Proton Induced Structural Reorganization of a Few Carbonyl Molecules in the Ground and Excited States

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Quantum chemical valence parameters have been used to analyze the structural reorganization of carbonyl molecules like acrolein, glyoxal, propynal, and formamide after protonation. The effect of proton at the carbonyl oxygen is countable in the electronic configuration of the molecule as a whole. Structures in different electronic states are analyzed with respect to calculated values of bond orders and net charge densities on the atoms. Correlation has been made between the extent of structural changes in the protonated molecules and proton affinities of the molecules. Prominent structural reorganizations have been observed after protonation of the carbonyl molecules in comparison to the changes in the free molecules. The directionality of protonation and the π polarization of the C=O bond is also observed to be dependent on the type of substituents attached to the carbonyl group.

INTRODUCTION

Interest in the chemical bond that exists between atoms in a molecule, which may be stable or unstable, continues. A strict quantum theoretical description of a molecule that views it as a collection of oppositely charged particles, the nuclei and the electrons, interacting via the coulomb field, does not require a complete description of any explicit use of the concepts such as atoms, bonds, or valence on which the classical model of a molecule is based. However, once the relevant Schrödinger equations have been solved accurately or approximately, the need for interpreting the theoretical results and connecting them to an easily visualizable classical model of a molecule arises. Of particular interest is the possibility of constructing quantum chemical analogues of the parameter of classical or conventional chemistry such as valency, bond multiplicity, free valency, reactivity, etc. The possibility of establishing correspondence of this kind exists primarily due to the exclusive dependence of the apparatus of practical quantum chemistry on the LCAO-MO-SCF framework. Armstrong[1] et al. extended the pioneering ideas of Wiberg[2] in their attempt to interpret closed shell LCAO-MO-SCF wave functions in terms of bond multiplicity indices and valencies. Mayer[3−6] developed the analysis further, providing new insight into the problem especially when the basis set used for the LCAO expansion is nonorthogonal. A number of redefinitions have also been attempted.[7−10]

A molecule in the ground state is often denoted by a single determinant LCAO-MO-SCF wave function, whereas a molecule in the electronically excited state cannot be easily expressed by a conventional structural description in terms of electron pair bonds, lone pairs, etc. Structural modeling of molecules in excited states has not received much attention. So it is worthwhile to attempt suggestive generation and analysis of quantum chemical valence parameters of molecules in excited states and examine the structural models implied by these results.

THEORY

Within the basic framework of the single determinant LCAO-MO-SCF model we have the following description in terms of a set of n occupied molecular spin orbitals (ϕ_i) which are a linear combination of say N ($N \geq n$) atom centered nonorthogonal functions (α_i).

$$\psi \, (1.2...n) = \mathcal{A} \, (\phi_i...\phi_n)$$

$$\Phi \, (\phi_1\phi_2...\phi_n) = \mathrm{X} \, (\chi_1\chi_2...\chi_n)T$$

$$\langle \chi | \chi \rangle = S, \, T^+ST = 1$$

$$\bar{\mathbf{P}} = T \, T^+, \, \mathbf{P} = \sum_{i=1}^{\mathrm{OCC}} n_i T_i T_i^+ = \overline{2\mathbf{P}}$$

if all the n spin orbitals are paired. **P** is a representation of the OEDM (one electron density matrix) in the ϕ basis. Clearly this representation corresponds to the closed shell SCF model or the open shell unrestricted Hartree−Fock theory of the molecules. Within the limitations of the models mentioned above, one can define the atomic LCAO-atomic charge density operator $Z_A - \hat{q}_A$, such that

$$q_A = Z_A - \langle q_A \rangle = Z_A - \sum_{\mu \in A} \sum_{\nu \in B} \mathbf{P}_{\mu\nu}S_{\nu\mu}$$

Z_A being the nuclear charge of the atom A. $\langle q_A \rangle$ is clearly the Mulliken's gross charge density on atom A and is an atomic invariant. The chemists' notion of partial charges on the atoms of a molecule can thus be recovered from the OEDM represented in the ϕ_{basis}. Along with the so called partial charges on the atoms in the molecules, chemists' model of molecules involve the very useful notion of bond order between a pair of atoms in a molecule, a notion which practically corresponds to the multiplicity or number of the bonds holding the pair of atoms together. The quantum chemical analogue of this quantity, the so called quantum chemical bond order, has been defined for closed shell single

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determinant wave function as follows:

