_{\mu\nu} (PS)_{\nu\mu}.$$

A more general definition that covers open-shell (UHF) states as well, has also been successfully used,

$$\begin{aligned}B_{AB} &= \sum_{\mu \in A} \sum_{\nu \in B} ((PS)_{\nu\mu}) + \sum_{\mu \in A} \sum_{\nu \in B} (P^s S)_{\mu\nu} (P^s S)_{\nu\mu}, \quad \text{with} \\ P &= P^\alpha + P^\beta, \quad P^s = P^\alpha - P^\beta, \quad P^\alpha = T^\alpha T^{\alpha+}, \quad P^\beta = T^\beta T^{\beta+}.\end{aligned}$$

B_{AB} measures the fluctuation of atomic charges on atoms A and B (Giambiagi *et al* 1985), i.e. $B_{AB} = \langle (\hat{q}_A - \langle q_A \rangle)(\hat{q}_B - \langle q_B \rangle) \rangle$.

If the gross population of an AO basis function (χ_μ^A) on an atom A in the molecule is q_μ^A , the potential bonding power of that particular AO is

$$b_\mu^A = 2(q_\mu^A) - (q_\mu^A)^2.$$

Summing over all the basis functions centred on atom A, we get what has been called valency (V_A) of the atom A in the molecule,

$$V_A = \sum_{\mu \in A} b_\mu^A = \sum_{\mu \in A} (2q_\mu^A - (q_\mu^A)^2).$$

Mayer's (1983, 1986) definition of atomic valence (V_A^M) is a straightforward generalization of Wiberg's valence where the basis set of expansion is nonorthogonal,

$$V_A^M = 2 \sum_{\mu \in A} (PS)_{\mu\mu} - \sum_{\mu\nu} (PS)_{\mu\nu} (PS)_{\nu\mu}.$$

For the open shell state (UHF), we have

$P = P^\alpha + P^\beta$, $P^s = P^\alpha - P^\beta$, this leads to a residual or free valence (f_A) for the atom A

$$f_A = \sum_{\mu \in A} \sum_{\nu \in A} (P^s S)_{\mu\nu} (P^s S)_{\nu\mu}.$$

We represent the molecule in its lowest singlet and triplet excited states by the following type of wave function ($S = 0$ corresponds to singlet, $S = 1$ to triplet)

$${}^{1,3}\psi_{i \rightarrow j} = (1/\sqrt{2})(|\phi_1 \bar{\phi}_1 \cdots \phi_i \bar{\phi}_j \cdots \phi_n \bar{\phi}_n| + (-1)^S |\phi_1 \bar{\phi}_1 \cdots \phi_j \bar{\phi}_i \cdots \phi_n \bar{\phi}_n|).$$

Orbitals are optimised by the master equation of Mcweeny and Sutcliffe (1969), and solved iteratively by the orthogonal gradient method (Medhi *et al* 1993)

$$V = (hTP_1 + Z) = ST\lambda. \quad (1)$$

The *CI* problem requires us to solve the equation

$$HC = CE. \quad (2)$$

The *CI* coefficients are used to construct the one electron density matrix (ρ_1) in the $MO(\phi)$ basis, the density matrix in the χ basis as follows,

$$P = T\rho_1 T^+, \quad P = P^D + P^S.$$

P^D represents the component of the OEDM coming from the doubly occupied orbitals and P^S , the component contributed by the singly occupied orbital. The P and P^S matrices can now be used for the determination of the quantum chemical valence parameters B_{AB} , V_A , f_A etc.

