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Substituent effect on the stability and electronic properties of naphthalene and azulene: A computational investigation

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Abstract: In this research, substituent effect on the stability and electronic properties of naphthalene and azulene studied. Hydrogen atoms of the studied molecules were replaced with methyl, fluoride and chloride substituents. Calculations were done at the M062X/6-311G(d,p) level of theory. Bicyclobutane mechanism was considered for the rearrangement of azulene to naphthalene and substituent effect on the activation energy values were illustrated with the density functional calculations. Harmonic oscillator model of aromaticity (HOMA) parameters were used to illustration of aromoaticity in the studied molecules. Also, frontier orbital analysis in the azulenes and naphthalenes were reported.

Introduction

The thermal rearrangement of azulene to naphthalene is an example of the conversion of an aromatic molecule to another [1]. This reaction is occurred by flash vacuum thermolysis above 800 °C or static thermolysis above 400 °C. Various mechanisms have been reported about this rearrangement [2-11]. Computational study of radical-promoted and intramolecular mechanisms of this rearrangement has been reported [12]. In other investigation, The Car–Parrinello metadynamics method explored different reaction mechanisms [13]. Also, this rearrangement explored through the bent bond and antiperiplanar hypothesis orbital model [14].

In the current research, we have attempted to study the Substituent effect on the stability and electronic properties of naphthalene and azulene.

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Results and discussion
Energetic aspect

Energy values of the azulene, naphthalene, fluorinated, chlorinated and methylated azulene and naphthalene molecules (Figure 1) are listed in Table 1 at the M062X/6-311G(d,p) level of theory. It can be found, naphthalene is more stable than azulene in the presence of all substituents (X=F, Cl, Me). Larger relative energy value is observed in the presence of X=Me than X=H (Table 1). In contrast, ΔE values are decrease in the presence of X=F and Cl substituents than X=H.

Bicyclobutane Mechanism

Bicyclobutane mechanism of azulene-to-naphthalene rearrangement is indicated in Figure 2. Energy and relative energy values of the bicyclobutane (BCB) and transition states for the formation of the bicyclobutane and for its subsequent rearrangement to naphthalene are calculated at the M062X/6-311G (d,p) level of theory (Tables 1 and 2). The two transition states are

found at 84.50 and 81.50 kcal/mol higher than azulene.   Very high activation energies limit extent in the
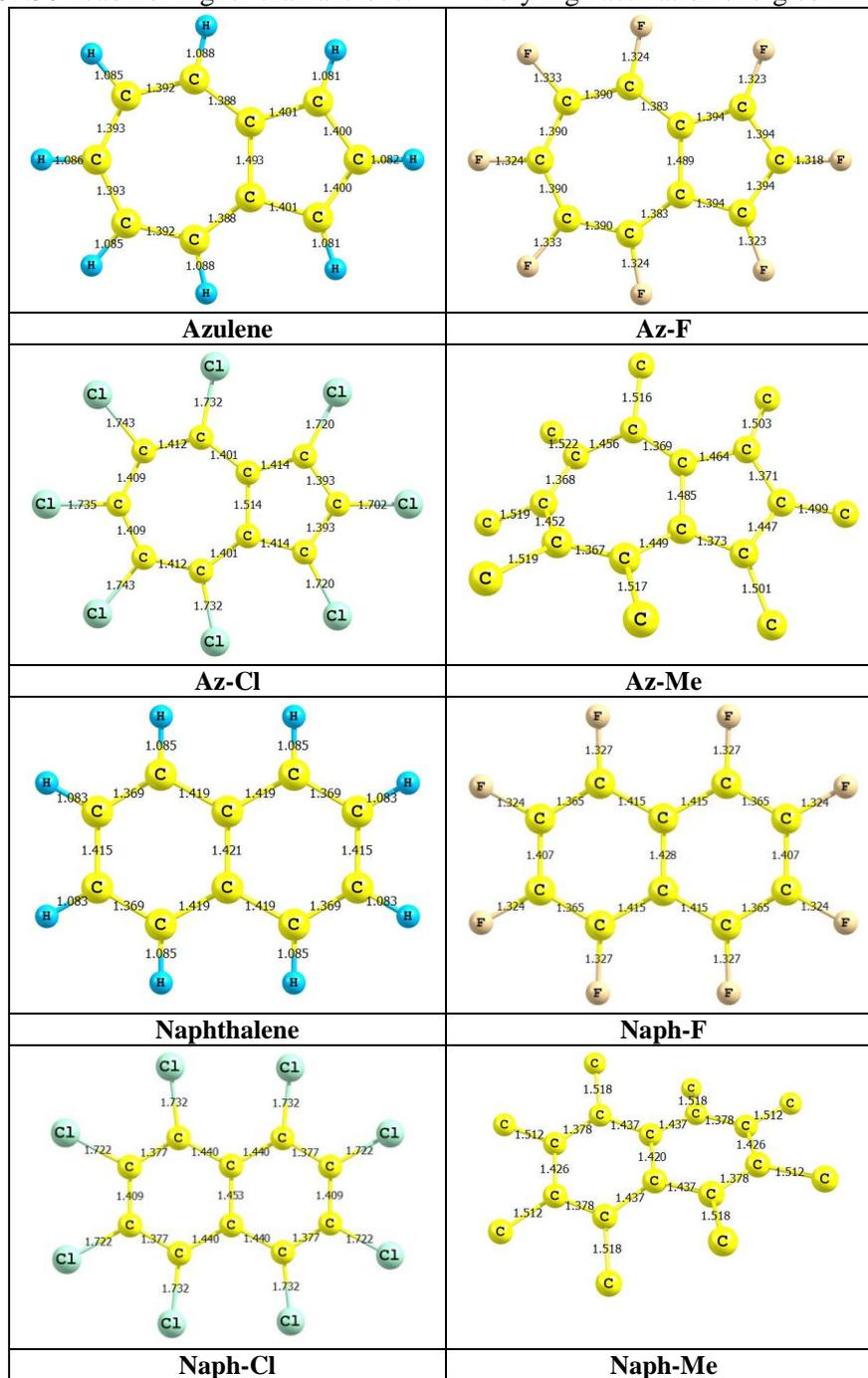
Figure 1. Optimized geometries of azulene, naphthalene, fluorinated, chlorinated and methylated azulene and naphthalene molecules.

