SAKARYA UNIVERSITY
JOURNAL OF SCIENCE

e-ISSN: 2147-835X
http://www.saujs.sakarya.edu.tr

Received
15-01-2018
Accepted
10-05-2018

Doi
10.16984/saufenbilder.379170

SAKARYA
UNIVERSITY

Theoritical calculations of LASO molecule by using DFT/B3LYP and DFT/HSEH1PBE levels: A detailed vibrational, NMR and NLO analysis

Hacer Gümüş[1]

Abstract

L-arginine semi-oxalate (LASO) molecule $[C_6H_{15}N_4O_2^+.C_2HO_4^-]$ was synthesized and its IR and ^1H NMR and ^{13}C NMR spectroscopy were studied by P. Vasudevan et al. In this study, the geometric structure determination of LASO molecule was optimized to obtain its molecular geometric structure by using the Gaussian program. The theoretical harmonic vibrational wavenumbers of LASO molecule were also calculated. The calculated theoretical data were checked with the experimental data. The experimental and the theoretical data were seen compatible with each other. Further more; LASO molecule is studied by means of NMR spectra. Finally, the analysis of nonlinear optical (NLO) properties, molecular orbitals (MO), molecular surfaces and Mulliken, APT and NBO populations were viewed. All theoretical calculations have been fulfilled by employing the Density Functional Theory (DFT) at B3LYP/6-311++G(d,p) and HSEH1PBE/6-311++G(d,p) levels.

Keywords: LASO, IR, NMR, NLO and DFT.

1.INTRODUCTION

L-arginine complexes are made up of zwitterionic positively charged semi-oxalate ions and amino acid molecules. Firstly, different molecules are collected into separate variable sheets. The fundamental monad in the arginine sheet is a centrosymmetric dimer, while the semi-oxalate ions constitute hydrogen-bonded structure ring in their sheet. In the L-arginine complex each semi-oxalate ion is encircled by arginine molecules and L-arginine complex may be defined as a subsumption compound [2]. Molecular structure of LASO molecule have been examined by P. Vasudevan et al. [1] and its FT-IR and the NMR spectroscopy and the thermal analyses have been done experimentally. The experimentally defined molecular structure and the atom numbers have been shown in Figure 1.

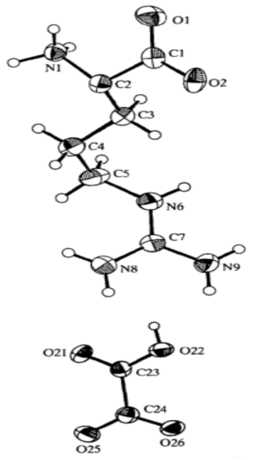


Figure 1. The asymmetric unit of LASO molecule, showing the atomic numbering scheme.

2. DETAILS OF THE COMPUTATION

The whole molecular structure calculations of LASO molecule at fundamental level performed by Gaussian program [3] and GaussView 5 software [4]. Calculated

---

[1] Kocaeli Üniversitesi, Dr. Öğrt. Üyesi Hacer GÜMÜŞ (hacerpir@gmail.com)

bond lengths and calculated bond angles, IR and NMR spectra, electric and electronic features, mulliken, APT and NBO populations and molecular surfaces for LASO molecule have been reached by using B3LYP [5,6] and HSEH1PBE [7-10] methods at 6-311++G(d,p) level [11]. Theoretical geometric structure of LASO which performed with B3LYP level has been displayed in Figure 2.

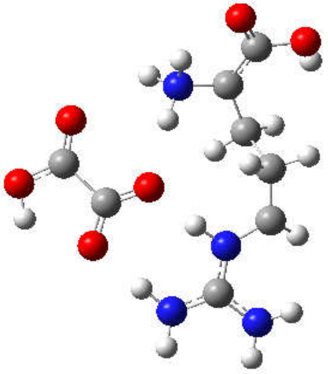


Figure 2. Optimized molecular structure of LASO.