3. Results and discussions

We shall now discuss the change in bond orders and the total net charge densities on the atoms in molecules (irrespective of separate π and σ net charge densities) to formulate structural patterns in different excited states. Table 1 summarises the computed bond orders and net charge densities on different atoms of formaldehyde in the ground, ${}^{1,3}n\pi^*$ and ${}^3\pi\pi^*$ states at the respective equilibrium geometry. $n \rightarrow \pi^*$ excitation reduces C=O bond order by $\approx 40\%$ relative to the ground state, while $\pi \rightarrow \pi^*$ reduces it by 50%. $n\pi^*$ and $\pi\pi^*$ excitations therefore reduce the carbon atom to a virtually trivalent state ($V_A \approx 3$) leading to non-planar geometry around the carbonyl carbon atom. Computed charge densities on different atoms show that considerable electron density has migrated from oxygen to the carbon atom following $n\pi^*$ excitation. Such migration is less in the $\pi\pi^*$ state. The C–O BO together with the atomic charge densities suggests that the ground state structure of formaldehyde is almost exclusively dominated by the contribution from structures 1 and 2, while the excited states could be neatly described by 3.

Table 1. Computed bond orders and net charge densities on different atoms in the ground and excited states of H_2CO .

System state	Bond order		Net charges on		
	C–O	C–H	C	O	H
Ground	2.03	0.94	0.32	–0.24	–0.04
$1n\pi^*$	1.15	0.94	0.06	–0.12	0.03
$3n\pi^*$	1.19	0.93	0.02	–0.08	0.01
$3\pi\pi^*$	0.99	0.96	0.17	–0.14	–0.01

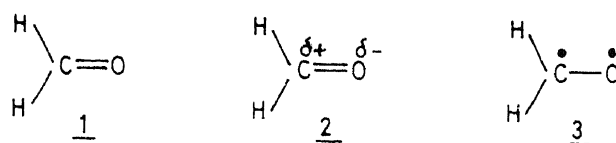
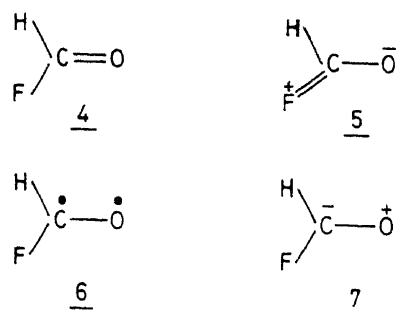


Table 2. Computed bond orders and net charge densities on different atoms in the ground and excited states of HFCO.

System state	Bond order			Net charges on			
	C-O	C-F	C-H	C	O	F	H
Ground	1.94	0.95	0.93	0.56	-0.29	-0.23	0.14
1nπ*	1.08	0.98	0.91	0.30	-0.12	-0.18	0.15
3nπ*	1.10	0.97	0.90	0.28	-0.11	-0.18	0.15
3ππ*	0.98	1.03	0.95	0.28	-0.16	-0.13	0.15



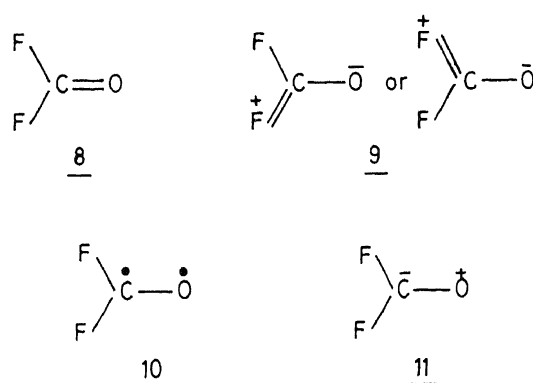
Substitution of one or both hydrogen atoms of the formaldehyde molecule gives rise to extensive structural changes depending on the type of substituent, which can be either electron-withdrawing, electron-donating or unsaturated. As we can see from the data in table 2, a single fluorine substitution in H_2CO results in significant reduction of $\text{C}=\text{O}$ bond order even in the ground state. This may be due to the π polarization of the $\text{C}=\text{O}$ bond caused by the strongly σ withdrawing effect of the F-substituent. $n\pi^*$ and $\pi\pi^*$ excitations reduce the $\text{C}=\text{O}$ bond order further and the carbon centre becomes nearly trivalent in the HFCO molecule. The $\text{C}-\text{H}$ BO is unaffected by excitation. But the $\text{C}-\text{F}$ BO increases marginally following $\pi\pi^*$ excitation. In addition to the normal structure 4, HFCO in the ground state has a small contribution from the structure as shown by 5. In the excited state, 6 and 7 should be the most important structures that contribute.