azulene-naphthalene rearrangement at the highest temperatures (above 1000 °C).

When hydrogen atoms replace with Me, F, and Cl, ΔE(TS1) values decrease. Smallest ΔE(TS1) value is observed in the presence of X=Cl.   After, replacing of hydrogen atoms with F, ΔE(TS2) values increase.

hydrogen atoms with Me, and Cl ΔE(TS2) values decrease. This value is larger in the presence methyl than Cl substituent. In contrast, After, replacing of hydrogen atoms with F, ΔE(TS2) values increase. These lower activation energies in compared to non-substituted molecules show that rearrangement can be

occurred at the lower temperatures in the presence of　　chloride substituent.
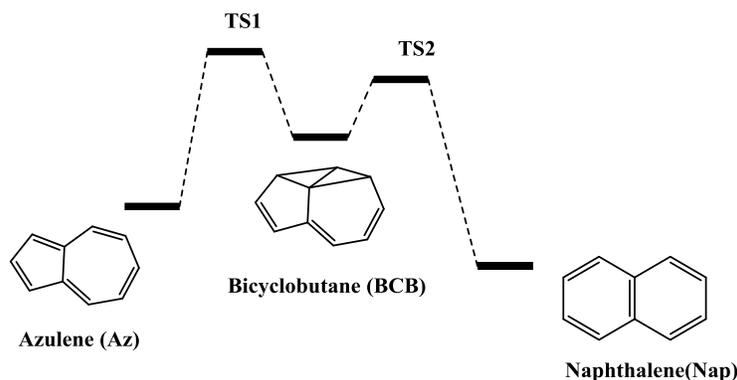
Figure 2. Bicyclobutane Mechanism of Azulene-to-Naphthalene Rearrangement.

Electronic spatial extent (ESE)

The surface area covering the volume around any molecules is reflected as its ESE, which defines its receptivity from an external electric field. Table 3 reveals the larger ESE values for the azulene than naphthalene molecule in the present of selected substituents. ESE values decrease as X=Cl>Me>F>H.

Table 1. Energy (E, a.u) of azulenes, bicyclobutanes (BCB) and transition states for the formation of the bicyclobutanes and for its subsequent rearrangement to naphthalenes at 6-311G(d,p) level of theory.

