



A theoretical study on the thermodynamic parameters for some imidazolium crystals

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ABSTRACT

We present a thermodynamic calculations of mechanical, electronic and chemical bonding in 1,3-diisopropyl-4, 5-dimethylimidazolium cyano-1-phenylthienolate (1), 1,3-diisopropyl-4,5-dimethylimidazolium-2-nitrodiethylmalonate (2) and 1,3-dicyclohexyl-4, 5-dimethylimidazoliumDicyanomethylid (3). The geometries of all fragments of the three complexes were fixed at the geometry obtained from the X-ray data. Single point calculations were performed along with frequency calculations at B3LYP density functional theory.

Key words: Imidazolium; Thermodynamic; Entropy; abinitio; Electronic energy.

INTRODUCTION

The nucleophilic strength of *N*-Heterocyclic carbenes have been in the center of our interest [1- 3].As part of a long term research projects for synthesis and characterization compounds contain imidazolium salts, we have investigated different molecules and anions of this type [4-8]. As a continuation of these studies we have performed theoretical calculations for some imidazolium compounds that have previously synthesized and characterized by X-ray,1,3-diisopropyl-4,5-dimethylimidazolium cyano-1-phenylthienolate (1) [9], 1,3-diisopropyl-4,5-dimethylimidazolium-2-nitrodiethylmalonate (2) [10] and 1,3-dicyclohexyl-4, 5-dimethylimidazoliumDicyanomethylid (3) [11].There single crystal X-ray structure analysis revealed the formation of stable C–H···X (X = O, N) hydrogen bonds between imidazolium cation and anion species.

All calculations were carried out using GAUSSIAN09 program suite [12]. The geometries of all fragments of the three complexes were fixed at the geometry obtained from the X-ray data. Single point calculations were performed along with frequency calculations at B3LYP density functional theory [13, 14] with (6-311G(d,p)) basis set polarized with d and p orbitals.

These calculations were performed with an approximation is that all the equations used to obtain the thermodynamic properties assume non-interacting particles and therefore can be applied only to an ideal gas. This limitation will introduce some error, depending on the extent of the deviation form ideal system.

Partition functions for the electronic, vibrational, rotational and translational motions were used to determine the internal thermal energy, entropy and heat capacity at constant volume. The determined parameters later were used to calculate the thermodynamic properties.

Table (1) shows the calculated thermodynamic properties for the cation and ion for each case, as well as the complex made from the combination of the two fragments. Combining the two fragments is calculated to be exothermic and spontaneous as denoted by ΔH and ΔG .

Calculated entropy agree with the expected values of the combining two fragments in one complex.

Results obtained from the Gaussian output file were with variety of energy units, all were converted to J/mole. The thermodynamic parameters were obtained from the calculated electronic energy with added corrections for the total energy as the total entropy as $E_{\text{tot}} = E_t + E_r + E_v + E_e$ and $S_{\text{tot}} = S_t + S_r + S_v + S_e$ with subscripts denote the translation, rotation, vibration and electronic motion. To calculate the enthalpy and free energy, corrections must be added to the electronic energy (ϵ_0) as $H_{\text{corr}} = E_{\text{tot}} + k_B T$ and $G_{\text{corr}} = H_{\text{corr}} - TS_{\text{tot}}$ [15].

Calculated change in entropy, enthalpy and free energy, for the reaction between the two fragments to give the complex, were all negative. Interpreting these results is straight forward as two molecules combine to form one large molecule decreases the entropy. While combining positively and negatively charged molecules is exothermic and spontaneous, denoted by the negative sign of ΔH_{rxn} and ΔG_{rxn} .

Electrostatic potential (ESP), as well as, atomic charges of the three complexes were mapped as shown in figures 1, 2 and 3. The ESP map showed that the three charge distribution around the N and O atoms in the anionic fragment of the first complex (1) has the highest extent, while the negative charge is localized between the oxygen on the nitro group and the eclipsed oxygen in the second complex (2). For the last complex (3) the negative charge is mostly on the N atom away from the cationic fragment.

To conclude, the results presented in this theoretical study are compatible with the X-ray data performed for the same compounds.

Table (1): Calculated thermodynamic parameters for the three complexes in Joule/mole at 25°C.

