

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/51167730>

Structure and Electronic Properties of Amino Acid Ionic Liquids

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · JUNE 2011

Impact Factor: 2.69 · DOI: 10.1021/jp1093965 · Source: PubMed

CITATIONS

19

READS

52

2 AUTHORS:



Afshan Mohajeri

Shiraz University

68 PUBLICATIONS 556 CITATIONS

SEE PROFILE



Abolfazl Ashrafi

Shiraz University

3 PUBLICATIONS 40 CITATIONS

SEE PROFILE

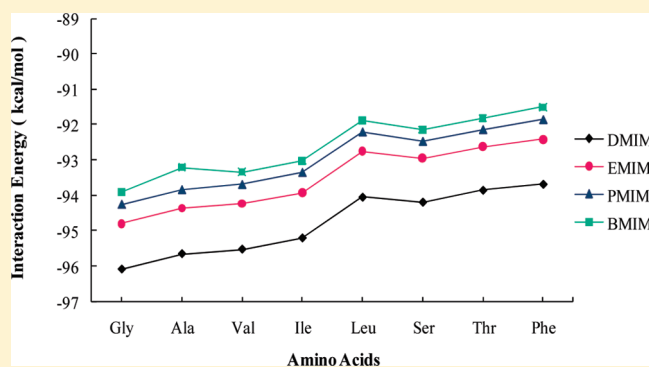
Structure and Electronic Properties of Amino Acid Ionic Liquids

Afshar Mohajeri* and Abolfazl Ashrafi

Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

Supporting Information

ABSTRACT: The interactions between eight amino acid based anions and four imidazolium-based cations have been investigated by density functional theory. The electronic and structural properties of the resulting amino acid ionic liquids (AAILs) have been unveiled by means of the atoms in molecules framework. The calculated interaction energy was found to increase in magnitude with decreasing alkyl chain length at imidazolium ring. Moreover, AAILs composed of an amino acid with some functional group such as aromatic ring had decreased interaction energy. Finally, several correlative relationships between glass transition temperature and interaction energy as well as density at bond critical point have been checked for 1-ethyl-3-methylimidazolium based ILs. Although the obtained correlations do not show excellent fits, a preliminary estimation of the glass transition temperature of different AAILs can be achieved by use of their electronic properties.



1. INTRODUCTION

Ionic liquids (ILs) are a class of novel compounds composed exclusively of organic cations (such as imidazolium, pyrimidinium, ammonium, phosphonium, etc.) and anions. ILs have very different properties from molecular liquids, making them promising substances for use in a variety of fields. ILs have captured the imagination of a large and steadily growing community of scientists due to their applications as reaction media,^{1–3} in batteries and supercapacitors,^{4,5} in solar and fuel cells,^{6,7} for electrochemical deposition of metals and semiconductors,⁸ for protein extraction and crystallization,⁹ in nanoscience,^{10,11} in physical chemistry,¹² and many others. Despite the enormous number of combinations of cations and anions, based on the diversity of organic ions, there are limited types of effective ions for ILs, having physical and chemical properties suitable for applications.

The physical and chemical properties of ILs depend on the nature and size of both their cation and anion constituents and they can be changed or modulated by changing the anion or cation or modifying the nature of substituents on cation. The presence of specific groups on the cation or on the anion is able to impart highly specific properties to the ionic liquid.^{13–15} Consequently, design of new ionic liquids has become one of the most active areas of research. For a rational design it is necessary to correlate the key physical and chemical properties of the already investigated ILs to their chemical structure. However, bulk properties such as melting point, viscosity, and density have been determined for many ionic liquids,¹⁶ and several attempts have been made to correlate these properties to structural features.¹⁷

Development of amino acid ionic liquids (AAILs) provides a great opportunity for novel generation of ILs which are promising

alternatives to used ILs.^{18–20} Since amino acids have both a carboxylic residue and an amino group in a single molecule, they can be used as either anions or cations. The advantages of using amino acids are their low cost, biodegradability²¹ and biological activity.²² Additionally, these are nontoxic and pharmaceutically acceptable.²³ These appealing features have attracted considerable attention in recent years. In 2005, Ohno et al. have synthesized a new kind of AAIL that is directly derived from naturally occurring amino acids.^{24,25} The properties of the resulting ionic liquids depend on the side groups of the amino acids involved. In a more recent investigation, Gao et al. have performed a theoretical study on the structure and cation–anion interaction of proline cation based AAIL [Pro]⁺[NO₃][–].²⁶ Li and co-workers studied the relationship between the interaction energy and the melting point of amino acid cation based ionic liquids.²⁷

