



A DFT study on the mono lithium and sodium salts of *N*-(2-hydroxyphenyl)salicylaldimine

Tareq Irshaidat*

Department of Chemistry, College of Sciences, Al-Hussein Bin Talal University, Ma'an, Jordan

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ABSTRACT

This computational organic chemistry study presents results based on density functional theory at the B3LYP/6-31G(d) and B3LYP/cc-PVTZ//B3LYP/6-31G(d) levels of theory. Other computational procedures (HF and MP2) are presented for model structures. Three main points were investigated: some of the electronic structure aspects, the relative stability of isomers, and aromaticity. The results suggest that the title salts are the first Schiff base systems in the literature to exist only in the N–H form, which is characterized as the zwitterion form. Also, the estimated delocalization of the π -electron density in the middle ring indicates that these compounds are the first examples of metalla-hetero[10]annulenes. Analysis of the electron density delocalization indicates that the title compounds are better conductors at the molecular level than the parent Schiff base, and therefore, can be considered as new building blocks for organic materials.

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1. Introduction

Salicylaldimines are easy to prepare and are characterized by their high stability, which makes them desirable for photochromic and thermochromic applications.^{1–3} Tautomerism in these Schiff bases is a major topic in physical organic chemistry. Tautomerism is postulated as an essential process for molecular electronic devices,^{4,5} optical switches,⁶ photodetectors⁷ and for photodynamic cancer therapy.⁸ These Schiff bases have been subject to extensive spectroscopic and crystallographic studies, which in general support the fact that the enol-form is more favored than the keto-form. However, a few examples of the keto-form in the solid state have been reported.^{9–12} The presence of the keto-form at room temperature remains uncertain due to the lack of solid experimental evidence. In addition to the enol-form and the keto-form, the zwitterionic-form has been included in discussions of tautomerism but has not been given much attention.¹³ This study presents new features of the electronic structure of salicylaldimines.

In the light of the importance of salicylaldimines to the theory of hydrogen bonding^{14–21} and due to their technological applications, we have studied the title compounds (Fig. 1). In a previous study,²² we found that replacement of the OH proton in salicylaldimines can enhance delocalization of the π system and decrease the band gap. The parent Schiff base in this study has two OH groups (Fig. 1), one is involved in hydrogen bonding and the other is a substituent on the second phenyl ring. Mono deprotonation of the

Schiff base with lithium or sodium hydride in the absence of coordinating solvents will produce the salt shown in Figure 1. Some of the physical organic aspects of this structure are the subject of this study. The results show that these metalla-heterocycles are more stable than the other possible isomers. The discussion focusses on ΔE values of different isomeric structures, calculated atomic charges; Mulliken, APT, NPA, and ChelpG, selected infrared stretching frequencies, calculated harmonic oscillator measure of aromaticity (HOMA) values, and selected HOMO–LUMO energy differences (band gap energies).

2. Computational methods

Gas phase calculations at the B3LYP level of theory and the standard basis set 6-31G(d)^{23–25} were employed to optimize all the structures in this study. Other computational procedures were compared for model compounds (Tables 1 and 2). All calculations were performed using the GAUSSIAN 03 series of programs.²⁶ Mulliken,²⁷ NPA,²⁸ atom polarizability tensor-based charges (APT),²⁹ and Chelpg³⁰ charges were calculated using the same software. The harmonic oscillator measure of aromaticity (HOMA)³¹ is a method used to describe the aromaticity based on the geometrical parameters. HOMA takes advantage of bond lengths inside the studied rings. The best illustration of this can be made by considering the conjugated cyclic system of formula C₆H₆. The value HOMA = 0 represents the system with localized double bonds which is known as the Kekulé structure, while HOMA = 1 is for the fully delocalized system, the known benzene ring. Values of HOMA less than unity and greater than zero are the most common.