Calc. value	1			2			3		
	cation	anion	complex	cation	anion	complex	cation	anion	complex
ϵ_0 Internal energy	-1420661.7	-1251342.0	-2672360.0	-1420413.7	-2045061.1	-3465807.5	-2033336.9	-589348.6	-2622973.9
ϵ_{ZPE}^a Zero point energies	833.0	316.0	1153.7	838.4	483.4	1325.6	1166.6	84.9	1254.3
E_{total} Total thermal energy	853.7	337.5	1197.5	858.4	507.7	1374.7	1194.3	96.3	1293.7
S_{total} Total entropy	0.371	0.382	0.553	0.365	0.413	0.612	0.428	0.290	0.524
H_{corr} Correction for enthalpy	856.2	340.0	1200.0	860.9	510.2	1377.2	1196.8	98.8	1296.2
G_{corr} Correction for free energy	745.5	226.1	1035.3	752.0	387.2	1194.7	1069.2	12.3	1139.9
ΔS_{rxn}		-0.201			-0.166			-0.194	
ΔH_{rxn}		-352.4			-326.7			-287.9	
ΔG_{rxn}		-292.5			-277.3			-230.1	

^a $\epsilon_{\text{ZPE}} = 0.5(\text{sum of all non-imagery frequencies})$

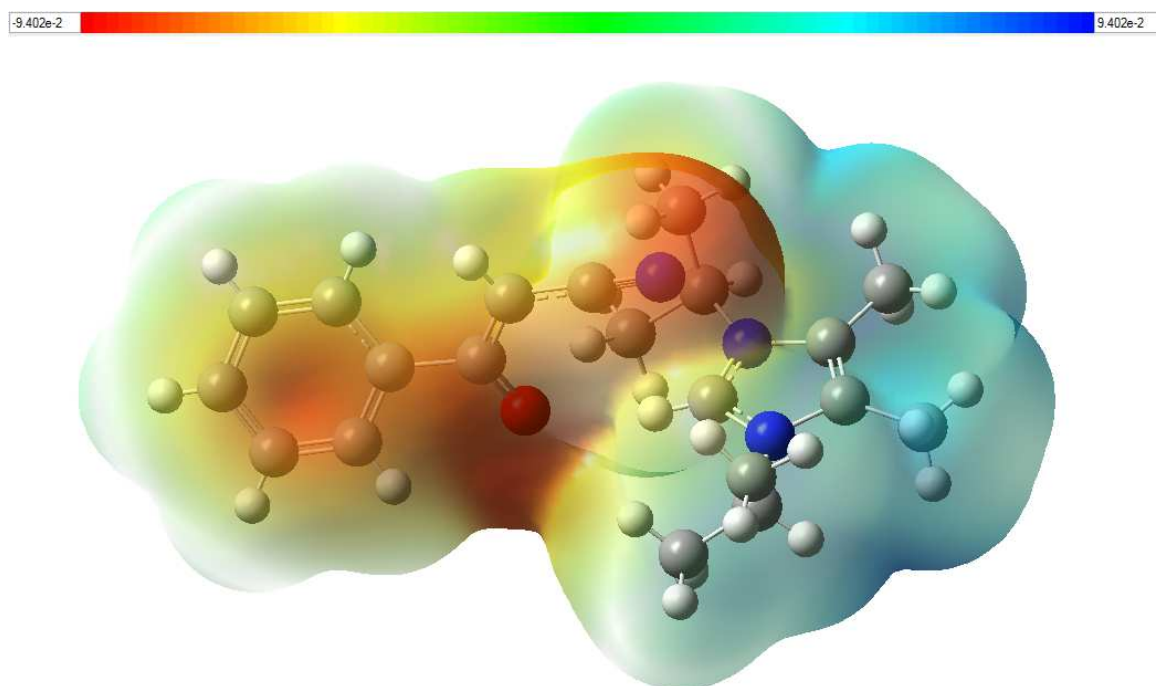


Figure 1: Electrostatic potential map for 1,3-diisopropyl-4,5-dimethylimidazolium cyano-1- phenylthiolate $C_{19}H_{27}N_3O$ (1) within the range from -9.4×10^{-2} an (red) to 9.4×10^{-2} an (blue)