In the current study we focus on the molecular interaction and conformational analysis of several AAILs which are composed of 1-alkyl-3-methylimidazolium cation and amino acid anions (Scheme 1).

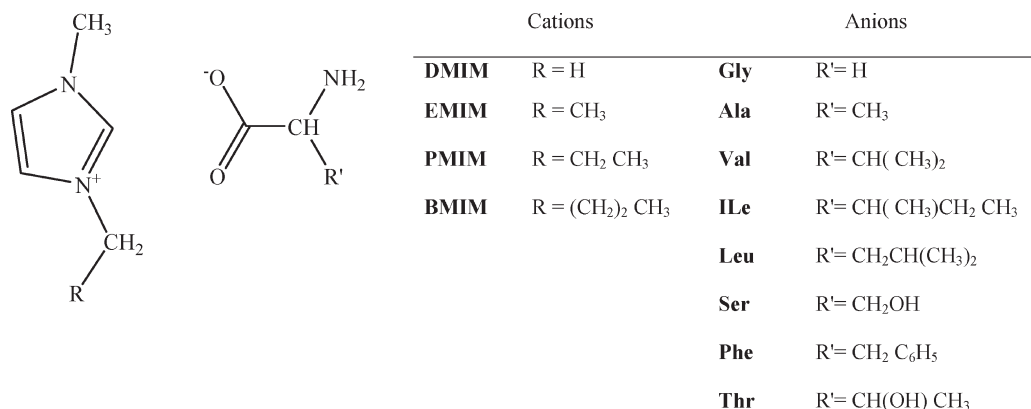
Possible conformers are simulated with respect to different molecular interactions between various cations and anions and the lowest energy conformers are obtained in the light of energy and geometry. The effects of alkyl side chain of the imidazolium ring and amino acid functional group on the nature of interaction have been investigated. Moreover, properties extracted from AIM analysis of the resultant complexes were used to provide

Received: September 30, 2010

Revised: April 27, 2011

Published: May 26, 2011

Scheme 1



proper correlations with the glass transition temperature of some studied ILs.

2. COMPUTATIONAL METHODS

The hybrid density functional theory method B3LYP together with the standard basis set 6-311++G** was used for the geometry optimization of all isolated cations and anions as well as the resulting ion pairs. Each optimization step was counterpoise²⁸ corrected for the basis set superposition error (BSSE). The supermolecule method was used in the calculation of interaction energy between the ion pairs. All of the calculations have been performed with the Gaussian 03 program.²⁹ Analysis of the topology of the electron density has been performed using Bader's theory of atoms in molecules.³⁰ The AIM2000 package was employed for calculating the bond critical points and visualizing the bond paths.³¹

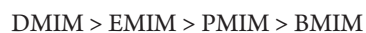
3. RESULTS AND DISCUSSION

Mutual orientations of cations and anions led to various conformers on the basis of molecular interaction. Herein, the geometries of ion pairs of 32 compounds composed of cations and anions shown in Scheme 1 were optimized in such a way that all the structural parameters of cations and anions as well as their relative position with respect to each other were free to be optimized. For that there probably exist different stable conformations for each ion pair. To make sure that the most stable geometries were gotten, different initial guess geometries were chosen for the studied AAILs. For example in the optimization of [EMIM][Gly], seven stable conformations were obtained during the optimization which are shown in Figure 1. As seen from this figure the interactions occur between oxygen atoms of Gly anion and several sites of imidazolium ring, including hydrogen atoms of methyl and methylene groups and the three hydrogens on the imidazolium ring. The optimized structure of conformation a in [EMIM][Gly] complex as well as hydrogen bond labeling is shown in Figure 2, as a representative ion pair. The total electronic energy calculated and the relative stabilization energies (with respect to the lowest energy conformer) for the seven stable conformers of [EMIM][Gly] ionic liquid are reported in Table 1. As seen from this table, the lowest energy conformers are a, b, e, and f in which the oxygen atoms of Gly anion interact with one of the ring's hydrogens at position C7