* Tel.: +962 799514989; fax: +962 3 2179050.
 E-mail address: tirshaidat@yahoo.com

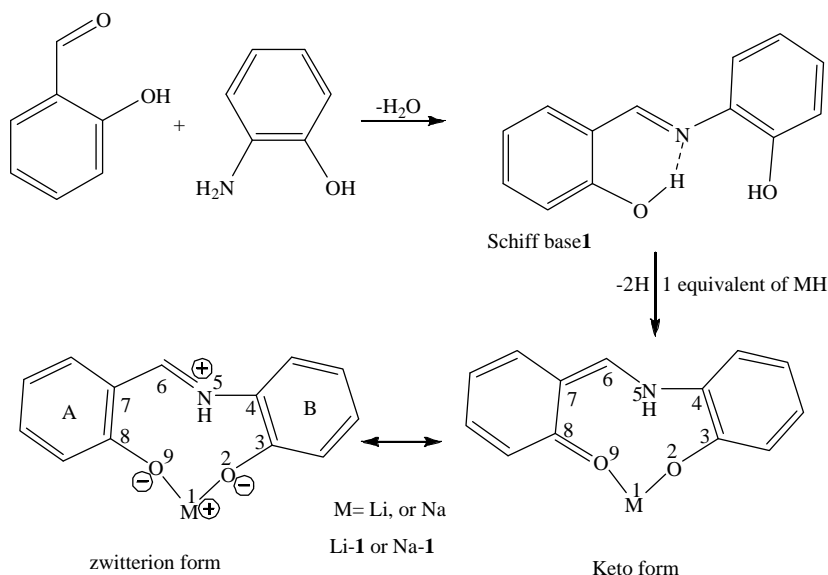


Figure 1. The two Schiff base salts investigated and the numbering system.

Table 1

Calculated HOMA values for geometries optimized using different computational procedures

Computational procedure	HOMA
B3LYP/3-21G	0.79
B3LYP/3-21G**	0.79
B3LYP/Lan12dz	0.72
B3LYP/SDD	0.72
B3LYP/6-31G(d)	0.90
B3LYP/6-311G(2d)	0.91
B3LYP/6-311++G(d,p)	0.91
MP2/6-311++G(d,p)	0.90

Table 2

Energy calculations for the isomerization reaction in Figure 3

Computational method	ΔE (kcal/mol)
B3LYP/6-31G(d)	13.7
MP2/6-31G(d)	12.6
B3LYP/6-311G(2d)	13.3
B3LYP/6-311++G(d,p)	12.8
HF/6-31G(d)//B3LYP/6-31G(d)	5.5
MP2/6-31G(d)//B3LYP/6-31G(d)	12.8
B3LYP/cc-PVTZ//B3LYP/6-31G(d)	13.6
B3LYP/cc-PVTZ//B3LYP/6-311++G(d,p)	13.3

3. Results and discussion

3.1. Choosing the method

In previous work,²² the functional B3LYP and the basis set 6-31G(d) were examined and found suitable to produce acceptable geometry for benzene (HOMA = 0.98) compared to the actual geometry (HOMA = 1), the accuracy in geometry optimization is 98%. On the other hand, the larger basis set 6-311+G(d,p)³² does not improve the geometry of benzene (HOMA = 0.99) significantly. The MP2 method³³ using the basis set 6-31G(d) produced a less accurate result (HOMA = 0.92). In addition to our own experience with the basis set 6-31G(d), the literature reports numerous studies in which this basis set was found to be suitable for both geometry optimization and energy calculations to obtain qualitative and semi-quantitative results.^{34,35}

3.2. Geometry optimization

To confirm that the basis set 6-31G(d) is suitable to optimize this type of structure, the basic skeleton of the metalla-heterocycle, MOCCNCCO (numbering in Fig. 1), was optimized (Fig. 2) using a variety of computational procedures, and the value of HOMA, as a criterion of the optimized geometries, was calculated for each (Table 1). Data in Table 1 show that the results from the basis sets 3-21G,³⁶ 3-21G**, Lan12dz,³⁷ and SDD³⁸ are not sufficiently close to those of larger basis sets and therefore these basis sets cannot be considered for final geometry optimization. On the other hand, the basis set 6-31G(d) can optimize the geometry (HOMA = 0.90) close to that optimized using other larger basis sets with a negligible difference among the calculated values of HOMA (0.01), which justifies using this basis set, 6-31G(d), to obtain acceptable results for these molecular systems.