3. CALCULATION RESULTS

3.1. Geometrical Parameters

LASO molecule $[C_6H_{15}N_4O_2^+.C_2HO_4^-]$ has P1 space group and triclinic crystal [2]. These results are taken from the data reported by Nagasuma R. Chandr et al. [2]. The calculated bond distances and the angles are listed in Table 1 together with the comparative experimental X-ray values [1]. As could easily seen from the Table 1, C-C bond distances have been calculated in the range of 1.40786-1.60788 Å and 1.403-1.586 Å in the same methods, respectively. The C-C bond distances are experimentally determined to be 1.518 and 1.534 Å [1]. The C_1-O_1 and C_2-N_1 bond length are observed at 1.240 and 1.491 Å, respectively [1]. These bond distances were calculated as 1.238, 1.487 Å and 1.236, 1.473 Å at B3LYP and HSEH1PBE levels, respectively. O1-C1-O2 angle was found at 117.85° [1], and this angle has been calculated at 117.59950° and 117.909° using B3LYP and HSEHPBE levels, respectively. In Table 1, there exists great harmony between experimental and theoretically calculated parameters of the LASO molecule.

3.2. IR spectra analysis

P. Vasudevan et al. [1] have recently investigated the infrared spectra of the LASO molecule and have assigned the bands vibrations [1]. The experimental vibrational frequencies of LASO molecule have been reported [1], and the experimental values are listed in Table 2. The vibrational frequencies have been calculated. The theoretically calculated vibrational spectra for LASO molecule using HSEH1PBE and B3LYP levels, and the assignments have been given in Table 2.

Table 1. Geometrical parameters of the LASO.

	Exp[1]	Theoretical	
	X-Ray	B3LYP	HSEH1PBE
Bond lengths (Å)			
N1-C2	1.491	1.487	1.473
O1-C1	1.240	1.238	1.236
C2-O2	1.259	1.384	1.372
C2-C1	1.531	1.407	1.403
C3-C2	1.526	1.487	1.483
C3-C4	1.524	1.607	1.586
C5-C4	1.518	1.477	1.474
C5-N6	1.457	1.391	1.384
C7-N6	1.326	1.331	1.326
C7-N9	1.327	1.359	1.352
C7-N8	1.329	1.342	1.334
C13-O11	1.200	1.334	1.200
C14-O15	1.232	1.253	1.248
C13-O12	1.290	1.203	1.324
O16-C14	1.255	1.253	1.250
Bond angles (°)			
O1-C1-O2	117.85	117.59	117.90
N1-C2-C3	108.23	116.28	116.51
O1-C1-C2	125.94	124.17	123.84
O2-C1-C2	116.07	118.22	118.24
C4-C3-C2	113.58	114.50	114.24
C3-C2-C1	111.21	128.13	127.53
N6-C5-C4	113.82	116.89	116.29
C5-C4-C3	109.95	114.97	114.68
N6-C7-N9	118.40	119.40	119.24
C7-N6-C5	124.54	127.06	126.73
O12-C13-C14	114.11	112.57	112.32
O11-C13-C14	120.90	123.73	123.59
C13-C14- O16	116.05	115.16	114.94

Table 2. Harmonic vibrational wavenumbers (cm^{-1}) assignments for the LASO molecule.

Assignments	Exp[1]	Theoretical	
		B3LYP	HSEH1PBE
NH_2 stretching	3384	3564	3471
NH_3 stretching	3179	3260	3340
NH_3 asymmetric stretching	3070	3212	3172
COO^- asymmetric stretching	1647	1732	1697
N-H asymmetric bending	1502	1577	1534
COO^- symmetric bending	1403	1427	1392
COO^- vibrations	1233	1294	1256
CH_2 wagging	1278	1281	1239
NH_3 rocking	1172	1175	1146
C-N stretching	1032	1033	1006
COO^- rocking	848	866	855
CH_2 rocking	722	733	714

The whole calculated vibrational wavenumbers were scaled with a scaling agents of 0.9970 [12] and 0.9614 [13,14] at HSEH1PBE and B3LYP levels. The calculated and the experimental infrared spectrum of the LASO molecule are displayed in Figure 3.