(Figure 2) and one hydrogen of methyl or methylene group. However, the energy differences between these four conformations are not very pronounced while for the other three conformers a significant reduction in the relative stability has been observed. This finding is in accord with previous experimental IR and NMR spectroscopy data³² and theoretical studies³³ which have demonstrated that among three hydrogens of the imidazolium ring, H16 positioned on C7 causes stronger interaction with anion.

In order to study the role of amino acid's functional groups and alkyl side chain of the imidazolium ring, similar structures were optimized for the interaction between different cations and anions presented in Scheme 1. The electronic properties of hydrogen bonds in conformer a of all the resultant AAILs were studied using different criteria, which are discussed in the forthcoming subsections.

Interaction Energies of Ion Pairs. The interaction energy is one of the most powerful measurements for estimating the strength of noncovalent interactions. Table 2 shows the interaction energies corrected with BSSE for the two conformers (a and f) of the AAILs investigated here. The calculated interaction energies in Table 2 demonstrate that for all 32 AAILs the difference between ΔE of conformations a and f is less than 1 kcal/mol. The variation of interaction energy for all studied ion pairs in their conformation a is presented in Figure 3. Considering configuration a for all ion pairs, it is observed that Gly forms more stable complexes with different studied cations. Also the stability of AAILs slightly decreases as the functional group of amino acids becomes larger. In the interaction between a specific amino acid with various cations, the following trend has been observed for the stability of conformation a of the resultant AAILs



However, increasing the alkyl side chain coincided with gradual decrease in interaction energy, because the side chain is not directly involved in the interaction.

AIM Analysis of Hydrogen Bonds. A topological analysis of the electron density reveals the existence of two bond critical points (BCPs) between the oxygens of anion (donor) and the hydrogen atoms of cation, indicating two hydrogen bonds of C=O...H—C type in the resultant complexes. The properties at the BCPs were analyzed in terms of the electron density

