

First Order Hyperpolarizabilities, NPA and Fukui Functions of Cyclohexanone by Density Functional Theory Method

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The molecular structure of cyclohexanone was calculated by the B3LYP density functional model with 6-311++G(d,p) basis set by Gaussian program. The results from natural bond orbital analysis have been analyzed in terms of the hybridization of atoms and the electronic structure of the title molecule. The formation of hydrogen bond was investigated using natural bond orbital calculation. The electron density based local reactivity descriptors such as Fukui functions were calculated. The dipole moment (μ) and polarizability (α), anisotropy polarizability ($\Delta\alpha$) and first order hyperpolarizability (β_{tot}) of the molecule have been reported. Thermodynamic properties of the title compound were calculated at different temperatures.

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1. Introduction

Cyclohexanone is a colorless, mobile liquid with an odor similar to that of pepper mint and acetone [1, 2]. It was first prepared by the dry distillation of calcium pimelate and later by Bouveault by the catalytic dehydrogenation of cyclohexanol [3]. It is used as a solvent in insecticides, wood stains, paint and varnish removers, spot removers, cellulose, and natural and synthetic resins and lacquers. The most important use of cyclohexanone is as a chemical intermediate in nylon manufacture: 97% of all cyclohexanone output is used either to make caprolactam for nylon-6 or adipic acid for nylon-66. Cyclohexanone is also used as a solvent and thinner for lacquers, especially those containing nitrocellulose or vinyl chloride polymer and copolymers and as a general solvent for synthetic resins and polymers. Cyclohexanone is used as a building block in the synthesis of many organic compounds, such as pharmaceuticals, insecticides, and herbicides [4, 5]. The objective of the present work is to investigate the nature of bonding in cyclohexanone (Fig. 1) by using natural bond orbital (NBO) analysis. We have shown that the results from NBO calculations can provide the detailed insight into the electronic structure of molecule.

2. Computational methods

All the calculations were performed using the Gaussian 03W software package [6] and Gauss-view molecular visualization program package [7]. The calculations of systems containing C, H, and O is described by the standard 6-311++G(d,p) basis set function of the density functional theory (DFT) [8, 9]. Geometry optimization

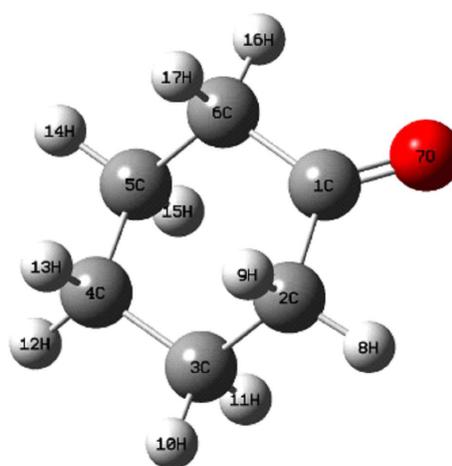


Fig. 1. The atom numbering system for cyclohexanone.

was performed utilizing Becker's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP) [10]. The population analysis has also been performed by the natural bond orbital method [11] at B3LYP/6-31G(d,p) and 6-311++G(d,p) level of theory using NBO program under Gaussian 03 program package.

Natural bond orbital analysis stresses the role of intermolecular orbital interaction in the complex, particularly charge transfer. This is carried out by considering all possible interactions between filled donor and empty acceptor NBOs and estimating their energetic importance by second-order perturbation theory. For each donor NBO (i) and acceptor NBO (j), the stabilization energy $E^{(2)}$ associated with electron delocalization between donor and acceptor is estimated as

$$E^{(2)} = q_i \frac{(F_{i,j})^2}{\varepsilon_j - \varepsilon_i},$$

where q_i is the orbital occupancy, ε_i , ε_j are diagonal

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elements and $F_{i,j}$ is the off-diagonal NBO Fock matrix element.