The pattern of effects of fluorine substitution observed in HFCO is expected to persist similarly as one goes from HFCO to F_2CO . This is found to be actually so, as the data in table 3 seem to indicate. The structural description of F_2CO in the ground state, consistent with the BO data, should involve canonical forms of the type in structures 8 and 9, while 10 and 11 appear to contribute strongly in the excited states.

Comparison of the CO bond order of H_2CO with that in CH_3CHO clearly shows that CH_3 substitution causes a decrease in $\text{C}-\text{O}$ bond order by 10% per methyl group in the ground state. This must be the result of π polarization of the $\text{C}=\text{O}$ bond (towards the oxygen atom) caused by the CH_3 group. The $\text{C}-\text{C}$ bond order in CH_3CHO is found to be systematically larger than the $\text{C}-\text{H}_a$ bond order (table 4) in

Table 3. Computed bond orders and net charge densities on different atoms in the ground and excited states of F_2CO .

System state	Bond order		Net charges on		
	C-O	C-F	C	O	F
Ground	1.86	0.95	0.78	-0.34	-0.22
$1n\pi^*$	0.98	0.96	0.53	-0.15	-0.19
$3n\pi^*$	0.97	0.96	0.53	-0.15	-0.19
$3\pi\pi^*$	0.96	0.97	0.53	-0.15	-0.19

**Table 4.** Computed bond order and net charge densities on different atoms⁺ in the ground and excited states of acetaldehyde.

System state	Bond order				Net charge on				
	C-O	C-C	CH _a	CH _m	C _a	O	C _m	H _a	H _m
Ground	1.90	1.09	0.92	0.90	0.92	-0.29	-0.01	-0.07	0.02
$1n\pi^*$	1.08	1.13	0.93	0.90	0.08	-0.14	0.07	0.01	0.00
$3n\pi^*$	1.11	1.12	0.93	0.90	0.05	-0.11	0.08	0.02	-0.02
$3\pi\pi^*$	0.96	1.19	0.95	0.90	0.12	-0.17	0.05	-0.02	0.00

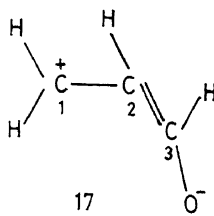
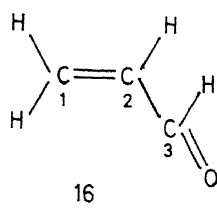
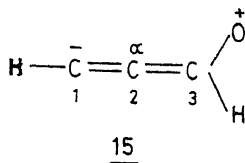
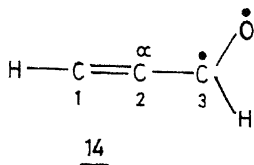
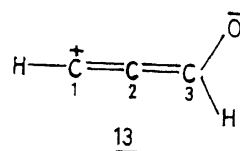
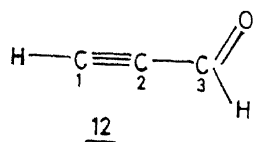
⁺C_m = methyl carbon atom, H_m = methyl hydrogen atom
H_a = aldehyde hydrogen atom

the excited states. We may speculate therefore that photochemical cleavage of the C-C bond would be less facile (Chandra and Sumathi 1990) than that of C-H_a bond in acetaldehyde. That is, the rupture of the C-C bond in $CH_3CHO \xrightarrow{h\nu} CH_3CHO^* \rightarrow H_3CCO\cdot + H$ will be energetically favoured compared to the cleavage into $H_3C\cdot + HCO\cdot$. The C-C bond order in the ground state is a bit higher than that expected for a single bond and C=O bond order is less than that expected of a C-O double bond (e.g. in H_2CO , it is 2.05).