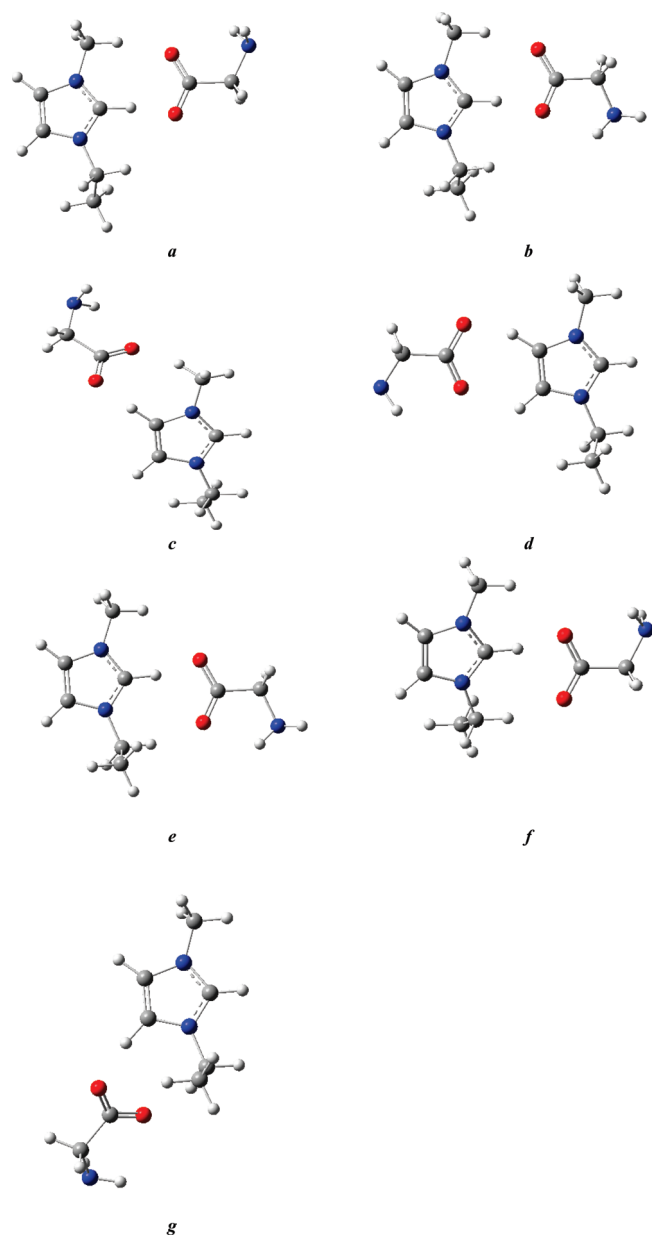


Figure 1. The seven more stable conformations of [EMIM][GLY].

(ρ_{BCP}) and the corresponding Laplacian ($\nabla^2 \rho_{\text{BCP}}$). The results for individual H-bond of conformer **a** in each complex are available in the Supporting Information (Table S1). It can be observed that the values of electron density are about 0.05 and 0.02 au for H-bond 1 and H-bond 2 in all 32 studied ionic liquids, respectively. The values of $\nabla^2 \rho_{\text{BCP}}$ are all positive with a range of 0.0130–0.134 au for H-bond 1 and 0.063–0.074 au for H-bond 2. These values are within the commonly accepted values for normal H-bonding,³⁴ thus demonstrating the typical closed-shell interactions of these complexes. The calculated values of the H-bond distance and electron density at BCPs reveal that imidazolium ring hydrogens makes stronger H-bonds in comparison to hydrogens of methylene groups.

For hydrogen bonds, there is a relationship between the interaction energy and topological parameters at the BCP.³⁵ Here, the existence of such a relationship has been checked for the investigated AAILs. Figure 4 presents the linear correlation

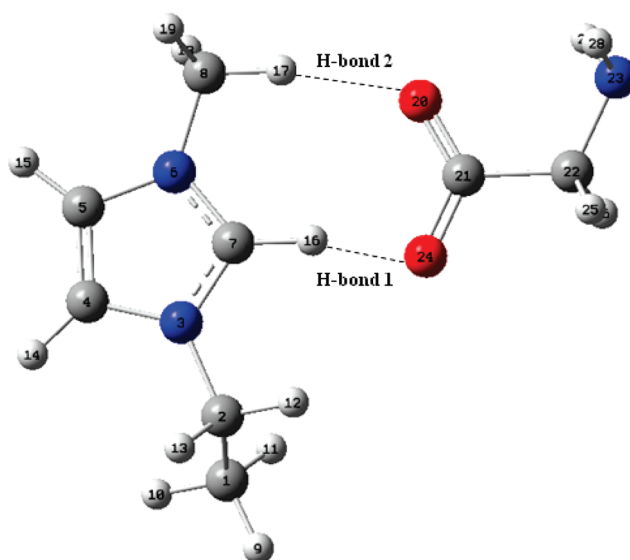


Figure 2. The optimized structure of conformation **a** and H-bond labeling in [EMIM][Gly] as representative example.

Table 1. Total Energy (in Hartree) and Relative Stabilization Energies (kcal/mol) for Different Conformations of [EMIM][Gly]

conformer	<i>E</i>	relative stabilization
a	−628.765470	0.00
f	−628.764758	0.45
b	−628.763989	0.93
e	−628.763757	1.07
g	−628.750951	9.13
c	−628.750640	9.31
d	−628.745464	12.55

between the interaction energy and sum of ρ_{BCP} of the two intermolecular BCPs in all studied ionic liquids ($R^2 = 0.836$).