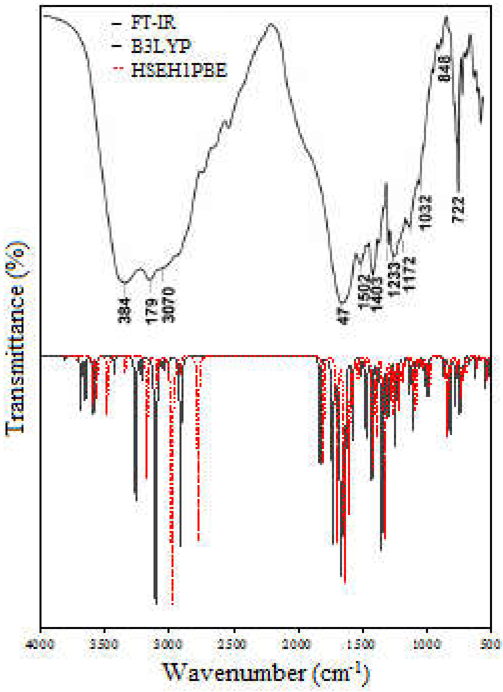


Figure 3. Infrared spectrum of the LASO molecule.

3.3. NMR spectra analyses

13C NMR and ^1H NMR were calculated within gage-including atomic orbital (GIAO) applying HSEH1PBE and B3LYP levels, and the obtained values were given in Table 3.

Table 3. The calculated and experimental ^{13}C and ^1H isotropic NMR chemical shifts for the LASO.

	Exp.	Theoretical (GIAO)	
		B3LYP	HSEH1PBE
^1H			
H_{N7}	3.741	13.965	14.480
H_{N8}	3.729	11.030	11.622
H_{O1}	3.716	9.723	9.945
H_{N1}	3.155	8.427	8.657
H_{N1}	1.852	8.068	8.393
H_{C5}	1.840	4.903	4.985
H_{N1}	1.831	4.900	4.982
H_{O2}	1.819	3.965	4.015
H_{N9}	1.811	3.681	3.834
H_{N8}	1.799	3.576	3.716
H_{N9}	1.783	3.528	3.618
H_{C3}	1.603	2.794	2.885
H_{C4}	1.584	2.733	2.789
H_{C3}	1.571	2.361	2.430
^{13}C			
C_1	173.948	171.232	165.046
C_{13}	166.353	169.831	164.025
C_{14}	156.780	165.950	159.844
C_6	153.450	148.222	142.661
C_5	54.005	106.394	98.714
C_2	40.449	69.214	59.162
C_3	27.415	38.394	30.742
C_4	23.849	37.203	29.830

The experimental and the calculated ^1H and ^{13}C isotropic chemical shifts of the LASO molecule have been given in Table 3. The ^{13}C chemical shift data for the whole calculations have the ranges ~171.232 from ~37.203 ppm at B3LYP method and ~165.046 from ~29.830 ppm at HSEH1PBE method, respectively. ^1H chemical shift data for the whole data have the ranges ~13.965 from ~2.231 ppm at B3LYP method and ~14.480 from~2.343 ppm at HSEH1PBE method, respectively.

3.4. Electronic analysis

Highest occupied molecular orbital energy (HOMO) and lowest unoccupied molecular orbital energy (LUMO) are the types of molecular orbitals. HOMO-LUMO energies display that the charge transfer within the molecule. The HOMO is electron giving ability whereas the LUMO means electron accepting ability. HOMO-LUMO energies were calculated as -6.528 and -4.891 eV and the results were presented in Table 4.

Table 4. Electronic properties of LASO.

	B3LYP	HSEH1PBE
E_{LUMO}	-4.891 eV	-4.899 eV
E_{HOMO}	-6.528 eV	-6.530 eV
$\Delta E = E_{LUMO} - E_{HOMO}$	1.636 eV	1.632 eV
I	6.528 eV	6.530 eV
A	4.892 eV	4.899 eV
χ	5.710 eV	5.714 eV
η	0.818 eV	0.816 eV
S	0.077 eV^{-1}	0.077 eV^{-1}
E_{TOTAL}	-984.53a.u.	-983.53 a.u.