3. Results and discussion

3.1. NPA atomic charges

NPA stands for natural population analysis and is based on the NBO scheme. Natural bond analysis classifies and localizes orbitals into three distinct groups: non-bonding natural atomic orbitals (NAOs), orbitals involved in bonding and antibonding (NBOs), and Rydberg type orbitals. The Rydberg type orbitals and NAOs are made up of basis sets of single atoms and the NBOs are a combination of basis set atomic orbitals of two atoms. This is similar to our notion of core electrons, lone pairs of electrons, and valence electrons, and works under the assumption that only the bonding orbitals should be made by combinations of two atoms' basis sets. Based on this model of electron partitioning, NPA then treats the NBOs as the Mulliken method treats all the orbitals. This method differentiates between the orbitals that will overlap to form a bond and those that are too near the core of an atom to be involved in bonding. This results in convergence of atomic partial charge to a stable value as the basis set size is increased. NPA also tends to predict larger charges than several other population analysis methods, so like Mulliken charges NPA is best used for comparing differences rather than determining absolute atomic charges.

TABLE I

NPA charges calculated by B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) methods.

Atom No.	B3LYP/ 6-31G(d,p)	B3LYP/ 6-311++G(d,p)
C1	0.264	0.588
C2	-0.497	-0.477
C3	-0.423	-0.382
C4	-0.426	-0.386
C5	-0.423	-0.382
C6	-0.497	-0.476
O7	-0.757	-0.556
H8	0.207	0.225
H9	0.119	0.214
H10	0.175	0.205
H11	0.19	0.194
H12	0.193	0.206
H13	0.183	0.188
H14	0.175	0.205
H15	0.19	0.194
H16	0.207	0.225
H17	0.119	0.214

NPA charges calculated by B3LYP methods are collected in Table I. It can be clearly shown that the carbon atom attached with oxygen atom has positive charge whereas other carbon atoms attached to hydrogen atoms have negative charge. It is worthy to mention that C1 alone of title molecule exhibits positive

charge while C2, C3, C4, C5, C6 atoms exhibit negative charges. Oxygen has a maximum negative charge value of about -0.757 . However all the hydrogen atoms exhibit a net positive charges. The presence of large negative charge on O atom and net positive charge on H atom may suggest the formation of intramolecular interaction in solid forms [12].

3.2. NBO analysis

NBO analysis provides an efficient method for studying intra and intermolecular bonding and interaction among bonds, and also provides a convenient basis for investigation charge transfer or conjugative interactions in molecular system [13]. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulting from the second order micro-disturbance theory are reported [14, 15]. The larger the $E(2)$ value, the more intensive is the interaction between electron donors and the greater the extent of conjugation of the whole system. Delocalization of occupation between occupied Lewis type (bond or lone pair) NBO orbital's and formally unoccupied (antibonding or Rydberg) non Lewis NBO orbital's correspond to a stabilizing donor-acceptor interaction. NBO analysis was performed on the molecule at the DFT/B3LYP/6-311++G(d,p) level in order to elucidate the intra molecular rehybridization and delocalization of occupation within the molecule. The molecular interaction is formed by the orbital overlap between $\sigma(\text{C-C})$ and $\sigma^*(\text{C-C})$ bond orbital which results in intramolecular charge (ICT) causing stabilization of the system. These interactions are observed as increase in occupation in C-C antibonding orbital that weakens the respective bonds. The occupation of conjugated double as well as the single bond of the conjugated ring ($\approx 1.9e$) clearly demonstrates strong delocalization inside the molecule.

Table II lists the calculated occupancies of natural orbitals. Three classes of NBOs are included, the Lewis-type (σ and π bonding or lone pair) orbitals, the valence non-Lewis (acceptors formally unfilled) orbitals and the Rydberg NBOs, which originate from orbitals outside the atomic valence shell. The calculated natural hybrids on atoms are also given in this Table II. As seen from Table II, the $\sigma(\text{C1-C2})$ bond is formed from $sp^{1.972}$ hybrid on carbon (which is the mixture of 34.25% s , 65.71% p , and 0.04% d atomic orbitals). On the other hand, $\sigma(\text{C4-H12})$ bond is formed from a $sp^{3.47}$ hybrid on hydrogen (which is the mixture of 22.35% s , 77.59% p , and 0.06% d orbitals). The $\pi(\text{C1-O7})$ is formed from $sp^{2.18}$ hybrid on oxygen (which is the mixture of 31.43% s , 68.40% p , and 0.18% d).