3.3. Energy calculation

In order to examine the performance of B3LYP/6-31G(d) in energy calculations, the ΔE of the model isomerization reaction shown in Figure 3 was calculated and the value was compared to

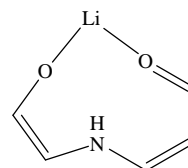


Figure 2. Structure of the model compound used to evaluate B3LYP/6-31G(d) for geometry optimization in comparison with other computational procedures.

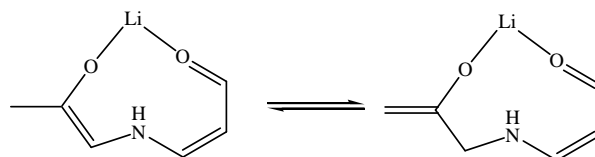


Figure 3. Model isomerization reaction used to compare the calculated ΔE obtained from a variety of computational procedures.

that calculated using other computational procedures. Lithium was selected as an example for this comparison. Table 2 shows that using HF/6-31G(d)³⁹ as the method for energy calculations of the optimized geometry with B3LYP/6-31G(d) is not suitable compared to all the other methods. The ΔE calculated using B3LYP/6-31G(d) is acceptable and comparable to that obtained using larger basis sets. To achieve further refinement of the calculated ΔE , the results from B3LYP/6-31G(d) and B3LYP/cc-PVTZ//B3LYP/6-31G(d) will also be presented.

4. Structure, selected charges, band gap, and HOMA

Many trials were run to optimize the acyclic form of these compounds, but in all cases the geometry was optimized to that appearing in Figure 4; lithium and sodium form bonds with the two oxygen atoms. The two tricyclic systems are planar which indicates that the electron pairs in the π -bonds and the nonbonding electron pairs on oxygen/nitrogen are conjugated.

The heat of reaction (ΔH) was calculated for the reaction of LiH and NaH with the Schiff base (according to Fig. 1). The calculated value for **Li-1** is -76.1 kcal/mol and for **Na-1** is -62.8 kcal/mol. The reaction is exothermic and the products appear to be more stable than the reactants. In order to understand why the acyclic form cannot be optimized, an estimation of the heat of formation of the acyclic form might be helpful. The closest acyclic model system is the formation of PhOLi and PhONa from PhOH and LiH and NaH, and their heats of formation were calculated in the same way. The values of ΔH are -43.5 kcal/mol and -31.4 kcal/mol for PhOLi and PhONa, respectively. Thus the cyclic form is more stable than the acyclic form by nearly 30 kcal/mol.

The value of HOMA for the segment OCCNCCCO (Fig. 1) of the enol-form is 0.24 (Table 3). The salt **Li-1** has a HOMA value for

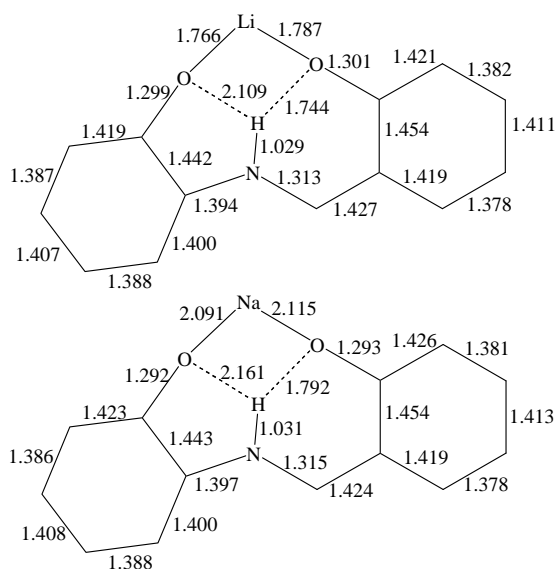


Figure 4. Structures of **Li-1** and **Na-1** and bond lengths in Ångstroms.