In propynal, on the other hand, the computed C₂-C₃ bond order (table 5) in the ground state is about 10% more than that expected for a single C-C bond, while the C₁-C₂ BO is $\approx 10\%$ less than that of an ideal triple bond. One can therefore rationalise

Table 5. Computed bond order and net densities on different atoms in the ground and excited states of propynal.

System state	Bond order				Net charges on				
	C≡C	C-C	C-O	C ₃ -H ₅ C ₁ -H ₆	C ₁	C ₂	C ₃	O	H ₅ H ₆
Ground	2.84	1.11	1.88	0.92 0.98	-0.02	-0.05	0.34	-0.28	-0.05 0.06
1 $\pi\pi^*$	2.76	1.19	1.10	0.90 0.98	-0.08	0.01	0.11	-0.12	0.02 0.06
3 $\pi\pi^*$	2.78	1.16	1.12	0.90 0.97	-0.09	0.01	0.08	-0.10	0.26 0.06
3 $\pi\pi^*$	2.60	1.34	0.97	0.94 0.98	-0.04	0.01	0.15	-0.16	0.01 0.07



the observed BOs in terms of mixing of the canonical structures in 12 and 13. The computed C-H bond orders and charge densities on the atoms differentiate the aldehyde hydrogen (H₅) from the typical acetylenic hydrogen (table 5). $n\pi^*$ excitation is predicted to cause a further decrease in C₁≡C₂ BO and an increase in the C₂-C₃ bond order. The decrease in the C=O bond order upon excitation is about 40%, relative to the ground state value. These changes in BOs can be rationalised in terms of mixing of the canonical structures in 14 and 15. The allene structure in 15, which results from electronic charge transfer, has the effect of lengthening C≡C bond and decreasing the corresponding BO and an opposite effect on the C-C bond. The computed BOs nicely mirror these expectations, based on the classical concept of structures extended to electronically excited states of molecules. The bond order in the ground state of the acrolein molecule points to a model that confirms the structural description of the molecule in terms of 16, i.e. a double bond between the C₁ and C₂ atoms (BO = 1.94), a

single bond between C₂ and C₃ (BO = 1.09) and a double bond between C₃ and the oxygen atom (BO = 1.88). The slightly reduced values of the C₁-C₂ and C₃-O BOs could be taken to imply that the canonical structure in 17 also contributes in the ground state, a proposition that may be credible in view of the π donor ability of the CH₂=C- unit.

A survey of the literature shows that the ground and excited ^{1,3}n π^* states of propynal have been studied extensively by optical spectroscopy (Corey *et al* 1964; Wiesner 1975; Blount *et al* 1980). Molecular dimensions in the ground state have been determined by microwave studies, which have confirmed a planar ground state structure. From the computed BOs (table 5) in the ³ $\pi\pi^*$ state of propynal, the canonical structure of the type in 17 is predicted to contribute the most. It is tempting to conclude on the basis of the picture which emerges that photochemical cleavage of the C₂-C₃ bond would be more facile than that of the C-H_a bond. However, the barriers to the corresponding processes may be quite different and cleavage may not be controlled by their equilibrium bond orders alone.

In the ground state of the glyoxal molecule, the *trans* conformer represents the global minimum, the CO bond (table 6) order in the ground state is significantly less than ≈ 2 i.e. the value observed for H₂CO in the ground state. Simultaneously, the C-C bond order is about 10% above that expected for a C-C single bond. Ignoring the limitations of the small basis set used in our calculations, this would tend to suggest that there are two canonical structures (18 and 19) that contribute significantly to the ground state of glyoxal with 18 as the dominant one. Structure 19 would arise out of π donation by the -CHO unit in glyoxal whose π electrons are conjugated. The fairly large positive charge on the carbonyl carbon atom and the net negative charge on the carbonyl oxygen atom are both found to be higher than the corresponding quantities in formaldehyde. This supports the concept of π polarization towards the oxygen atom implied by 18 and 19.