In Table III the perturbation energies of donor-acceptor interactions are presented. In our title molecule cyclohexanone $\sigma(\text{C2-H9}) \rightarrow \pi^*(\text{C1-O7})$ and $\sigma(\text{C6-H17}) \rightarrow \pi^*(\text{C1-O7})$ has 6.26 kJ/mol and hence they give strong stabilization to the structure. From Table II it is noted that the maximum occupancies 1.98263, 1.98120, 1.98356, 1.98010 are obtained for

TABLE II

Occupancy of natural orbitals (NBOs) and hybrids of cyclohexanone calculated by B3LYP method with 6-311++G(d,p) basis set for C, H and O atoms.

Donor Lewis type ^a NBOs	Occupation	Hybrid ^b	NAO(%) ^c
σ C1-C2	1.98263	$sp^{1.92}$	$s(34.25\%)p(65.71\%)d(0.04\%)$
σ C1-O7	1.99612	$sp^{2.18}$	$s(31.43\%)p(68.40\%)d(0.18\%)$
σ C2-H8	1.9812	$sp^{3.23}$	$s(23.63\%)p(76.31\%)d(0.06\%)$
σ C3-H1	1.97928	$sp^{3.58}$	$s(21.80\%)p(78.13\%)d(0.07\%)$
σ C4-H1	1.97828	$sp^{3.47}$	$s(22.35\%)p(77.59\%)d(0.06\%)$
σ C6-H1	1.95971	$sp^{3.66}$	$s(21.45\%)p(78.48\%)d(0.07\%)$
LP(1) O7	1.97691	$sp^{0.75}$	$s(58.07\%)p(42.91\%)d(0.02\%)$
σ^* C1-C	0.06204	$sp^{1.92}$	$s(34.25\%)p(65.71\%)d(0.04\%)$
σ^* C1-O	0.01368	$sp^{2.18}$	$s(31.43\%)p(68.40\%)d(0.18\%)$
σ^* C2-H	0.01047	$sp^{3.23}$	$s(23.63\%)p(76.31\%)d(0.06\%)$
σ^* C3-H11	0.01731	$sp^{3.58}$	$s(21.80\%)p(78.13\%)d(0.07\%)$
σ^* C4-H12	0.01207	$sp^{3.47}$	$s(22.35\%)p(77.59\%)d(0.06\%)$
σ^* C6-H17	0.01446	$sp^{3.66}$	$s(21.45\%)p(78.48\%)d(0.07\%)$

^a LP(n)A is a valence lone pair orbital (n) on A atom.

^b Hybrid on A atom in the A-B bond or otherwise, as indicated.

^c Percentage contribution of atomic orbitals in NBO hybrid.

σ (C1-C2), σ (C2-H8), σ (C3-C4) and σ (C5-H14), respectively. Therefore, the results suggest that the σ (C1-C2), σ (C2-H8), σ (C3-C4), and σ (C5-H14) are essentially controlled by the p -character of the hybrid orbitals.

The same kind of interaction is calculated in the same kind of interaction energy, related to the resonance in the molecule, where electron donating from σ (O7) to σ^* (C1-C2) shows less stabilization 1.88 kJ/mol and further π (O7) to σ^* (C1-C2) leads to strong stabilization energy of 19.88 kJ/mol. The strong intra-molecular hyper conjugation interaction of the σ and the π electrons of C-H to the anti C-H bond in the ring lead to stabilization of some part of the ring as evident from Table III.