the same segment equal to 0.57, and for **Na-1** the HOMA value is 0.59. In **Na-1**, the HOMA value is slightly higher than that in **Li-1**, which might be attributed to differences in the sizes of the two ions Li^+ and Na^+ . Figure 5 presents selected conjugated systems with 10π electrons ($4n + 2$ rule of aromaticity; $n = 2$) and the calculated HOMA values for the entire π -system. The HOMA values for **Li-1** (0.57) and **Na-1** (0.59) predict that they will have π -electron delocalization over the OCCNCCCO segment similar to that for pyrano-pyrrole aromatic heterocyclic systems (HOMA: 0.45–0.59). Bonding of lithium and sodium to the Schiff base enhanced the delocalization of the nonbonding electrons of the nitrogen and oxygen atoms significantly, which might be attributed to the presence of an empty p-orbital on lithium and sodium of sufficient energy to overlap with the rest of the conjugated system. This similarity with pyrano-pyrroles also suggests that **Li-1** and **Na-1** have similar aromatic character, which is clarified in Section 7.

The calculated average charge (Table 3) for O-9 (Fig. 1) became closer to one-unit-atomic charge in **1-Li** (-0.794) and **1-Na** (-0.773) with respect to the enol-form (-0.640). This suggests that **1-Li** and **1-Na** demonstrate charge delocalization in the segment N5–C6–C7–C8–O9 and therefore these structures are best described as zwitterions. This analysis can also be interpreted numerically and qualitatively by calculating the changes in the HOMO–LUMO gap (the band gap). The enol-form has a band gap equal to 3.91 eV while **Li-1** has a value of 2.93 eV, and **Na-1** has a value of 2.79 eV. The decrease in the band gap means that the electron density is less localized and hence the molecular structures include charge separation. This result is consistent with the conclusion based on the calculated average charge of O-9 that the structures **Li-1** and **Na-1** are the zwitterions shown in Figure 1.

5. IR vibrations

The stretching frequencies of the CO and NH groups were identified by determining the vibrational modes of each diatomic segment based on B3LYP/6-31G(d) calculations. The structure of **Li-1** has the following stretching frequencies: CO (1670 cm^{-1}) and NH (3303 cm^{-1}). In addition, the NC bond stretches at the same frequency as that for CO. This is important and indicates that the CO and the CN bonds have nearly the same force constant. This result is in full agreement with those from the HOMA calculations (0.57) and supports that the π -electron density is delocalized. In **Na-1**, the CO group stretches at 1670 cm^{-1} and the N–H stretches at 3292 cm^{-1} . The difference compared to **Li-1** can be explained by an increase in the bond length between sodium and oxygen. Similar to **Li-1**, **Na-1** also has the CN bond stretching at the same frequency as for CO. The stretching frequency for CO in both cases (1670 cm^{-1}) is less than the typical value for C=O groups in aldehydes and ketones, supporting the fact that there is charge separation as predicted by the atomic charges calculations.

6. Isomers

The Schiff base **1** can act as a ligand for lithium and sodium and can form new structures as shown in Figure 6. The structure **M-1a** was found to be the least stable (Table 4) while structure **M-1** re-

Table 3

Band gap (eV), atomic charges on O-9 and their average charge, and the values of HOMA for the segment OCCNCCCO

Structure	Band gap	Mulliken	APT	NPA	ChelpG	Average charge	HOMA
1-enol	3.91	-0.649	-0.675	-0.687	-0.547	-0.640	0.24
1-keto	3.16	-0.604	-0.590	-0.652	-0.587	-0.608	0.40
1-Li	2.93	-0.713	-0.745	-0.867	-0.852	-0.794	0.57
1-Na	2.79	-0.704	-0.712	-0.843	-0.832	-0.773	0.59