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

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

$$B_{AB} = \sum_{\mu \in A} \sum_{\nu \in B} \{(PS)_{\mu\nu}(PS)_{\nu\mu}\} + \sum_{\mu \in A} \sum_{\nu \in B} \{(P^S S)_{\mu\nu}(P^S S)_{\nu\mu}\}$$

with

$$\mathbf{P} = p^\alpha + p^\beta, \quad \mathbf{P}^S = p^\alpha - p^\beta$$
$$p^\alpha = T^\alpha T^\alpha, \quad p^\beta = T^\beta T^{\beta+}$$

B_{AB} is thus defined has an interacting statistical interpretation,[8-11] i.e., B_{AB} measures the connection between the fluctuations of atomic charges on atoms A and B from their respective average values.

The idea of the molecular orbital picture of valency was first introduced by Wiberg.[2] If the gross population of an AO basis function (χ_μ^A) on atom A in the molecule is q_μ^A, the potential bonding power of these particular AOs in the molecule is supposed to be

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

Summing over all the basis function centered on atom A we get what has been called free valency (V_A) of the atom A in the molecule.

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

Wiberg's definition of valency was proposed in connection with the ZDO theories of π electron systems. The ab initio generalization of the concept by Mayer is of a rather recent vintage. Mayer's definition[3-6] is a straightforward generalization of Wiberg's valence when the basis set of expansion is nonorthogonal.

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

If the system is in an open-shell state and represented by a UHF wave function, we have

$$\mathbf{P} = \mathbf{P}^\alpha + \mathbf{P}^\beta, \quad \mathbf{P}^S = \mathbf{P}^\alpha - \mathbf{P}^\beta$$

It is easy to show that this leads to a residual or free valence (f_A) for the atom A is given by

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

With this theoretical background we propose to examine the usefulness of the quantum chemical valence parameters in the context of structural modeling of some atoms in the ground and excited states. We represent the molecule in its lowest singlet and triplet excited states by the following wave function ($S = 0$ corresponds to the singlet and $S = 1$ to the triplet):

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

It requires the variational optimization of the orbital $\phi_1...\phi_n$ which requires the solution of the so called Master equation of Mcweeny.[11]

$$V = (hTP_1 + Z) = ST\lambda \tag{1}$$

This equation is solved iteratively by a variant of OGM (orthogonal gradient method)[12] which involves the construction of the following sequence iteratively until desired degree of convergence is achieved

$$T_i \to T_{i+1} \to S^{-1}V_i(V_iS^{-1}V)^{-1/2}$$

The CI coefficients at convergence are used to construct the one electron density matrix (ρ_1) in MO(ϕ) basis. Once ρ_1 is determined the optimized expansion coefficient T can then be condensed into a representation of the density matrix in the χ basis as follows

$$\mathbf{P} = T\rho_1 T^+$$

For the simplest choice of ψ where we have a fixed set of doubly occupied (core) and a set of singly occupied orbitals (valence) it is possible to partition ρ_1 into ρ_1^D and ρ_1^S and define

$$P^D = (T\rho_1^D T^+)$$
$$P^{S^1} = (T\rho_1^S T^+)$$

where P^D is the ODM for the core (doubly occupied) orbitals and P^S is the same for the singly occupied orbitals. The P^D and P^S matrices can now be used for the determination of the quantum chemical valence parameters B_{AB}, V_A, f_A, etc.

RESULTS AND DISCUSSION

With this theoretical background we have computed net charges and bond orders on different atoms of the molecules using the MCSCF(OGM)[12] method. Computed bond orders and net charge densities on different atoms in the ground and excited states of protonated acrolein, glyoxal, propynal, and formamide molecules are shown in Tables 1−4. Variation of CO bond lengths between free and protonated molecules and changes in proton affinities (PA) in the ground and excited states are shown in Table 5.

Acrolein. The effect of protonation on the CO bond length follows the expected trend;[14-16] the proton polarizes the π electron density within the CO bond and toward the oxygen atom of the C=O moiety (Figure 1 and Figure 2). The response of electron density in the C−O bond to the added proton is however seen to exhibit some dependence on the orientation of the −CHO unit about the C−C single bond indicating the relative stabilities of cis and trans geometries. Protonation is seen to cause substantial increase in the stability of the cis conformation in the ground and $n\pi^*$ states. A marginal lowering of stability of trans geometry is predicted to occur as a result of protonation. Protonation is seen to cause the anticipated changes in the

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Table 1. Computed Bond Orders and Net Charge Densities on Different Atoms of Protonated Acrolein in the Ground and Excited States