In the lowest n π^* states of the glyoxal molecule, the CO bond order is reduced by $\approx 20\%$ (40% in H₂CO) and C-C BO increases by about the same amount. The comparatively larger C-O bond orders in the n π^* excited states of glyoxal relative to those in H₂CO may be explained by the fact that there are two structures in the n π^* states, which contribute significantly each having one of the equivalent C=O units with the π bond intact (18 or 19, 20 or 21). This also explains why the net electron density on the oxygen atom in the n π^* state of glyoxal is much larger compared to that in formaldehyde. In the $\pi\pi^*$ state, the situation is more or less the same except that structures of the type 22 or 23 may apparently provide better explanation.

Table 6. Computed bond order and net charge densities on different atoms in the ground and excited states of glyoxal.

System state	Bond order			Net charge densities on		
	C-C	C-O	C-H	C	O	H
Ground	1.09	1.89	0.89	0.25	-0.22	0.04
1n π^*	1.24	1.52	0.89	0.20	-0.21	0.01
3n π^*	1.26	1.51	0.89	0.20	-0.20	0.01
3 $\pi\pi^*$	1.87	1.05	0.95	0.17	-0.16	0.02

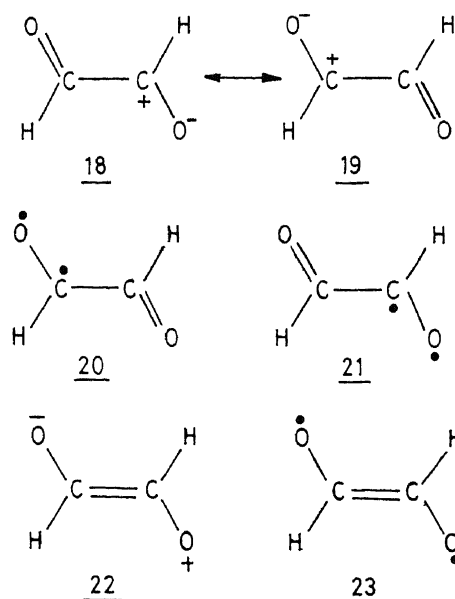
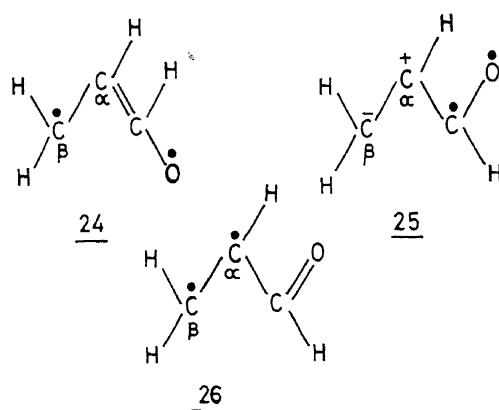


Table 7. Computed bond order and net charge densities on different atoms in the ground and excited states of acrolein.

System state	Bond order					Net charges on					
	C ₁ C ₂	C ₂ C ₃	C ₃ O ₄	CH	CH _a	C ₁	C ₂	C ₃	O	H	H _a
Ground	1.94	1.09	1.88	0.96	0.92	0.07	-0.03	0.32	-0.29	-0.01	0.01
1nπ*	1.69	1.32	1.09	0.96	0.92	-0.02	0.04	0.13	-0.14	-0.01	0.01
3nπ*	1.79	1.27	1.11	0.96	0.92	-0.01	0.04	0.10	-0.11	-0.01	0.01
3ππ*	1.23	1.75	1.00	0.96	0.92	-0.01	0.03	0.17	-0.18	0.00	0.00



In the $n\pi^*$ excitation of acrolein one observes changes specially in the C₁-C₂ and C₃=O bond orders (table 7). In the language of the classical VB model, acrolein in $n\pi^*$ state therefore dominantly resembles the canonical structure 24. The increase in C₂-C₃ BO and decrease in C₁-C₂ BO tend to suggest further that contributions from the structures 25 or 26 may be sizable. Significant contributions from 25 in the

$n\pi^*$ state would further suggest that the state of hybridization of the C_1 atom may change from sp^2 (planar) to sp^3 (pyramidal). Furthermore, increase in C_2-C_3 BO implied by contributions from 25 would affect rotation around the C_2-C_3 bond, presumably free in the ground state where a single bond is supposed to connect the C_2 and C_3 atoms.