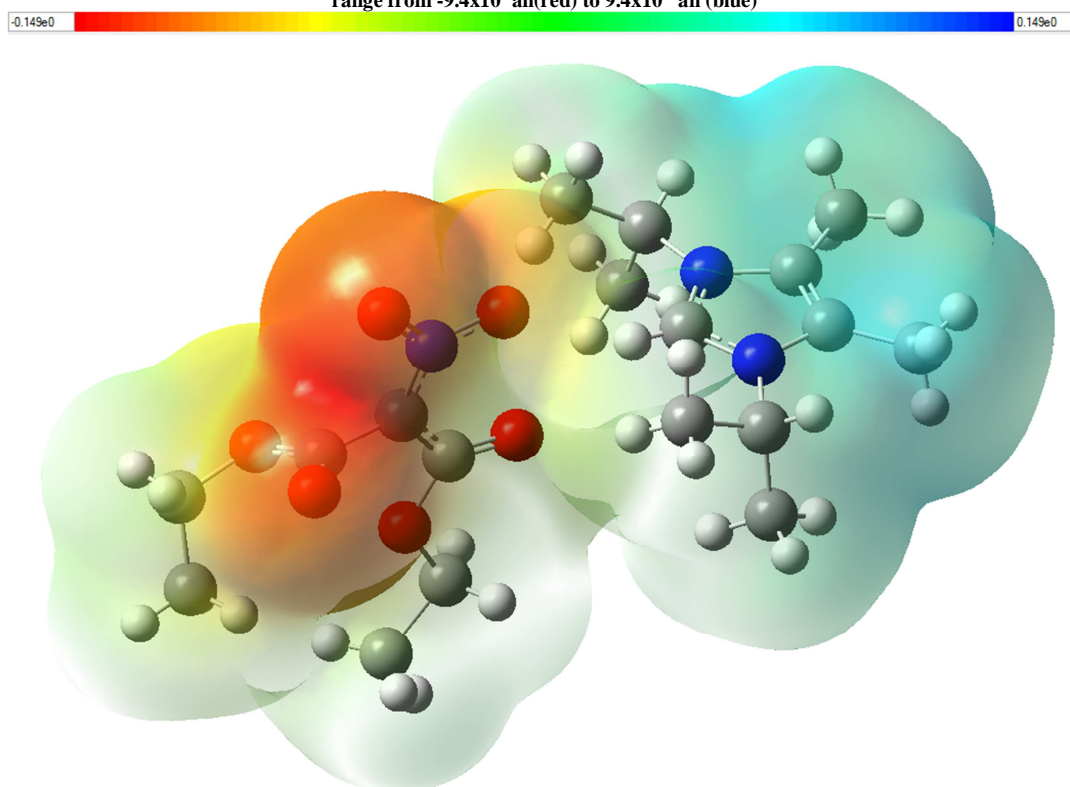


Figure 2: Electrostatic potential map for 1,3-diisopropyl-4,5-dimethylimidazolium-2-nitrodiethylmalonate $C_{18}H_{31}N_3O_6$ (2) within the range from -0.15 an (red) to $+0.15$ an (blue)