Another parameter that is usually closely associated with the strength of a hydrogen bond (in $\text{X}-\text{H}\cdots\text{Y}$) is the elongation that the formation of this bond causes in the $\text{X}-\text{H}$ bond.³⁶ This elongation has been observed in the $\text{C}-\text{H}$ bond of the cations in ILs under investigation. Along with the elongation of the $\text{C}-\text{H}$ bond length, vibrational frequency of this bond suffers a substantial reduction upon formation of a H-bond. The amounts of this red shift for individual H-bond of the considered AAILs are reported in the last column of Table S1 in the Supporting Information. In accord with the obtained interaction energies, the computed values of $\Delta\nu$ show that the largest shifts in $\text{C}-\text{H}$ frequency have occurred in DMIM complexes while the smallest variations are observed in BMIM and PMIM containing ILs. Among all studied amino acids the weakest interaction in Phe containing complexes suffers a red shift less than 700 cm^{-1} ; this quantity climbs to nearly 790 cm^{-1} for the Gly as better proton acceptors.

Correlation between Glass Transition Temperature and Electronic Properties. The available experimental results for the glass transition temperature (T_g) of EMIM-based AAILs²⁴ (see Table 3) offers a good opportunity to check the correlation between calculated electronic properties of AAILs and T_g values. AAILs composed of an amino acid with some functional group

Table 2. Interaction Energies Corrected with BSSE (kcal mol⁻¹) for Conformations a and f for Studied AAILs

	Gly	Ala	Val	Ile	Leu	Ser	Thr	Phe
DMIM-a	-96.10	-95.66	-95.53	-95.21	-94.05	-94.19	-93.85	-93.68
DMIM-f	-95.74	-95.12	-95.17	-94.86	-93.77	-94.01	-93.70	-93.47
EMIM-a	-94.86	-94.37	-94.24	-93.93	-92.75	-92.95	-92.62	-92.42
EMIM-f	-94.41	-93.98	-94.03	-93.73	-92.65	-92.74	-92.39	-92.39
PMIM-a	-94.25	-93.84	-93.70	-93.36	-92.21	-92.48	-92.15	-91.87
PMIM-f	-94.02	-93.41	-93.46	-93.17	-92.09	-92.44	-92.14	-91.78
BMIM-a	-93.91	-93.21	-93.34	-93.03	-91.89	-92.14	-91.82	-91.51
BMIM-f	-93.68	-93.09	-92.12	-92.81	-91.76	-91.18	-91.87	-91.46

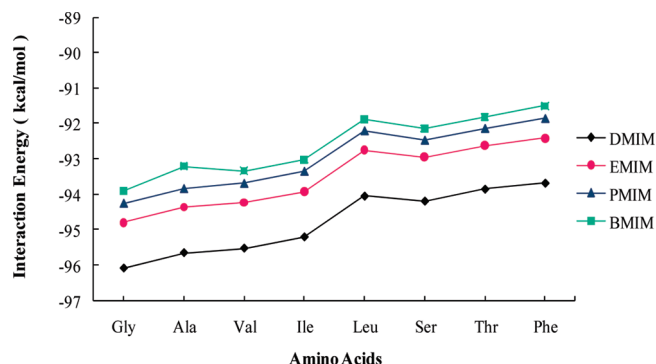


Figure 3. Interaction energy variation for conformation a in all studied AAILs.

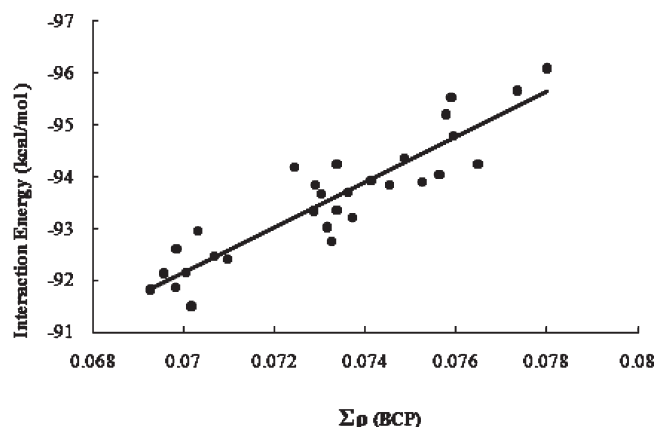


Figure 4. Relationship between the interaction energy and sum of densities at BCPs for all studied AAILs in conformation a.