The gap among HOMO-LUMO energies characterizes chemically stability of a molecule [15] and this has been calculated as 1.636 eV at the B3LYP method. The calculated molecular orbital image was displayed in Figure 4. Negative-positive charges have been symbolized by greeen-red colors.

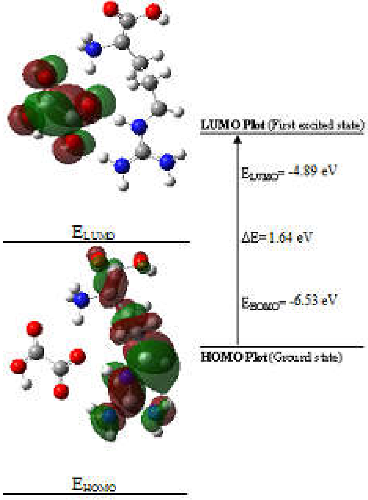


Figure 4. Molecular frontier orbital pictures of the LASO.

3.5. Electric analysis

Nonlinear optical properties of some organic matters have been researched in photonic materials recently [16]. Nonlinear optical properties are the crucial factors in quantum chemistry [17]. In this paper, we have presented the values of the total static dipole moment (μ), the mean polarizability (<α>), the anisotropy of the polarizability (Δα) and the mean first-order hyperpolarizability (<β>) as defined [18] in the following equations:

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2}$$

$$\prec \alpha \succ = \left(\frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}\right)$$

$$\Delta\alpha = \left(\frac{\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + \left(\alpha_{zz} - \alpha_{xx}\right)^2}{2}\right)^{1/2}$$

$$\prec \beta \succ = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2}$$

where

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$
$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$
$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

Nonlinear optical (NLO) analysis has been performed by using the following procedure:

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2}$$
$$\mu = ((4.8)^2 + (3.6)^2 + (0.5)^2)^{1/2}$$
$$\mu = 6.02$$

$$< \alpha >= \left(\frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}\right)$$
$$< \alpha >= \left(\frac{277.6 + 190.9 + 107.3}{3}\right)$$
$$< \alpha >= 191.9 a.u. = 28.10^{-24} esu$$

$$\Delta\alpha = \left(\frac{\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + \left(\alpha_{zz} - \alpha_{xx}\right)^2}{2}\right)^{1/2}$$
$$\Delta\alpha = \left(\frac{(277.6 - 190.9)^2 + (190.9 - 107.3)^2 + (107.3 - 277.6^2)}{2}\right)^{1/2}$$
$$\Delta\alpha = 147.4 a.u. = 22.10^{-24} esu$$
$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz} = 21640 - 7957 - 561 = 13122$$
$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz} = 4945 + 13225 + 174 = 31292$$
$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz} = -233 - 3288 + 811 = -2710$$

$$< \beta >= \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2}$$
$$< \beta >= \left((13122)^2 + (31292)^2 + (-2710)^2\right)^{1/2}$$
$$< \beta >= 34040 a.u. = 294082.10^{-33} esu$$

The calculated values of LASO molecule at B3LYP/6-311++G(d,p) level were given in Table 6.

Table 4. Total static dipole moment (μ), the mean polarizability (<α>), the anisotropy of the polarizability (Δα), the mean first-order hyperpolarizability (<β>) LASO.

Property	B3LYP/6311++G(d,p)
μ_x	4.8 Debye
μ_y	3.6 Debye
μ_z	0.5 Debye
μ	6.02 Debye
α_{xx}	277.6 a.u.
α_{yy}	190.9 a.u.
α_{zz}	107.3 a.u.
<α>	191.9 a.u.
Δα	147.4 a.u.
β_x	13122 a.u.
β_y	31292 a.u.
β_z	-2710 a.u.
<β>	34040 a.u.

where dipole moment of 6.02 Debye, polarizability of 28.10^{-24}, anisotropy of the polarizability of 22.10^{-24} and first-order hyperpolarizability of 294082.10^{-33} have been calculated at B3LYP method for LASO molecule.