X	E(Az)	E(TS1)	E(BCB)	E(TS2)	E(Naph)
H	-385.7507	-385.6113	-385.6724	-385.6209	-385.8119
Me	-700.1651	-700.0673	-700.1269	-700.0703	-700.2275
F	-1179.5919	-1179.4613	-1179.5262	-1179.4485	-1179.6510
Cl	-4062.4620	-4062.3802	-4062.4361	-4062.3777	-4062.5221

Table 2. Relative energy (ΔE, kcal/mol) of azulenes, bicyclobutanes (BCB) and transition states for the formation of the bicyclobutanes and for its subsequent rearrangement to naphthalenes at 6-311G(d,p) level of theory.

X	ΔE(Az)	ΔE(TS1)	ΔE(BCB)	ΔE(TS2)	ΔE(Naph)
H	0.00	87.50	49.15	81.50	-38.35
Me	0.00	61.36	23.98	59.49	-39.19
F	0.00	81.95	41.24	89.99	-37.07
Cl	0.00	51.34	16.28	52.89	-37.72

Table 3. Electronic spatial extent (ESE, a.u), wavenumber of S0→S1 transition and HOMA values of azulenes and naphthalenes at 6-311G(d,p) level of theory.

X	ESE(Az)	ESE(Naph)		λ(Az)	λ(Naph)		7-membered	5-membered	6-membered
H	1300.87	1284.38		512.08	261.46		0.5834	0.3914	0.8048
Me	4795.10	4838.44		469.55	294.78		0.1447	0.0059	0.6736
F	4161.31	4128.08		520.15	270.63		0.6137	0.4581	0.8121
Cl	8580.53	8527.86		599.15	307.41		0.3251	0.1117	0.5628

Bond distances

Optimized geometries of the studied molecules are presented in Figure 1. It can be deduced the geometries of fluorinated and chlorinated molecules are planar.

But, geometries of the methylated molecules are non-planar.

The C–C bond lengths of the studied molecules are presented Figure 1. It can be found, the C–C bond

lengths values are between the single and double bond for all molecules. A single C–C bond is 1.527 Å in C_2H_6 molecule at the M062X/6-311G(d,p) level of

theory. A double C=C bound is 1.324 Å at the same level of theory. Here, the C–C bond length are on average, similar to that found for benzene (1.391 Å). This feature implies a resonant character of five and

seven-membered rings in azulene and six-membered in naphthalene. Azulene structure is formed of two fused ionic aromatic cycles, one of them being an electronically deficient tropylium cation and other an electronically rich cyclopentadienyl anion (Figure 3).

Naphthalene(Nap)   **Azulene (Az)**

(a)

(b)
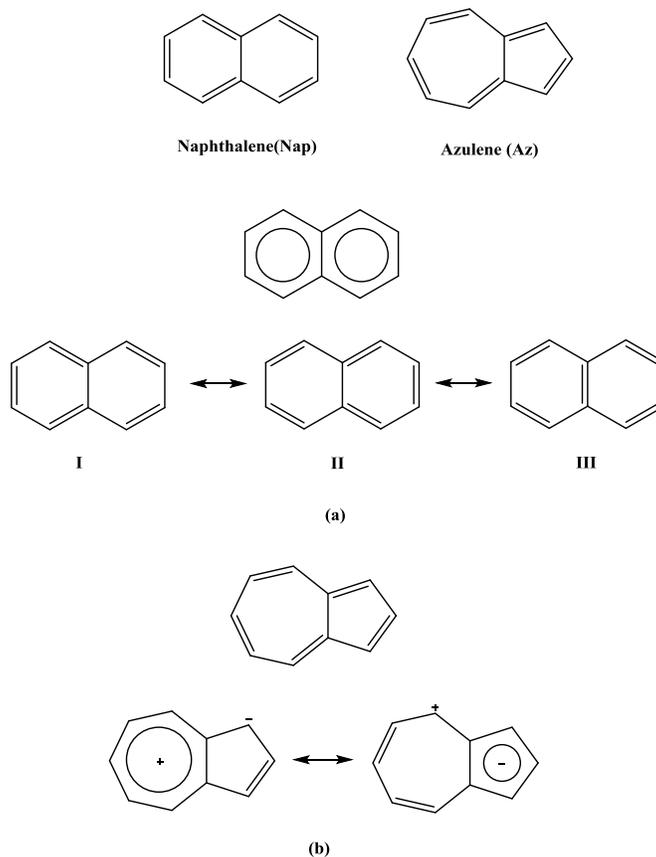
Figure 3. Possible resonance structures of naphthalene and azulene molecules.