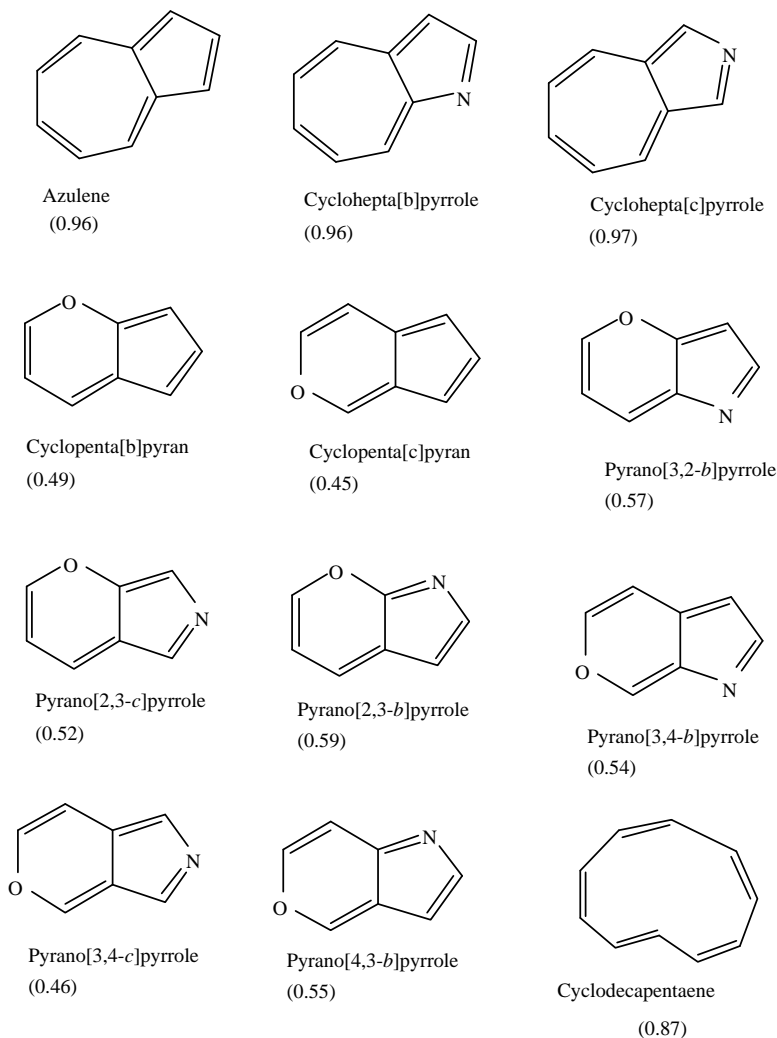


Figure 5. Selected 10 electron π -systems and the calculated values of HOMA in parentheses.

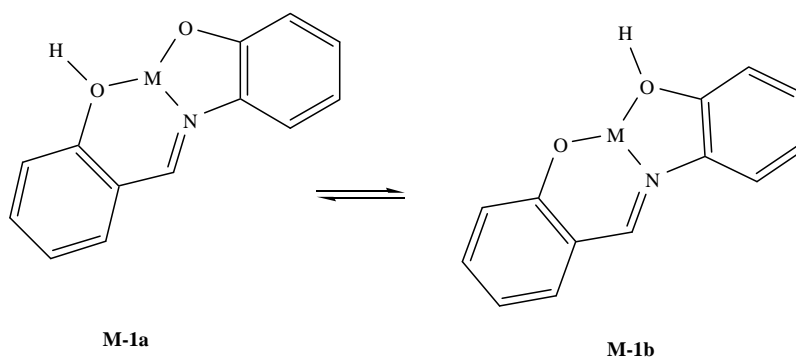


Figure 6. Possible isomers of Li-1 and Na-1.

mains the most stable. The relative stability was calculated using two methods. The results are similar to each other and predict the dominance of **M-1**, more clearly, in the case of sodium.