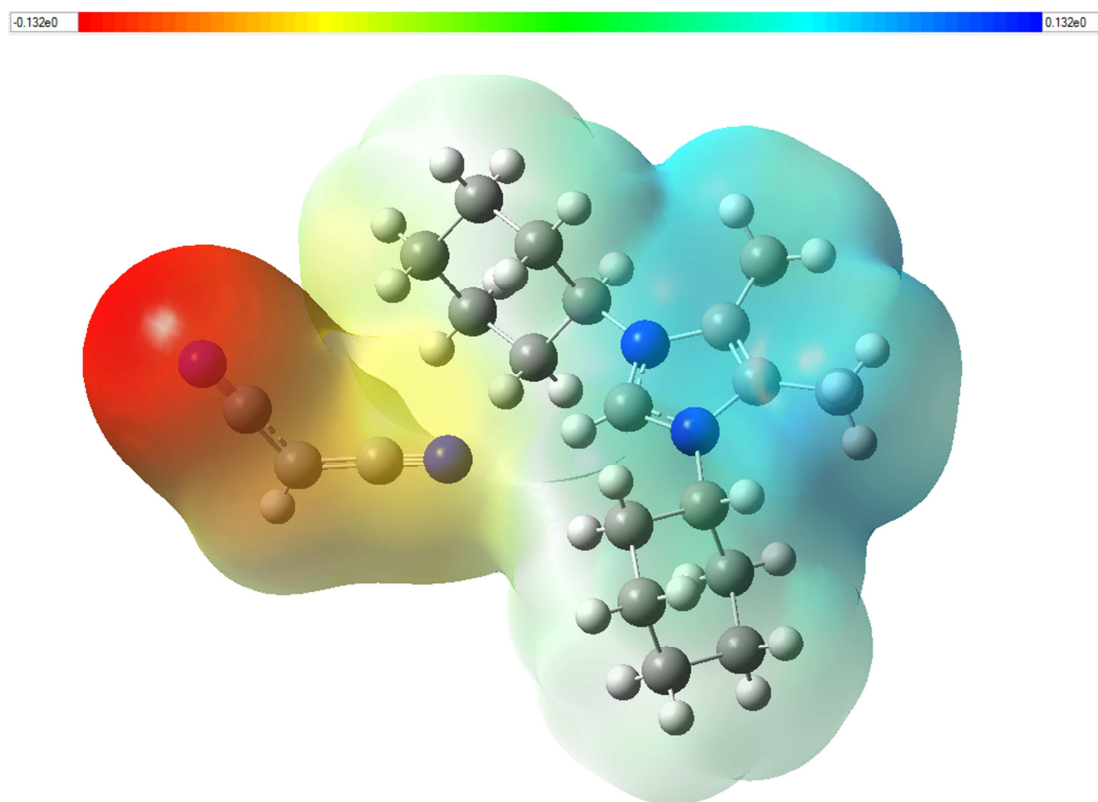


Figure 3: Electrostatic potential map for 1,3-dicyclohexyl-4,5-dimethylimidazolium Dicyanomethylid $C_{20}H_{30}N_4$ (3) within the range from -0.132e0 (red) to +0.132e0 (blue)

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REFERENCES

- [1] AJ Arduengo; H Bock; H Chen; M Denk; DA Dixon; JC green; WA Hermann; NL Joens; M Wagner; R West. *J. Am. Chem. Soc.*, **1994**, 116, 6641.
- [2] AJ Arduengo. *Accounts of Chemical Research*, **1999**, 32, 11.
- [3] N Kuhn; A Al-Sheikh. *Coord. Chem. Rev.*, **2005**, 249, 829.
- [4] AJ Arduengo; HVR Dias; RL Harlow; M Kleine. *J. Am. Chem. Soc.*, **1992**, 114, 5530.
- [5] E Mallah; Q Abu-Salem; K Sweidan; N Kuhn; C Maichle-Mößmer; M Steimann; M Ströbele; and M Walker. *Z. Naturforsch.* **2011**, 66b, 545-548.
- [6] E Mallah; K Sweidan; J Engelman; M Steimann; N Kuhn; M E Maier. *Tetrahedron*, **2012**, 68, 1005.
- [7] E Mallah; K Sweidan; W Abu Dayyih; M Steimann; and M Sunjuk. *Acta Cryst.* **2014**, E70, o1227–o1228.
- [8] Y J Kim; A Streitwieser. *J. Am. Chem. Soc.*, **2002**, 124, 5757.
- [9] K Sweidan; N Kuhn; and C Maichle-Mößmer. *Z. Kristallogr. NCS.* **2009**, 224, 295.
- [10] N Kuhn; C Maichle-Mößmer; M Steimann; and K Sweidan. *Z. Naturforsch.*, **2007**, 62b, 101.
- [11] N Kuhn; M Steimann; and K. Sweidan. *Z. Naturforsch.* **2005**, 60b, 123.
- [12] Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; 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.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas,

O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, (2004).

[13] A DBecke.*J. Chem. Phys.*, **1993**, 98, 5648.

[14] C Lee; W Yang; R GParr.*Phys rev.***1988**, B, 37, 785.

[15] J B Foresman; A EFrissch. Exploring chemistry with electronic structure methods.