Aromaticity

One of the structural aromaticity indices is harmonic oscillator model of aromaticity (HOMA) [23, 24]. HOMO measures the molecular aromaticity by relating the amount of bond distance equalization in that compound with a hypothetical reference. The zero and one HOMA indices are attributed to a model non aromatic system and a system with full π-electron delocalization, respectively.

Computed HOMA values were listed in Table 3. The higher HOMA value reveals the more ''aromatic'' the ring. Therefore, the delocalization of the π-electrons of the system are increased. Hit can be deduced, the

higher HOMA in the presence of F substitution, representing enhance in local aromaticity.

Molecular orbital analysis

The energies of the frontier orbitals (HOMO, LUMO), the corresponding HOMO–LUMO energy gaps, hardness, chemical potential and electrophilicity values of the azulene and naphthalene molecules are given in Table 4. Plots of frontier orbitals of naphthalene and azulene are revealed in Figure 4.
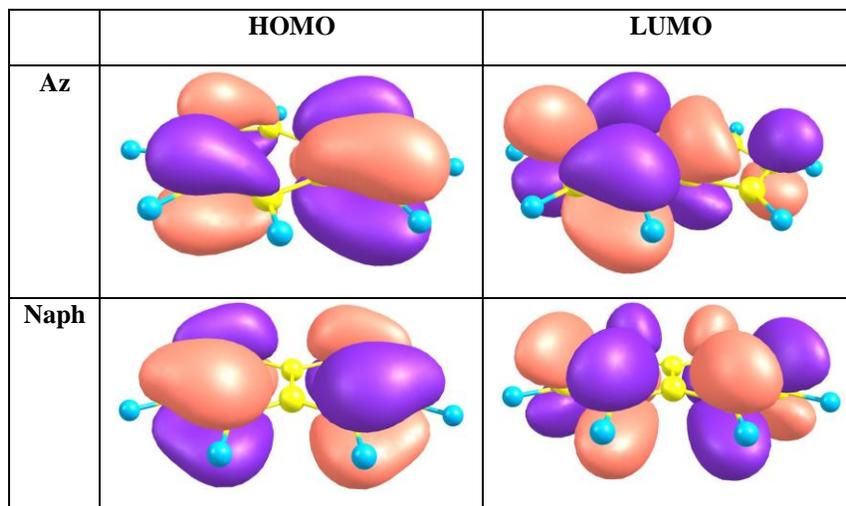
	HOMO	LUMO
Az		
Naph		

Figure 4. Plots of frontier orbitals of azulene and naphthalene molecules.

As seen shown in Table 4, HOMO energy of naphthalene is less than azulene. On the other hand, LUMO energy of naphthalene is more than azulene. HOMO-LUMO gap and hardness of naphthalene are larger than azulene. As expected from the principles of

minimum energy (MEP), and maximum hardness (MHP) [25-29].

Table 4. Frontier orbital energies (E, eV), HOMO-LUMO gap (eV), hardness (η, eV), chemical potential (μ, eV) and electrophilicity (ω, eV) of azulenes and naphthalenes at 6-311G(d,p) level of theory.

X	Az						Naph					
	E(HOMO)	E(LUMO)	Gap	η	μ	ω	E(HOMO)	E(LUMO)	Gap	η	μ	ω
H	-6.61	-1.34	5.27	2.63	-3.98	3.00	-7.31	-0.34	6.97	3.49	-3.83	2.10
Me	-5.93	-0.68	5.25	2.62	-3.30	2.08	-6.36	-0.04	6.32	3.16	-3.20	1.62
F	-7.66	-2.49	5.17	2.59	-5.07	4.97	-8.18	-1.36	6.82	3.41	-4.77	3.34
Cl	-7.60	-2.95	4.65	2.32	-5.28	5.99	-8.02	-2.06	5.96	2.98	-5.04	4.26

Table 5. Thermochemical parameters of azulenes, naphthalenes and isomerization reaction of these molecules at 6-311G(d,p) level of theory. G and H are Gibbs's free energy and enthalpy in a.u. ΔG_r and ΔH_r are changes of Gibbs's free energy and enthalpy in kcal/mol.