				Bond Orders				
states	C_1C_2	C_2C_3	C_3O	OH^+	C_1H_6	C_1H_7	C_2H_8	C_3H_5
ground	1.77	1.24	1.43	0.82	0.92	0.96	0.96	0.94
$^1n\pi^*$	1.67	1.34	0.85	0.80	0.96	0.96	0.90	0.90
$^3n\pi^*$	1.70	1.30	0.86	0.80	0.96	0.96	0.90	0.90
$^3\pi\pi^*$	1.22	1.64	0.84	0.81	0.96	0.96	0.97	0.91

				Net Charges on				
states	C_1	C_2	C_3	O	H^+	H_6	H_7	H_8	H_5
ground	0.22	−0.09	0.53	−0.22	0.37	0.02	0.06	0.08	0.23
$^1n\pi^*$	0.07	0.05	0.15	0.08	0.39	0.03	0.06	0.06	0.11
$^3n\pi^*$	0.07	0.05	0.14	0.08	0.39	0.02	0.06	0.06	0.11
$^3\pi\pi^*$	0.05	0.16	0.12	0.03	0.38	0.04	0.07	0.08	0.06

Table 2. Computed Bond Orders and Net Charge Densities on Different Atoms of Protonated Glyoxal in the Ground and Excited States

			Bond Orders			
states	C_1C_2	C_1O_3	C_2O_4	O_3H^+	C_1H_5	C_2H_6
ground	1.15	1.54	1.83	0.88	0.94	0.95
$^1n\pi^*$	1.37	1.27	1.32	0.90	0.92	0.95
$^3n\pi^*$	1.39	1.29	1.31	0.90	0.91	0.95
$^3\pi\pi^*$	1.70	1.03	1.04	0.87	0.94	0.96

			Charge Density on			
states	C_1	C_2	O_3	O_4	H^+	H_5	H_6
ground	0.44	0.21	−0.01	−0.08	0.31	0.07	0.08
$^1n\pi^*$	0.23	0.30	−0.07	0.04	0.29	0.12	0.08
$^3n\pi^*$	0.30	0.22	0.09	−0.10	0.28	0.13	0.07
$^3\pi\pi^*$	0.12	0.34	−0.06	0.10	0.33	0.07	0.09

Table 3. Computed Bond Orders and Net Charge Densities on Different Atoms of Protonated Propynal in the Ground and Excited States

			Bond Orders			
states	C_1C_2	C_2C_3	C_3O	OH^+	C_3H_5	C_1H_6
ground	2.71	1.23	1.48	0.88	0.94	0.94
$^1n\pi^*$	2.69	1.22	0.85	0.80	0.90	0.97
$^3n\pi^*$	2.70	1.21	0.83	0.79	0.88	0.97
$^3\pi\pi^*$	2.35	1.47	0.77	0.80	0.95	0.96

			Charge Density on			
states	C_1	C_2	C_3	O	H^+	H_5	H_6
ground	0.19	−0.08	0.51	−0.11	0.38	0.12	0.11
$^1n\pi^*$	0.08	0.00	0.19	0.09	0.39	0.13	0.11
$^3n\pi^*$	0.08	0.00	0.18	0.09	0.40	0.13	0.11
$^3\pi\pi^*$	0.12	0.09	0.13	0.05	0.39	0.07	0.08

Table 4. Computed Bond Orders and Net Charge Densities on Different Atoms of Protonated Formamide in the Ground and Excited States
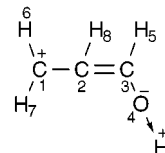
			Bond Orders			
states	H^+O	C_2O	C_2N	NH_5	NH_6	C_2H_7
ground	0.901	1.298	1.571	0.925	0.926	0.947
$^1n\pi^*$	0.819	0.867	1.229	0.931	0.906	0.931
$^3n\pi^*$	0.799	0.883	1.277	0.929	0.915	0.858
$3\pi\pi^*$	0.858	0.768	1.264	0.865	0.723	0.829

			Net Charges on			
states	H^+	O	C	N	H_5	H_6	H_7
ground	0.272	−0.174	0.501	−0.119	0.216	0.222	0.082
$^1n\pi^*$	0.339	0.105	0.186	−0.110	0.191	0.206	0.083
$^3n\pi^*$	0.322	0.100	0.199	−0.104	0.192	0.194	0.095
$^3\pi\pi^*$	0.281	0.031	0.217	−0.115	0.225	0.289	0.071