Table 3. The Glass Transition (°C) of EMIM-Based ILs

AAILs	T_g^a
EMIM-Gly	-65
EMIM-Ala	-57
EMIM-Val	-52
EMIM-Ile	-52
EMIM-Leu	-51
EMIM-Thr	-40
EMIM-Phe	-36

^a T_g values are taken from ref 24.Table 4. Regression Equations between Electronic Properties and Glass Transition Temperature of EMIM-Based Ionic Liquids (Conformation a)^a

properties	α	β	R^2
ΔE_{int}	9.0	796.2	0.796
ρ_{BCP} (H-bond 1)	-5074.8	217.4	0.923
ρ_{BCP} (H-bond 2)	-2491.7	458.2	0.646

^a The regression equation is $Y = \alpha X + \beta$, where Y is glass transition temperature (T_g) and X can be one of the properties listed in the first column.

such as a hydrogen bonding group or aromatic ring has an increased glass transition temperature. Moreover, an increase in the alkyl side chain coincided with gradual increase of T_g , probably due to an increase of van der Waals force between alkyl side chains. Thus, the electronic structure of ILs is an important parameter to determine T_g .

Table 4 collects the corresponding parameters of the linear regression equations between calculated properties of conformer a including interaction energy and density at BCPs with glass transition temperature for EMIM-based AAILs. In view of resultant correlation coefficients, it could be concluded that density at BCPs of the H-bonds 1 exhibits a rather good correlation with T_g ($R^2 = 0.923$) while the use of ρ_{BCP} at H-bond 2 makes the correlation worse. Thus, density at BCPs of the H-bonds 1 can be recommended as a proper descriptor for prediction of the glass transition temperature of AAILs.

4. CONCLUSIONS

Systematic investigation of electronic structure and molecular interactions in amino acid ionic liquids composed of 1-alkyl-3-methylimidazolium cations and eight amino acid anions have been presented. Several stable conformers were simulated with respect to different orientation of cation and anion and the electronic properties of hydrogen bond interaction have been analyzed for the lowest energy conformers. The calculated interaction energies of the two lowest energy conformations span over a range of -91.18 to -96.10 kcal/mol. Among all studied amino acids and imidazolium cations, Gly and DMIM, respectively, were found to form the most stable complexes with their counterion.

Moreover, it was shown that in each ion pair two H-bonds of $\text{C}=\text{O} \cdots \text{H}-\text{C}$ type form which are different in nature. The calculated values of electron density at BCPs of H-bond 1, in which the imidazolium ring hydrogen is involved, is more than two times the values obtained for H-bond 2 where one hydrogen of methyl or the methylene group is involved. In the last part,

correlative relationships between glass transition temperature and interaction energy as well as density at BCPs have been checked for EMIM-based ILs. It is found that density at BCPs of the H-bonds 1 exhibits the best correlation with T_g ($R^2 = 0.923$). However, although the obtained correlations do not show excellent fits, they can be used in a predictive manner for estimation of glass transition temperature of different AAILs through the use of their electronic properties.

■ ASSOCIATED CONTENT

Supporting Information. Binding distances, electron density at BCP, Laplacian of electron density at BCP, and shift in C–H stretching vibrational frequency (Table S1). This material is available free of charge via the Internet at <http://pubs.acs.org>

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: amohajeri@shirazu.ac.ir.