3.3. Fukui functions

DFT is one of the important tools of quantum chemistry to understand popular chemical concepts such as electronegativity, electron affinity, chemical potential and ionisation potential. In order to solve the negative Fukui function problem, different attempts have been made by various groups [16]. Kolandaivel et al. [17] introduced the atomic descriptor to determine the local reactive sites of the molecular system. In the present study, the AM1-optimised molecular geometry was utilized in single-point energy calculations, which have been performed at the DFT for the anions and cations of the conformers using the ground state with doublet multiplicity. The individual atomic charges calculated by NPA and Mulliken population analysis (MPA) have been used to calculate the Fukui function. Table IV shows the f_k^0 , f_k^+ and f_k^- values for the title molecule calculated by NPA and MPA gross charges at DFT level of theory with the basis set (B3LYP/6-311G++(d,p)). It has been found that both NPA and MPA scheme methods predict that the oxygen atom O7 has a higher f_k^+ value

TABLE III

Second order perturbation theory analysis of Fock matrix in NBO basis in cyclohexanone.

Donor (i)	Type	Occupation	Acceptor (j)	Type	Occupation (e)	$E(2)^a$ [kJ/mol]	$E(j) - E(i)^b$	$F(i, j)^c$
C1-C2	σ	1.98263	C3-H10	σ^*	0.01275	1.53	1.03	0.035
			C6-H16	σ^*	0.01047	1.18	1.03	0.031
C2-C3	σ	1.97394	C1-O7	σ^*	0.01368	2.14	1.22	0.046
			C1-O7	π^*	0.08186	1.97	0.63	0.032
C2-H8	σ	1.9812	C1-C6	σ^*	0.06204	3.49	0.89	0.05
			C3-C4	σ^*	0.01376	2.67	0.88	0.043
C2-H9	σ	1.95969	C1-O7	σ^*	0.01368	1.34	1.11	0.035
			C1-O7	π^*	0.08186	6.26	0.52	0.052
C3-C4	σ	1.98356	C3-H11	σ^*	0.01731	2.76	0.88	0.044
			C2-H8	σ^*	0.01047	1.65	1.01	0.036
C3-H11	σ	1.97928	C5-H14	σ^*	0.01274	1.65	1.01	0.036
			C2-H9	σ^*	0.01447	2.71	0.87	0.043
C4-H12	σ	1.97828	C4-H13	σ^*	0.01784	2.97	0.87	0.046
			C2-C3	σ^*	0.01383	3.13	0.86	0.047
C4-H13	σ	1.97902	C5-C6	σ^*	0.01382	3.13	0.86	0.047
			C3-H11	σ^*	0.01731	2.89	0.88	0.045
C5-H14	σ	1.9801	C5-H15	σ^*	0.01731	2.89	0.88	0.045
			C1-C6	σ^*	0.06204	2.75	0.88	0.044
C6-H16	σ	1.9812	C3-C4	σ^*	0.01376	2.87	0.88	0.045
			C1-C2	σ^*	0.06204	3.49	0.89	0.05
C6-H17	σ	1.95971	C4-C5	σ^*	0.01376	2.67	0.88	0.043
			C1-O7	σ^*	0.01368	1.34	1.11	0.035
O7	σ	1.97691	C1-O7	π^*	0.08186	6.26	0.52	0.052
			C1-C2	σ^*	0.06204	1.88	1.07	0.04
O7	π	1.89261	C1-C6	σ^*	0.06204	1.88	1.07	0.04
			C1-C2	σ^*	0.06204	19.88	0.65	0.103
			C1-C6	σ^*	0.06204	19.88	0.65	0.103

$E(2)^a$ means energy of hyper conjugative interaction (stabilization energy); b energy difference between donor and acceptor i and j NBO orbitals, $F(i, j)^c$ is the Fock matrix element between i and j NBO orbitals.

for nucleophilic attack. From the values reported in the Table IV the reactivity order for the electrophilic case was H12 > H10 > H14 for MPA analysis. On the other hand, for nucleophilic attack O11 has greater reactivity value. The attack for radical case was H12 > H10 > H14 for MPA. If one compares the three kinds of attacks, it is possible to observe that the electrophilic attack has bigger reactivity compared to the nucleophilic and radical attack.