In the photoaddition of allene and other olefins to the $\alpha\beta$ unsaturated carbonyl compounds, a key step in the synthesis of polycyclic-bridged natural products, one finds enough examples where the allenes approach from the sterically more hindered side of the enone. In order to explain this, Wiesner (1975) proposed a general rule for predicting the stereochemistry of such photoadducts. He postulated that the reaction is controlled by the excited state of enone which suffers conversion at the β carbon atom (C_1) following the electronic excitation. Wiesner's empirical rule (Wiesner 1975; Chandra and Sumathi 1990) is the consideration of the change in charge distribution of the $\alpha\beta$ unsaturated carbonyl compounds upon photoexcitation. According to Corey (1964), the lowest excited singlet state of an $\alpha\beta$ unsaturated carbonyl compound has a positively charged C_α and a negatively charged C_β . Our calculations support this contention and suggest that the structure 24 also contributes to the $n\pi^*$ state in addition to structures 25 and 26. The negative charge on C_β may be assumed to have been accommodated in an orbital dominantly centred on C_β which therefore pyramidalises. The orbital accommodating the negative charge may then be directed either upwards or downwards, depending upon the local steric environment. One wonders at this point what the controlling factor of the reaction is, if not the geometry in the excited state.

Corey *et al* (1964), postulated that a π complex is formed between the olefin and the excited carbonyl compound. The complex becomes a diradical which then cyclises to form the product. Photoexcitation in an $\alpha\beta$ unsaturated carbonyl like acrolein will initially lead to the $^1n\pi^*$ state. Since intersystem cross-over from $^1n\pi^*$ to either the $^3n\pi^*$ or $^3\pi\pi^*$ may be quite rapid, the charge distribution, bond order indices and geometry in all the three states are important for the reaction. Table 8 shows the total energy in the $^1,^3n\pi^*$ states of acrolein for a number of values of the out-of-plane angle at C_β . It is clear that the equilibrium geometry of the molecule remains planar in all the three states. From our analysis it appears that the rationale behind the success of Wiesner's rule cannot be found in the geometry of the excited states thereby mirroring Corey's view (Corey *et al* 1964). Nevertheless, considering

Table 8. Total energy in the $n\pi^*$ states of acrylaldehyde for different degrees of out-of-plane bending at the terminal carbon atom (C_β).

State	Out-of-plane angle at C_β	Total energy (a.u.)
$^1n\pi^*$	0	-40.84965
	10	-40.84179
	20	-40.83827
	30	-40.82943
$^3n\pi^*$	0	-40.85710
	10	-40.85426
	20	-40.84889
	30	-40.83165

the great success of Wiesner's rule, one may be tempted to suggest that in the initial stages of this reaction the carbonyl compound perhaps pyramidalises at C_β , a feature that is not unexpected, in view of its near trivalent character ($V_A \approx 3$) and rather flat energy surface created by pyramidalisation at C_β .

4. Conclusion

The INDO-MC-SCF orthogonal gradient method investigations on carbonyl bases show that there is a strong polarization within the carbonyl moiety in the excited $n\pi^*$ states. Electron-donating substituents enhance the polarization of the carbonyl chromophore whereas σ -withdrawing substituents have the opposite effect. Extensive structural reorganization within the carbonyl bases can occur in excited states. Quantum chemical bond order indices based on natural orbital description have been shown to be useful in understanding the structural changes and reactivity of the carbonyl systems and provide a natural means of transcription of the computed molecular electronic structure in terms of classical structural concepts.

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