Molecules of **M-1** can, in principle, dimerize. The effect of this on the relative stability of the monomer versus the dimer was simulated by considering the interaction of **M-1** with one dimethyl ether (OMe_2) molecule. The calculated energies indicate that the addition of OMe_2 is a favored process and **M-1-OMe₂** is more than 10 kcal/mol more stable than the dissociated species. The effect of addition of OMe_2 (dimerization) on the relative stabilities of the

Table 4
Relative energies for **M-1a**, **M-1b**, and **M-1**

Method	Na-1a	Na-1b	Na-1
B3LYP/6-31G(d)	0.0	-7.73	-15.82
B3LYP/cc-pVTZ//B3LYP/6-31G(d)	0.0	-7.91	-14.92
	Li-1a	Li-1b	Li-1
B3LYP/6-31G(d)	0.0	-7.51	-9.80
B3LYP/cc-pVTZ//B3LYP/6-31G(d)	0.0	-7.69	-8.94

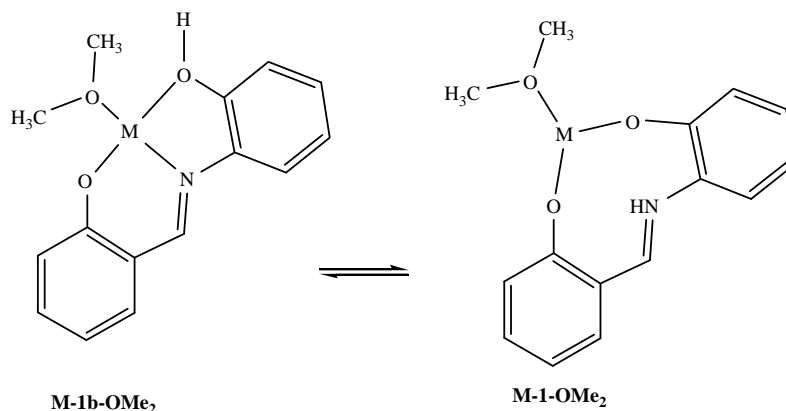


Figure 7. Simulation of dimerization using dimethyl ether as a model compound.

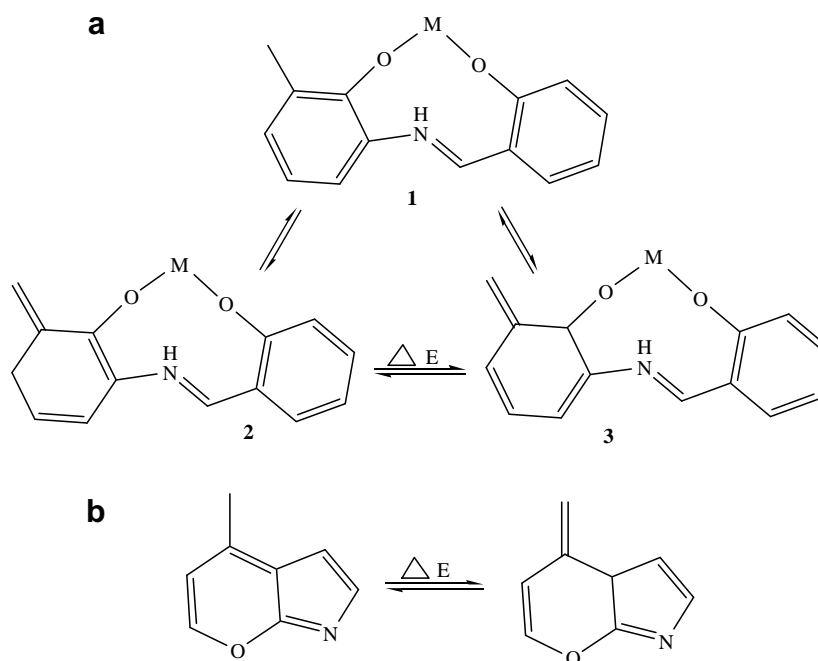


Figure 8. (a) Isomerization reactions proposed to estimate the induced stabilization gained by bonding to Li and Na in the OCCNCCCO unit, and (b) isomerization of pyrano[2,3-*b*]pyrrole for comparison.