3.4. First order hyperpolarizability calculations

Polarizabilities and hyperpolarizabilities characterize the response of a system in an applied electric field [18]. They determine not only the strength of molecular interactions as well as the cross-sections of different scattering and collision processes, but also the non-linear optical properties (NLO) of the system [19, 20]. In order to investigate the relationships among photocurrent generation, molecular structures and NLO, the polarizabilities and hyperpolarizabilities of title compound was calculated using B3LYP/6-31G(d,p) and B3LYP/6-311++G(d,p) based on the finite-field approach. The first order hyperpolarizability (β) of title molecule along with related properties (μ , α , and α_0) are reported in Table V. The calculated value of dipole moment was found to be 1.2107 D at B3LYP/6-31G(d,p) and 1.3651 at

TABLE IV

Condensed Fukui functions calculated by B3LYP/6-311++G(d,p) from NPA and MPA schemes.

Atoms	MPA			NPA		
	f_k^+	f_k^-	f_k^0	f_k^+	f_k^-	f_k^0
C1	0.2491	0.131	0.3672	-0.2845	0.2757	-0.0044
C2	-0.4105	-0.0614	-0.7596	0.3209	-0.2395	0.0407
C3	-0.2796	-0.0526	-0.5066	0.2001	-0.1948	0.0027
C4	-0.5465	-0.0084	-1.0845	0.1909	-0.1948	-0.002
C5	-0.2795	-0.0526	-0.5063	0.2001	-0.1948	0.0027
C6	-0.4105	-0.0614	-0.7596	0.3208	-0.2395	0.0407
O7	0.2347	0.3753	0.094	0.8317	-0.2717	0.28
H8	0.0866	0.0673	0.1059	-0.0915	0.142	0.0149
H9	0.3012	0.0979	0.5044	-0.0757	0.105	0.0147
H10	0.4328	0.0799	0.7857	-0.0574	0.1022	0.0224
H11	0.0692	0.064	0.0743	-0.0816	0.1033	0.0109
H12	0.4911	0.0566	0.8255	-0.0837	0.1064	0.0114
H13	0.1723	0.0552	0.2894	-0.0839	0.0899	0.003
H14	0.4327	0.0799	0.7855	-0.0574	0.1022	0.0224
H15	0.0692	0.064	0.0743	-0.0816	0.1033	0.0109
H16	0.0866	0.0673	0.1058	-0.0916	0.1212	0.0148
H17	0.3011	0.0978	0.5044	-0.0757	0.1049	0.0146

6-311++G(d,p). In addition to the isotropic polarizabilities and polarizabilities anisotropy invariant were also calculated. The calculated anisotropy of the polarizability α of cyclohexanone is 119.39 at B3LYP/6-31G(d,p) and 137.01 a.u. at B3LYP/6-311++G(d,p) level. The B3LYP/6-31G(d,p) calculated first order hyperpolarizability value (β_0) of cyclohexanone is equal to 5.239×10^{-31} esu. Total dipole moment of title molecule is slightly smaller than those of urea and first order hyperpolarizability of title molecule is approximately four times greater than those of urea (1.3×10^{-31} esu). This result indicates the nonlinearity of the title molecule.

TABLE V

The B3LYP/6-31G(d,p) and 6-311G++(d,p) calculated electric dipole moments (Debye), polarizability (a.u), β components and β_{tot} (10^{-31}) esu value of cyclohexanone.

Para- meters	B3LYP/ 6-31 G(d,p)	B3LYP/ 6-311++ G(d,p)	Para- meters	B3LYP/ 6-31 G(d,p)	B3LYP/ 6-311++ G(d,p)
μ_x	1.2	1.353	β_{xxx}	37.87	37.556
μ_y	0.0569	0.0642	β_{xxy}	2.0421	3.326
μ_z	-0.1506	-0.1701	β_{xyy}	-3.683	-20.861
μ	1.2107	1.3651	β_{yyy}	-0.245	-3.847
α_{xx}	68.562	78.661	β_{xxz}	2.604	2.108
α_{xy}	0.356	0.433	β_{xyz}	-1.181	-2.253
α_{yy}	64.244	72.962	β_{yyz}	-2.127	9.896
α_{xz}	-4.499	-5.567	β_{zzz}	26.384	28.784
α_{yz}	0.176	0.191	β_{yzz}	0.943	1.7311
α_{zz}	54.616	62.147	β_{zzz}	0.694	7.089
α_0	62.474	71.256	β_{tot} (esu)	5.239×10^{-31}	6.124×10^{-32}
α	119.39	137.01			