■ REFERENCES

- (1) Wassercheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, 39, 3772.
- (2) Wassercheid, P.; Keim, W. *Angew. Chem.* **2000**, 112, 3926.
- (3) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, Germany, 2008.
- (4) Shobukawa, H.; Tokuda, H.; Susan, A. B. H.; Watanabe, M. *Electrochim. Acta* **2005**, 50, 3872.
- (5) Buzzeo, M. C.; Evans, R. G.; Compton, R. G. *ChemPhysChem* **2004**, 5, 1106.
- (6) Wang, P.; Zakeeruddin, S. M.; Comte, P.; Exnar, I.; Gratzel, M. *J. Am. Chem. Soc.* **2003**, 125, 1166.
- (7) Wang, P.; Zakeeruddin, S. M.; Moser, J.-E.; Gratzel, M. *J. Phys. Chem. B* **2003**, 107, 13280.
- (8) El Abedin, S. Z.; Endres, F. *Chem. Phys. Chem.* **2006**, 7, 58.
- (9) Du, Z.; Yu, Y.-L.; Wang, J.-H. *Chem.—Eur. J.* **2007**, 13, 2130.
- (10) Lee, B. S.; Chi, Y. S.; Lee, J. K.; Choi, I. S.; Song, C. E.; Namgoong, S. K.; Lee, S. G. *J. Am. Chem. Soc.* **2004**, 126, 480.
- (11) Antonietti, M.; Kuang, D.; Smarsly, B.; Zhou, Y. *Angew. Chem.* **2004**, 116, 5096.
- (12) Endres, F.; El Abedin, S. Z. *Phys. Chem. Chem. Phys.* **2006**, 8, 2101.
- (13) Fei, Z.; Zhao, D.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J. *Chem.—Eur. J.* **2004**, 10, 4886.
- (14) Itoh, H.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **2004**, 126, 3026.
- (15) Zhao, D.; Fei, Z.; Geldbach, T.; Scopelliti, R.; Dyson, P. J. *J. Am. Chem. Soc.* **2004**, 126, 15876.
- (16) Chiappe, C.; Pieraccini, D. *J. Phys. Org. Chem.* **2005**, 18, 275.
- (17) Kddermann, T.; Wertz, C.; Heintz, A.; Ludwig, R. *Angew. Chem., Int. Ed.* **2006**, 45, 3697.
- (18) Tao, G. H.; He, L.; Sun, N.; Kou, Y. *Chem. Commun.* **2005**, 28, 3562.
- (19) Plaquevent, J. C.; Levillain, J.; Guillen, F.; Malhiac, C.; Gaumont, A. C. *Chem. Rev.* **2008**, 108, 5035.
- (20) Chen, X.; Li, X.; Hu, A.; Wang, F. *Tetrahedron: Asymmetry* **2008**, 19, 1.
- (21) Gathergood, N.; Garcia, M. T.; Scammells, P. J. *Green Chem.* **2004**, 6, 166.
- (22) Docherty, K. M.; Kulpa, C. F., Jr. *Green Chem.* **2005**, 7, 185.
- (23) Pretti, C.; Chiappe, C.; Pieraccini, D.; Gregori, M.; Abramo, F.; Monnia, G.; Intorre, L. *Green Chem.* **2006**, 8, 238.
- (24) Fukumoto, K.; Yoshizawa, M.; Ohno, H. *J. Am. Chem. Soc.* **2005**, 127, 2398.
- (25) Ohno, H.; Fukumoto, K. *Acc. Chem. Res.* **2007**, 40, 1122.
- (26) Gao, H.; Zhang, Y.; Wang, H. J.; Liu, J.; Chen, J. *J. Phys. Chem. A* **2010**, 114, 10243.
- (27) Li, W.; Wu, X.; Qi, Ch.; Rong, H.; Gong, L. *J. Mol. Struct. (THEOCHEM)* **2010**, 942, 19.
- (28) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, 19, 553.
- (29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; 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.; 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.; Pople, J. A. *Gaussian 03, revision B.03*; Gaussian, Inc.: Pittsburgh, PA, 2003.
- (30) Bader, R. F. W. *Atoms in Molecules, A Quantum Theory*; Oxford University Press: New York, 1990.
- (31) Bader, R. F. W. *AIM2000 Program, ver 2.0*; McMaster University: Hamilton, ON, Canada, 2000.
- (32) Wulf, A.; Fumino, K.; Michalik, D.; Ludwig, R. *ChemPhysChem* **2007**, 8, 2265.
- (33) Talaty, E. R.; Raja, S.; Storhaug, V. J.; Dölle, A.; Carper, W. R. *J. Phys. Chem. B* **2004**, 108, 13177.
- (34) Koch, U.; Popelir, P. L. A. *J. Phys. Chem. A* **1995**, 99, 9747.
- (35) Mohajeri, A.; Fadaei, F. *J. Phys. Chem. A* **2008**, 112, 281.
- (36) Hobza, P.; Spirko, V.; Selzle, H. L.; Schlag, E. W. *J. Phys. Chem. A* **1998**, 102, 2501.