Table 5. Variation of CO Bond Lengths between Free and Protonated Molecules and Change in PA in the Ground and Excited States

molecule	states	r_{CO} (free)[a]	r_{CO} (protonated)[a]	$COH^{+\ b}$	change in PA[c]
glyoxal	ground	1.266	1.296	120.6	0.003
	$^1n\pi^*$	1.279	1.317	113.7	0.026
	$^3n\pi^*$	1.281	1.320	114.3	0.024
	$^3\pi\pi^*$	1.357	1.361	116.8	0.044
propynal	ground	1.269	1.286	119.0	0.027
	$^1n\pi^*$	1.340	1.355	180.0	0.018
	$^3n\pi^*$	1.320	1.350	180.0	0.019
	$^3\pi\pi^*$	1.385	1.390	180.0	0.012
acrolein	ground	1.265	1.288	180.0	0.028
	$^1n\pi^*$	1.334	1.360	180.0	0.018
	$^3n\pi^*$	1.334	1.356	180.0	0.027
	$^3\pi\pi^*$	1.368	1.377	180.0	0.028
formamide	ground	1.300	1.327	115.7	0.007
	$^1n\pi^*$	1.380	1.392	122.1	0.000
	$3n\pi^*$	1.370	1.382	138.5	0.069
	$^3\pi\pi^*$	1.362	1.358	98.4	0.063

[a] All the bond lengths are in Å. [b] All the angles are in deg. [c] All the PAs are in au.
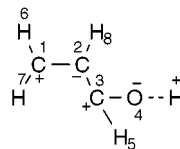
Figure 1. Computed structure of protonated acrolein molecule in the ground state.

Figure 2. Computed structure of protonated acrolein molecule in the $^{1,3}n\pi^*$ excited states.

bond lengths, i.e., further elongation of the C=O and shortening of C–C bond. Side by side the C=C bond length registers an increase in all the states following protonation. Considerable reorganization of π electron density must have therefore occurred in the field of the added proton. One feature of this reorganization must be an increase of electron density in the C–C region and a decrease from the C=C region. Protonation coordinate COH^+ is constant in all states; r_{OH^+} displays small variation.

Table 1 summarizes bond order (BO) indices between different pairs of atoms along with net charge densities in different atom centers in protonated acrolein in the ground and excited states. Protonation is seen to cause a substantial decrease in $C_1–C_2$ BO in the ground state and a small but noticeable decrease in the corresponding quantities in the excited states. Simultaneously protonation increases the $C_2–C_3$ BO in the ground state by about 20%. In the $n\pi^*$ states the corresponding BOs increase only marginally, while it is seen to register an increase in the $C_2–C_3$ BO in the ground state after protonation. One can explain this as a consequence of enhanced contribution of the structure of Figure 1. The computed charge densities on different atoms in the ground state of protonated acrolein shows the kind of charge
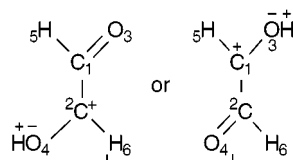
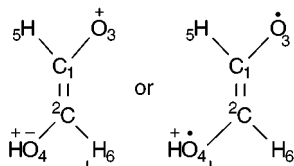**Figure 3.** Computed structure of protonated glyoxal molecule in the ground state.

Figure 4. Computed structure of protonated glyoxal molecule in the $^3\pi\pi^*$ excited state.

alternation that is implied by the structure in Figure 1. In the $n\pi^*$ states, however, the structure in Figure 2 contributes significantly even before protonation so that protonation does not cause any further dramatic increase in the C_2-C_3 BO. In the $^3\pi\pi^*$ state the structure of the type in Figure 2 is also a major contributor, and protonation perhaps causes polarization. Because of the π electron density accumulated in the C_2-C_3 bond region in the $^3\pi\pi^*$ state the C_2-C_3 BO decreases a little after protonation.