3.5. Thermodynamic properties

On the basis of vibrational analysis, the statically thermodynamic functions: heat capacity ($C_{p,m}^0$), entropy (S_m^0), and enthalpy changes (ΔH_m^0) for the title molecule are obtained from the theoretical harmonic frequencies and listed in Table VI. From Table VI it can be observed that these thermodynamic functions are increasing with temperature ranging from 100 to 1000 K due to the fact that the molecular vibrational intensities increase with temperature. The correlation equations between heat capacity, entropy, enthalpy changes and temperatures are fitted by quadratic formulae and the corresponding fitting factors (R^2) for these thermodynamic properties are 0.9997, 0.9997 and 0.9995, respectively. The corresponding fitting equations are as follows and the correlation graphics of those are shown in Fig. 2.

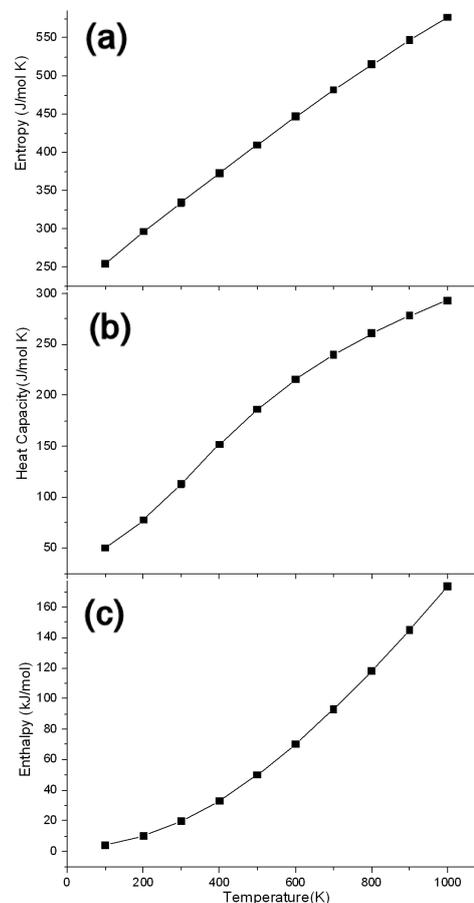


Fig. 2. Correlation graph of (a) entropy and temperature for cyclohexanone, (b) heat capacity and temperature for cyclohexanone, (c) enthalpy and temperature for cyclohexanone.

$$C_{p,m}^0 = 32.6359 + 0.5998T - 2.22 \times 10^{-4}T^2 (R^2 = 0.9997),$$

$$S_m^0 = 32.6359 + 0.5998T - 2.60 \times 10^{-4}T^2 (R^2 = 0.9997),$$

$$H_m^0 = -8.3430 + 0.0989T + 1.57 \times 10^{-4}T^2 (R^2 = 0.9995).$$

All the thermodynamic data supply helpful information for the further study on the cyclohexanone. They can be used to compute the other thermodynamic energies according to relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics in thermochemical field [21]. Notice: all thermodynamic calculations are done in gas phase and they could not be used in solution.

TABLE VI

Thermodynamic properties at different temperatures at B3LYP/6-311++G(d,p) level for cyclohexanone.

T [K]	S [J/mol K]	C_p [J/mol K]	ΔH [kJ/mol]
100	253.89	49.92	3.99
200	296.46	77.5	10.29
298.15	333.74	112.68	19.57
300	334.44	113.39	19.78
400	372.37	151.85	33.05
500	410.08	186.59	50.02
600	446.77	215.91	70.18
700	481.95	240.39	93.04
800	515.43	260.98	118.13
900	547.21	278.45	145.13
1000	577.34	293.37	173.74

4. Conclusions

According to our results the following conclusions are derived for the cyclohexanone.