X	G(Az)	G(Naph)	ΔG_r	H(Az)	H(Naph)	ΔH_r
H	-385.6353	-385.6937	-36.64	-385.5962	-385.6560	-37.52
Me	-699.8412	-699.8973	-35.19	-699.7740	-699.8344	-37.88
F	-1179.5511	-1179.6070	-35.11	-1179.4948	-1179.5526	-36.27
Cl	-4062.4360	-4062.4938	-36.29	-4062.3785	-4062.4375	-37.06

The calculated electrophilicity (ω) values are listed in Table 4. It can be observed the smaller ω values for naphthalene than azulene. This trend is compatible with the minimum electrophilicity principle (MElP) [30, 31].

Thermodynamics of rearrangement

Thermodynamics parameters of the azulen-naphthalene rearrangement are listed in Table 5 at the M062x/6-311G(d,p) level of theory. The following reaction is considered:

Azulene → Naphthalene ΔX=X(naphthalene)-X(Azulene); X=G, H

The free energy changes (ΔG_r) and enthalpy change (ΔH_r) values of reaction are calculated in 298 K and 1 atm (Table 5). Negative ΔG_r values indicate that this reaction is spontaneous thermodynamically. ΔG_r values increase as X=H < Cl < Me < F. on the other hand, negative ΔH_r values show that this rearrangement is exothermic thermodynamically. ΔH_r values enhance as X=H < Me < Cl < F.

Electronic spectrum

The $s_0 \rightarrow s_1$ electronic transition of the studied azulene and naphthalene molecules are investigated. The wavelength (λ_{max}) and oscillator strength (f) of the transitions obtained using TD-DFT computations are gathered in Table 3. In the azulenes, this transition is attributed to HOMO → LUMO transition (98%). In the naphthalene, this transition is attributed to HOMO → LUMO+1 (50%) and HOMO-1→LUMO (50%) transitions. In the fluorinated naphthalene, this transition is attributed to HOMO → LUMO+1 (69%) and HOMO-1→LUMO (30.1%) transitions. In the chlorinated naphthalene, this transition is attributed to HOMO → LUMO+1 (96.9%) and HOMO-1→LUMO (1.1%) transitions. In the methylated naphthalene, this transition is attributed to HOMO → LUMO (96.5%) and HOMO-1→LUMO (3.1%) transitions. Molecular orbital analysis show that $s_0 \rightarrow s_1$ electronic transition is attributed to $\pi \rightarrow \pi^*$ transition. It can be found red-shift of transition with replacing of hydrogen atoms with F and Cl substitutions in azulene. But, blue shift is observed with replacing of hydrogen atoms with Me substitutions in azulene. When replacing of hydrogen atoms with F, Cl and Me substitutions in naphthalene, red shift is observed.

Conclusion

Computational investigation of substituent effect on the stability and electronic properties of naphthalene and azulene at M06-2X/6-311G(d,p) level of theory indicated naphthalene is more stable energetically than azulene. Replacing of hydrogen atoms in azulene and naphthalene with X=F, Cl, Me did not change this stability of molecules. This stability trend was compatible with the principles of minimum energy (MEP) and maximum hardness (MHP) and minimum electrophilicity principle (MElP). ESE values of azulene were Larger for the than naphthalene molecule in the present of selected substituents. Harmonic oscillator model of aromaticity (HOMA) values

revealed that F substitution caused a higher aromaticity than the other substitutions. TD-DFT study results illustrated $s_0 \rightarrow s_1$ electronic transition of these systems is attributed to $\pi \rightarrow \pi^*$ transition.

Computational Methods

The Gaussian 09 was employed for conducting calculations [15]. Geometry optimization was performed utilizing the standard 6-311G(d,p) basis set [16-19] and the hybrid functional of Truhlar and Zhao (M06-2X) [20]. Computed vibrational frequencies were shown that the optimized structures have no imaginary frequency. Harmonic oscillator model of aromaticity (HOMA) parameters were computed using the Multiwfn 3.5 package [21]. The electronic spectra were provided using TD-DFT [22] at the M06-2X/6-311G(d,p) level of theory.

References

[1] Heilbronner, E.; Plattner, P.A.; Wieland, K., *Experientia*. **1947**, *3*, 70.

[2] Scott, L.T., *Acc. Chem. Res.* **1982**, *15*, 52.

[3] Alder, R.W.; Whittaker, G., *J. Chem. Soc., Perkin Trans. 2*. **1975**, 714.

[4] Alder, R.W.; Wilshire, C., *J. Chem. Soc., Perkin Trans. 2*. **1975**, 1464.