3.6. Electrostatic potential (ESP) and molecular electrostatic potential (MEP) analysis

MEPs are the technique of ESP map on iso-electron density surface. MEP has been founded commonly as a beneficial proportion to clarify hydrogen bonding. MEP is originated from it and at the same time wiews the dimension of the molecule, image as well as positive, negative and neutral electrostatic potential fields in terms of color classification [19]. Therotically calculated 3D MEP surfaces of LASO molecule have been performed from optimized molecular structure at B3LYP level. Polarization effect is clearly visible in

Figure 5.

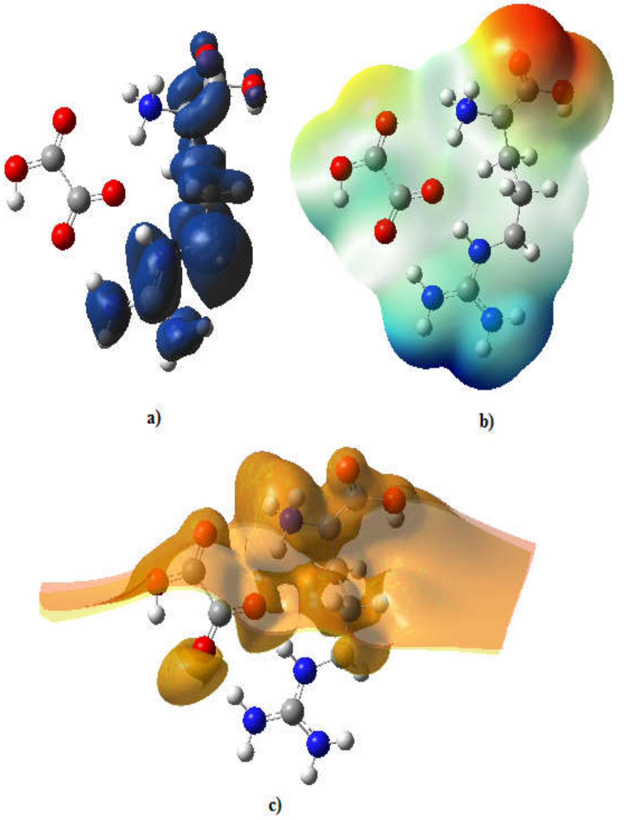
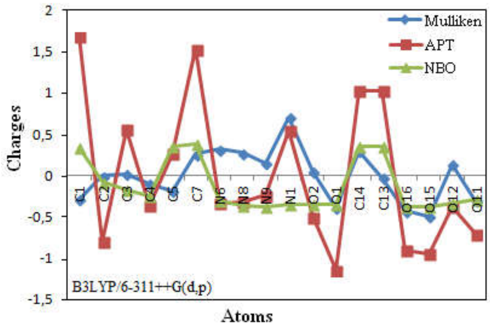


Figure 5. a) Spin density b) MEP and c) ESP pictures of LASO calculated at B3LYP level.

3.7. Mulliken, APT and NBO charge analysis

Between the orbital based definitions of atomic populations we put into utterances the famed Mulliken 20] population anatomy method and the density matrix based normal population anatomy [21-23]. The Mulliken charges analysis is one of the oldest and simplest method, with the electrons being divided up amongst the atoms according to the degree to which different atomic AO basis functions contribute to the overall wave function [24]. The Mulliken charge analysis of the LASO molecule has been calculated with HSEH1PBE and B3LYP methods of theory. Mulliken, APT and NBO atomic charge on each atom of the LASO have been presented in the graphical representation shown in Figure 6.



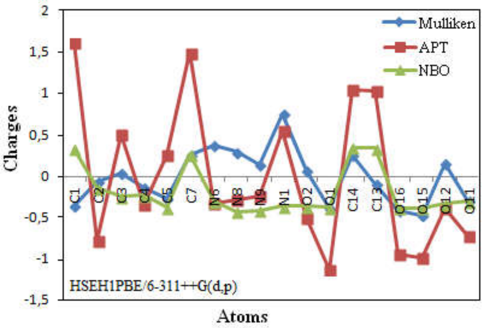


Figure 6. Charge analysis of LASO.