1. The NBO analysis has provided the detailed insight into the type of hybridization and the nature of bonding in cyclohexanone. The $\sigma(\text{C4-H12})$ bonds are formed from an $sp^{3.47}$ hybrid on hydrogen atom and $\pi(\text{C1-O7})$ bond is formed from an $sp^{2.18}$ on oxygen. The strongest electron donation occurs from $\pi(\text{O7})$ to $\sigma^*(\text{C1-C2})$ orbitals.

2. The predicted first order hyperpolarizability shows that the molecule might have a reasonably good NLO behavior. The Mulliken atomic charges analysis shows that charge transfer occurs within the molecule. NBO results reflect the charge transfer mainly due to C–O group.

References

- [1] W.J. Krasavage, J.L. O'Donoghue, G.D. Divinzenzo, in: *Patty's Industri Hygiene and Toxicology*, Eds. G.D. Clayton, E.E. Clayton, Vol. 2C, 3rd ed., Wiley, New York 1982, pp. 4722, 4780.
- [2] M. Windholz, *The Merck Index*, 10th ed., Merck & Co., Rahway, NJ 1983, p. 391.
- [3] D.M. Considine, *Chemical and Process Technology Encyclopedia*, McGraw-Hill, New York 1974, p. 337.
- [4] *Chemyclopedia 87*, American Chemical Society, Washington DC 1987, p. 62.
- [5] G.G. Hawley, *The Condensed Chemical Dictionary*, 10th ed., Van Nostrand Reinhold, New York 1981, p. 297.
- [6] D.C. Young, *Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems (Electronic)*, Wiley, New York 2001.
- [7] A. Frish, A.B. Nielsen, A.J. Holder, *Gauss View User Manual*, Gaussian Inc., Pittsburgh, PA 2001.
- [8] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Suzerain, M.A. Robb, J.R. Cheeseman Jr., J.A. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Gaussian 03, Revision A.1*, Gaussian Inc., Pittsburgh 2003, for ref. [8] and [9] compare also [Gaussian 09](#).
- [9] P.C. Hariharan, J.A. Pople, *Theor. Chim. Acta* **28**, 213 (1973).
- [10] P.C. Hariharan, J.A. Pople, *Mol. Phys.* **27**, 209 (1974).
- [11] A.D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- [12] A.E. Reed, R.B. Weinstock, F. Weinhold, *J. Chem. Phys.* **83**, 735 (1985).
- [13] L. Xiao-Hong, L. Xiang-Rua, Z. Xian-Zhou, *Comput. Theor. Chem.* **969**, 27 (2011).
- [14] M. Snehalatha, C. Ravikumar, I.H. Joe, N. Sekar, V.S. Jayakumar, *Spectrochim. Acta* **72A**, 654 (2009).
- [15] C. James, A. Amal Raj, R. Reghunathan, I.H. Joe, V.S. Jayakumar, *J. Raman Spectrosc.* **37**, 138 (2006).
- [16] J. Liu, Z. Chen, S. Yuan, J. Zhejiang, *Univ. Sci. B* **6**, 584 (2005).
- [17] R.K. Roy, K. Hirao, S. Krishnamurthy, S. Pal, *J. Chem. Phys.* **115**, 2901 (2001).
- [18] P. Kolandaivel, G. Praveen, P. Selvarengan, *J. Chem. Sci.* **117**, 591 (2005).
- [19] C.R. Zhang, H.S. Chen, G.H. Wang, *Chem. Res. Chin.* **U20**, 640 (2004).
- [20] Y. Sun, X. Chen, L. Sun, X. Guo, W. Lu, *Chem. Phys. Lett.* **381**, 397 (2003).
- [21] O. Christiansen, J. Gauss, J.F. Stanton, *Chem. Phys. Lett.* **305**, 147 (1999).
- [22] R. Zhang, B. Dub, G. Sun, Y.X. Sun, *Spectrochim. Acta A* **75**, 1115 (2010).