Glyoxal. Protonation is predicted to cause shortening of the C–C bond length in the ground and $^{1,3}n\pi^*$ states and its elongation in the $^3\pi\pi^*$ state. The pattern of the changes in the C=O bond length caused by protonation is rather interesting. The equivalence between the carbonyl groups in glyoxal is lost following protonation, and this is reflected in the difference in C=O bond order data in the protonated and unprotonated carbonyl groups (Table 2). In the ground state protonation is seen to cause lengthening of both the C=O bonds, the effect being much larger in the protonated HC=O fragment. In the lowest $n\pi^*$ and $\pi\pi^*$ states, however, we predict elongation of the C=O bond in the H–C=O··H$^+$ moiety and decrease of C=O length of the distant CHO unit. These features suggest that π electron polarization of the two C–O bonds caused by a proton must therefore be opposite in nature. From the BO and net charge density data C=O bond order is found to be less than 2 in the protonated and unprotonated C=O group. BO of protonated C=O is found to be less than unprotonated C=O group. C–C bond order is slightly more than a C–C single bond in the $n\pi^*$ and $\pi\pi^*$ states. Out of the two structures in Figures 3 and 4, it is possible to determine which one contributes more in different states. In the ground state, the structure shown in Figure 3 is more likely, and in the $^3\pi\pi^*$ state the structure shown in Figure 4 may be more appropriate. The structure in Figure 4 would arise out of π donation by the –CHO unit in glyoxal which can be explained by the much higher order of the C–C bond order. In the case of trans conformers H(6) is found to be more acidic than the distant H of –CHO unit.

Propynal. Molecular dimensions in the ground state of propynal have been determined by microwave studies and confirmed a planar structure.[17−19] The banded absorption system was identified within $n\pi^*$ transition state typically associated with the >C=O chromophore. A quasi planar structure of propynal (about 3° out of plane angle) was proposed in the $n\pi^*$ state.[17−19]
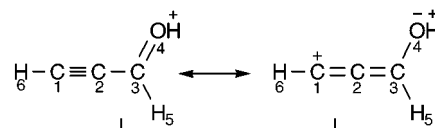

Figure 5. Computed structure of protonated propynal molecule in the ground state.
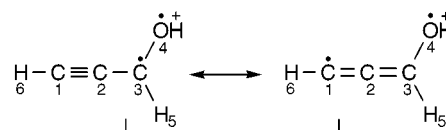

Figure 6. Computed structure of protonated propynal molecule in the excited ($^{1,3}n\pi^*$; $^3\pi\pi^*$) states.
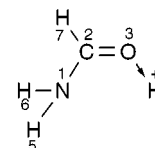

Figure 7. Computed structure of protonated formamide molecule in the ground state.
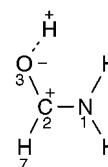

Figure 8. Computed structure of protonated formamide molecule in the excited ($^{1,3}n\pi^*$; $^3\pi\pi^*$) states.

The effects of protonation on the >C=O bond length and bond order are given in Table 3. The O··H$^+$ bond length is more or less constant for all the excited states (difference of 0.01 Å); the $\angle$C=O–H$^+$ is $\approx 119°$ in the ground state and linear in all the excited states. Protonation leads to further increase in C=O length and decrease in C–C length. These changes in geometrical parameters essentially reflect the kind of electronic reorganization that takes place in the bond region following protonation and excitation. Protonation is seen to cause substantial reduction in C–O bond order in the ground state (polarization of the π electron density in C=O bond) and smaller noticeable reduction of the same quantity in the excited states. The effect of π polarization is perceptible at the C≡C bond also which has much reduced bond order following protonation in any electronic state. The C–C bond order registers an increase upon protonation, the structure shown in Figure 5 contributes in the ground state, and the structure shown in Figure 6 contributes in the excited states. These changes in BOs confirm chemists' expectations. In propynal C–H (aldehydic) polarization is likely because of the delocalization of π electron in C≡C among the three carbon atoms, and CH (aldehydic) is found to be more acidic than H of the –C≡C–H group (Table 3). There is a change in hybridization due to H$^+$ in C_1 from sp to sp^2 in the $n\pi^*$ states.[14,15,20]

Formamide. Protonation of the formamide molecule in the ground and excited state is studied. Here H$^+$ is found to be cis to the NH$_2$ group in the ground and excited states (Figures 7 and 8). r_{OH^+} varies from 1.04 to 1.055 Å in all the states. The CO bond order is found to be slightly reduced, whereas the CN bond order increases in the ground state (Table 4). Prominent decrease of the C–H bond order

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compared to the N−H bond order is observable. Unlike other π substituents, protonation has little effect on the net charge density on the nitrogen atom in formamide. We have observed that H$^+$ has a strong affinity toward the lone pair electron of the oxygen atom, and electronic reorganization in the molecule takes place from the bonding electron of the neighboring bonds. This can be confirmed from the net charge density and BO data of protonated formamide molecule. In the ground state, protonation at the planar configuration is favored. The structure shown in Figure 7 contributes to the ground state, and planarity of the protonated molecule is lost in the excited states. However, H$^+$ is found to be out of plane with respect to the NH$_2$ group, and the carbonyl hydrogen atom is found to be trans to H$^+$. Similar to the observations made in the ground state, the nitrogen lone pair electron is not affected due to protonation in the nπ* and $\pi\pi$* excited states, and electronic reorganization may be expected among the bonding electrons. Elongation of C=O and reduction of C=O BO may be due to the migration of π electron to the oxygen atom after protonation. The configuration shown in Figure 8 is expected to be more stable in the excited states.