4. CONCLUSIONS

The geometry structure of the LASO molecule has been determined by HSEH1PBE and B3LYP methods. Calculated bond distances and angles compare well with the experimental data. Theoretical calculation of vibrational spectra and the harmonic vibration analysis have been performed and the vibration assignments have been checked with the experimental ones. The correlation factors between the theoretical (B3LYP/6-311++G(d,p)) and the experimental (that can be seen from the tables 1,2 and 3) ones for the LASO molecule have beenfound to be 0.9968, 0.9991 and 0.9493 respectively. Frontier MO, HOMO-LUMO energies were performed at B3LYP and HSEH1PBE levels. The LASO molecule exhibits strong effective intra- and intermolecular charge transfer and displays the first-hyperpolarizability of 294082.10^{-33} esu. The MEP plot clearly displays reactive parts, nucleophilic and electrophilic attack areas.

REFERENCES

[1] P. Vasudevan S. Gokul Raj, S. Sankar, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 106, pp. 210-215, 2013.l. 24, no. 6, pp. 51–63, 2013.

[2] Nagasuma R. Chandra, Moses M. Prabu, Jananı Venkatraman, S. Suresh and M. Vıjaya, *Acta Cryst. B*, vol. 54, pp. 257-263, 1998.

[3] M J Frisch et al. Gaussian 09, Revision D.01 (Wallingford, CT:Gaussian, Inc) 2009.

[4] GaussView, Version 5, R Dennington, T Keith and J Millam (Shawnee Mission, KS: Semichem Inc) 2009.

[5] A. D. Becke, *J Chem. Phys.*, vol. 98, pp. 5648, 1993.

[6] C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, vol. 37, pp.785, 1988.

[7] J. Heyd and G. Scuseria, *J. Chem. Phys*. Vol. 121, pp. 1187, 2004.

[8] J. Heyd and G. E. Scuseria *J. Chem. Phys.*, vol. 120, pp. 7274, 2004.

[9] J. Heyd, J. E. Peralta, G. E. Scuseria and R. L. Martin, *J. Chem. Phys.*, vol. 123, pp. 174101, 2005.

[10] J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.,* vol. 124, pp. 219906, 2006.

[11] M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.,* vol. 80, pp. 3265, 1984.

[12] J. B. Foresman, E Frisch, *Exploring Chemistry with Electronic Structure Methods, Gaussian, Inc., Pittsburgh, PA, USA*, 1993.

[13] A. Frish, A. B. Nielsen and A. J. Holder, *Gauss View User Manual, Gaussian Inc. Pittsburg, PA,* 2001.

[14] W. H. James, E. G. Buchanan, C. W. Müller, J. C. Dean, D. Kosenkov, L. V. Slipchenko, L. Guo, A. G. Reidenbach, S. H. Gellman and T. S. Zwier, *J. Phys. Chem. A,* vol. 115, pp. 13783, 2011.

[15] K. Fukui, *Science,* vol. 218, pp. 747, 1982.

[16] A. Cornelis van Walree, Okke Franssen, W. Albert Marsman, C. Marinus Flipseb and W. Leonardus Jenneskens; *J. Chem. Soc., Perkin Trans.* Vol. 2, 1997.

[17] D. Avci, A. Basoglu, Y. Atalay, *International Journal of Quantum Chemistry,* vol. 111, pp. 130-147, 2011.

[18] G. Maroulis, *Static hyperpolarizability of the water dimer and the interaction hyperpolarizability of two water molecules*, J. Chem. Phys., Vol. 113, No. 5, pp. 1813, 2000.

[19] R. G. Pearson, *Proceeding of the National Academiy of Sciences,* vol. 83, pp. 8440, 1986.

[20] R. S. Mulliken, *J. Chem. Phys.,* vol. 23, pp. 1833, 1955.

[21] A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, vol. 83, pp. 735, 1985.

[22] A. E. Reed and F. Weinhold, *J. Chem. Phys.*, vol. 83, pp. 1736, 1985.

[23] A. E. Reed, L. A Curtiss and F. Weinhold, *Chem. Rev.,* vol. 88, pp. 899, 1988.

[24] C. Cramer, *Essentials of Computational Chemistry: Theories and Models, Second Edition, John Wiley and Sons Ltd.*, 2004.