[5] Alder, R.W.; Whiteside, R.W.; Whittaker, G.; Wilshire, C., *J. Am. Chem. Soc.* . **1979**, *101*, 629.

[6] Becker, J.; Wentrup, C.; Katz, E.; Zeller, K.P., *J. Am. Chem. Soc.* **1980**, *102*, 5110.

[7] Zeller, K.P.; Wentrup, C., *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *368*, 852.

[8] Fowler, P.W.; Manolopoulos, D.E.; Ryan, R.P., *Carbon.* **1992**, *30*, 1235.

[9] Alder, R.W.; Whittaker, G., *J. Chem. Soc., Perkin Trans. 2*. **1975**, 712.

[10] Eggen, B.R.; Heggie, M.I.; Jungnickel, G.; Latham, C.D.; Jones, R.; Briddon, P.R., *Science*. **1996**, *272*, 87.

[11] Slanina, Z.; Zhao, X.; Uhlik, F.; Ozawa, M.; Osawa, E., *J. Organomet. Chem.* **2000**, *599*, 57.

[12] Alder, R.W.; East, S.P.; Harvey, J.N.; Oakley, M.T., *J. Am. Chem. soc*. **2003**, *125*, 5375.

[13] Stirling, A.; Iannuzzi, M.; Laio, A.; Parrinello, M., *ChemPhysChem*. **2004**, *5*, 1558.

[14] Deslongchamps, P., *Tetrahedron 82 (2021)* **2021**, *82*, 131956.

[15] Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalman, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmaylov, A.F.; Bloino, J.; Zheng, G.;

Sonnenberg, J.L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; T. Nakajima; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J.A.; Jr.; Peralta, J.E.; Ogliaro, F.; Bearpark, M.; Heyd, J.J.; Brothers, E.; Kudin, K.N.; Staroverov, V.N.; Kobayashi, R.; J. Normand; Raghavachari, K.; Rendell, A.; Burant, J.C.; Iyengar, S.S.; J. Tomasi; Cossi, M.; Rega, N.; Millam, J.M.; Klene, M.; Knox, J.E.; Cross, J.B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Martin, R.L.; Morokuma, K.; Zakrzewski, V.G.; Voth, G.A.; Salvador, P.; Dannenberg, J.J.; Dapprich, S.; Daniels, A.D.; Farkas, O.; Foresman, J.B.; Ortiz, J.V.; Cioslowski, J.; Fox, D.J. *Gaussian 09*, Revision A.02; Gaussian, Inc.: Wallingford CT, 2009.

[16]   Hay, P.J., *J. Chem. Phys.* **1977**, *66*, 4377.

[17]   Krishnan, R.; Binkley, J.S.; Seeger, R.; Pople, J.A., *J. Chem. Phys.* **1980**, *72*, 650.

[18]   McLean, A.D.; Chandler, G.S., *J. Chem. Phys.* **1980**, *72*, 5639.

[19]   Wachters, A.J.H., *J. Chem. Phys.* **1970**, *52*, 1033.

[20]   Zhao, Y.; Truhla, D.G., *J. Phys. Chem. A.* **2006**, *110*, 5121.

[21]   Lu, T.; Chen, F., *J. Comp. Chem.* **2012**, *33*, 580.

[22]   Runge, E.; Gross, E.K.U., *Phys. Rev. Lett.* **1984**, *52* 997.

[23]   Krygowski, Y.M., *J Chem Inf Comput Sci.* **1993**, *33*, 70.

[24]   Cyranski, M.K.; Krygowski, T.M., *J Chem Inf Comput Sci.* **1996**, *36*, 1142.

[25]   Ayers, P.W.; Parr, R.G., *J. Am. Chem. Soc. .* **2000**, *422*, 2010.

[26]   Parr, R.G.; Chattaraj, P.K., *J. Am. Chem. Soc. .* **1991**, *113*, 1854.

[27]   Pearson, R.G., *J. Chem. Educ. .* **1987**, *64*, 561.

[28]   Pearson, R.G., *Acc. Chem. Res. .* **1993**, *26*, 250.

[29]   Pearson, R.G., *J. Chem. Educ.* **1999**, *76*, 267.

[30]   Chamorro, E.; Chattaraj, P.K.; Fuentealba, P., *J. Phys. Chem. A* **2003**, *107*, 7068.

[31]   Parthasarathi, R.; Elango, M.; Subramanian, V.; Chattaraj, P.K., *Theor. Chem. Acc. .* **2005**, *113*, 257.