Correlation between Structural Reorganizations and Change in PA. To establish if there is any correlation between structural changes and proton affinity, we have compared the proton affinities between the unrelaxed protonated molecule and the optimized (relaxed) protonated molecule. In the unrelaxed protonated molecule we assume that molecular configuration does not change after protonation. We observe that structural changes are much more prominent compared to the change in PA from the unrelaxed to the relaxed protonated molecules both in the ground and excited states.[12] Table 5 displays the correlation between structural changes and change in PAs for acrolein, glyoxal, propynal, and formamide molecules. In general we observe that the C=O bond length elongates after protonation, and variation of r_{CO} after protonation is quite large; but, on the other hand, change in PA is very small. Other parameters like C−H, double and triple bonds, and bond angles are not of much significance for these molecules. The changes in

these parameters after protonation may be due to π electron density migration toward the proton. Directionality of the proton, i.e., COH$^+$, parameter depends on the type of substituent attached to C=O and also the extent of π polarization within C=O group (which depends on the substituent).

REFERENCES AND NOTES

(1) Armstrong, D. R.; Perkins, P. G.; Stewart, J. J. P. *J. Chem. Soc. (Dalton Trans.)* **1973**, 893.
(2) Wiberg, K. A. *Tetrahedron* **1973**, *24*, 1083.
(3) Mayer, I. *Theor. Chem. Acta* **1985**, *67*, 315.
(4) Mayer, I. *Chem. Phys. Lett.* **1983**, *97*, 270.
(5) Mayer, I. *Int. J. Quant. Chem.* **1986**, *29*, 477.
(6) Mayer, I. *Int. J. Quant. Chem.* **1986**, *29*, 73.
(7) Natiello, M. A.; Reale, H. F.; Medrano, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 6750.
(8) Stradella, O. G.; Villar, H. O.; Castro, E. A. *Theor. Chem. Acta* **1987**, *70*, 67.
(9) Villar, H. O.; Dupis, M. *Chem. Phys. Lett.* **1987**, *142*, 59.
(10) Gopinathan, M. S.; Jug, K. *Theor. Chem. Acta* **1983**, *63*, 497; **1983**, *63*, 511.
(11) Mcweeny, R.; Sutcliffe, B. T. In *The Method of Molecular Quantum Mechanics*; Academic Press: New York, 1969.
(12) Medhi, C.; Das, K. K.; Bhattacharyya, S. P. *Pramana J. Phys.* **1993**, *40*, 65.
(13) de Giambiagi, M. S.; Giambiagi, M.; Jorge, F. E. *Theor. Chem. Acta* **1985**, *68*, 337.
(14) Corey, E. J.; Bars, J. D.; Lemahien, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570.
(15) Blount, J. F.; Gray, R. D.; Atwae, K. S.; Tsai, T. Y. R.; Wisner, K. *Tetrahedron Lett.* **1980**, *21*, 4413.
(16) de Mayo, P.; Nicholson, A. A.; Tehir, M. T. *Can. J. Chem.* **1970**, *48*, 225.
(17) Howe, J. A.; Goldstein, J. H. *J. Chem. Phys.* **1955**, *23*, 1223.
(18) (i) Constain, C. C.; Morton, J. R. *J. Chem. Phys.* **1951**, *31*, 387. (ii) Lin, C. T.; Moule, D. C. *J. Mol. Spect.* **1971**, *37*, 280.
(19) Brand, J. C. D.; Callomon, J. H.; Waston, J. K. G. *Discuss. Faraday Soc.* **1963**, *35*, 175; *J. Phys.* **1961**, *39*, 1508.
(20) Wisner, K. *Tetrahedron* **1975**, *31*, 1655.
(21) (a) Del Bene, J. E.; Vaccaro, A. *J. Am. Chem. Soc.* **1976**, *98*, 7526. (b) Del Bene, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 1673. (c) Del Bene, J. E.; Radovick, S. *J. Am. Chem. Soc.* **1978**, *100*, 6936.

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