Table 5
Relative energies of **M-1b-OMe₂** and **M-1-OMe₂**, in kcal/mol

Method	Na-1b-OMe ₂	Na-1-OMe ₂
B3LYP/6-31G(d)	0.0	-9.3
B3LYP/cc-pVTZ//B3LYP/6-31G(d)	0.0	-8.0
	Li-1b-OMe ₂	Li-1-OMe ₂
B3LYP/6-31G(d)	0.0	-7.4
B3LYP/cc-pVTZ//B3LYP/6-31G(d)	0.0	-6.3

Table 6
Isomerization energy (I.E.) for **2/3** equilibrium, in kcal/mol

Substrate	I.E. ^a	I. E. ^b
Schiff base 2/3 (H)	2.7	0.0
2/3 M = Li	11.5	8.8
2/3 M = Na	23.0	20.3

^a Isomerization energy for **2/3**.

^b Isomerization energy after correction with respect to hydrogen.

M-1 isomers, particularly **M-1b** (Fig. 7), was examined. The structures of **M-1-OMe₂** were found to be relatively more stable, which supports the dominance of **M-1** as the thermodynamically most stable isomer.

7. The induced aromaticity (stability) in the OCCNCCCO unit

Stabilization by aromaticity is an important property of conjugated cyclic molecules on their structure, reactivity, and stability. Aromaticity is generally evaluated by methods based on the geometry, the energy, and the magnetic criteria.^{40–47} Benzene is an excellent model compound for describing aromaticity by its stability and its chemical behavior. The various concepts of aromaticity are now well documented.⁴⁸ Which criterion is the best to represent aromaticity is still a matter of debate due to the limitations in the currently available indices.

To obtain an estimation for the induced aromaticity, the method proposed by Schleyer⁴⁹ was adopted in this study. Schleyer proposed that ΔE for the isomerization of toluene to 5-methylene-

cyclohexa-1,3-diene gives an idea on the stabilization energy gained by aromaticity. This idea was used in this study to evaluate the performance of different computational procedures in energy calculations shown in (Fig. 3 and Table 2). In addition, the aromaticity induced by lithium and sodium in **Li-1** and **Na-1** could be estimated. Figure 8 shows the proposed isomerization reactions to evaluate how much stabilization energy is gained in each case.

In addition, Figure 8b shows the proposed isomerization of pyrano[2,3-*b*]pyrrole, Table 5 a structure that has a similar HOMA value. Table 6 reveals that the isomerization 2/3 in the case of hydrogen does not show a considerable difference and indicates that **2** is more stable by 2.7 kcal/mol, and therefore can be set as a reference point. In the case of lithium, this isomerization requires about 11.5 kcal/mol of energy and with respect to hydrogen it is corrected to 8.8 kcal/mol. On the other hand, sodium appears to result in more stabilization energy, 23.0 kcal/mol, and after correction with respect to hydrogen it becomes 20.3 kcal/mol. Isomerization of the pyrano[2,3-*b*]pyrrole derivative (Fig. 8b) gives an aromatic stabilization energy equal to 25.0 kcal/mol. Based on these data, sodium results in greater aromatic stabilization energy than lithium, and qualitatively it might be possible to say that **Na-1** is nearly as aromatic as the pyrano[2,3-*b*]pyrrole system. This result is unprecedented and represents a unique and novel case of stabilization energy (aromaticity) induction. It should be mentioned that a similar isomerization reaction for cyclodecaheptaene, [10]annulene, was calculated by Schleyer using B3LYP/6-31G(d) and the value was found to be nearly 33 kcal/mol.⁴⁹ Qualitatively, the aromatic character in **Li-1** and **Na-1** compared to cyclodecaheptaene is one-third and two-third, respectively.

8. Conclusion

The calculations at the B3LYP level of theory identified two new Schiff base salts which exist in zwitterionic form (trapped NH form), which represent the first examples in the literature of aromatic metalla-hetero[10]annulenes. Stabilizing charge separation and delocalization⁵⁰ is important in hole/electron injection processes; an essential molecular/macromolecular activity in electronic materials. The two molecular structures **Li-1** and **Na-1** already stabilize charge separation intramolecularly therefore, derivatives (including further extended conjugation and oligomerization) of these two systems, and possibly other similar systems, can be investigated to fine-tune their physical properties, which make them candidates as building blocks for electronic materials.

Acknowledgments

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