HETEROCYCLES, Vol. 71, No. 3, 2007, pp. 589 - 596 © The Japan Institute of Heterocyclic Chemistry
Received, 30th November, 2006, Accepted, 12th January, 2007, Published online, 15th January, 2007, COM-06-10960

SOLVATION EFFECTS ON IMIDAZOLIUM SALTS THAT CONTAIN ALKYL SIDE CHAINS

Allan D. Headley,* S. R. S. Saibabu Kotti,[#] and Bukuo Ni

Department of Chemistry, Texas A&M University-Commerce, Commerce, TX 75429-3011, USA, E-Mail: Allan_Headley@tamu-Commerce.edu
[#]Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061, USA

Abstract – Solvation effects of imidazolium salts that contain alkyl side chains in the 1 and 3 positions have been analyzed using multi-linear regression equations. The major contribution for the solvation of these compounds comes from the solvents' hydrogen bond acceptor basicity contribution, in which there is an interaction between the solvent and H2 hydrogen of the imidazolium cation. Another solvation effect, which is minimal, comes from the solvents' hydrogen bond donor acidity contribution, which serves to solvate the anions. The nature of the anion plays a role in the solvation of the anions. Salts with hard anions are solvated to a lesser extent via the solvents' hydrogen bond acceptor basicity; whereas, salts with softer anions are solvated to a larger extent via this mode. There is not much discrimination in the solvation of imidazolium salts that contain the same anion and different alkyl groups in positions 1 and 3.

INTRODUCTION

Due to the unique combination of properties of rt ionic liquids (RTILs), they have become promising candidates as solvents for a wide variety of organic reactions.[1] Compared to conventional solvents, RTILs are recyclable, thermally stable over a very wide temperature range, and some maintain their liquid state at temperatures as high as 200 °C.[2] Due to these properties, they have become ideal "green solvents" for a wide array of reactions.[3] RTILs consist of cations and anions counterparts; cations are typically imidazolium or pyridium species and anions normally include halogen anions, AlX_4^-, BF_4^-, PF_6^-, $CF_3SO_3^-$ or $(CF_3SO_3)_2N^-$. A very important property of RTILs is that they are relatively polar compounds, and as a result are able to dissolve a wide variety of polar reactants and stabilize polar reaction intermediates.[4] Ionic liquids have been shown to influence the outcome of reactions in a number of ways, such as higher reaction rates and better reaction control.[5] By varying the structure of the cation or the anion of ionic liquids, their properties can be altered to influence the outcome of various organic reactions,[6] including asymmetric reactions.[7]

The ability of solvents to influence the outcomes of reactions depends to a large extent on significant solute/solvent interactions that exist. An important property of solvents is their ability to be involved in various types of interactions with reactants, reaction intermediates and products; and various relationships have been developed over the years to better understand the nature of solvent/solute interactions.[8] These relationships are often referred to as quantitative structure-property relationships (QSPR). The Hammett equation is one such relationship and it is based on the assumption that linear free energy relationships (LFER) exist between the structure and the property of compounds.[9]

The general LFER developed by Kamlet, Taft and co-workers to examine the effects of various solute/solvent interactions and how they affect property changes is shown in Equation 1.[10]

$$\textbf{Property = bulk/cavity term + dipolarity/polarizability term(s)}$$
$$\textbf{+ hydrogen bonding term(s) + constant} \qquad \textbf{(1)}$$

The bulk/cavity term is a measure of the energy that is needed to overcome the cohesive solvent/solvent interactions to form a cavity for the solute molecule. The dipolarity/polarizability terms are measures of the energies of solute/solvent dipole and induced dipole interactions that contribute to solvation. Hydrogen bonding terms measure specific interactions between solvent and solute. They reflect the ability of the solvent to accept a hydrogen bond(s) from the solute, which is described as the hydrogen bond acceptor basicity (HBAB), and the ability of the solvent to donate a hydrogen bond(s) to the solute, which is described as the hydrogen bond donor acidity (HBDA).

Over the years, a number of descriptors have been developed to quantify the various solute/solvent interactions, but those developed by Taft and co-workers are used routinely in LFER.[11] These descriptors, developed from thermodynamic and spectroscopic data for solvents and solutes, have been used in Equation 2 to successfully correlate the chemical, physical and biological properties of more than 200 compounds.[12]

$$\textbf{Property} = s\pi^* + a\alpha + b\beta + c \qquad \textbf{(2)}$$

For the multi-linear regression (MLR) equation 2, the solvatochromic parameters, π^* represents the dipolarity/polarizability contribution, α and β represent the solvents' hydrogen bond donor acidity (HBDA) and the hydrogen bond acceptor basicity (HBAB) properties, respectively. For Equation 2, linear statistical fitting between the variables is used; the goodness of the 'fit' is reflected by the regression coefficient (R), standard deviation (SD) and the ability of the equation to predict accurately the experimental values. The coefficients of the MLR equations, s, a, and b, indicate the significance of the different solute/solvent interactions for the property being analyzed. In this study, the nature of the interactions that exist between conventional solvents and imidazolium salts, which contain different alkyl groups and anions is examined using LFER analysis by examining the ^{1}H NMR chemical shift change of H2 of the imidazolium cation in different solvents. Solute/solvent interactions that increase the chemical shift values (further downfield) result in negative coefficients; whereas, interactions that decrease the chemical shift values (further upfield) result in positive coefficients. Significant interactions manifest themselves in larger coefficients, compared to interactions that are minimal, which exhibit smaller coefficients.

RESULTS AND DISCUSSION

Table 1 shows the results obtained in various deuterated solvents.

Table 1. Solvatochromic parameters,[13] along with the H2 ^1H chemical shift values of 1,3-dialkylimidazolium salts (Figure 1) in different deuterated solvents at 298 K. Solution concentrations are 0.45(±0.01) molL^{-1} for all compounds.

Entry	Solvent	π*	A	β	δH2 R= C_2H_5	δH2 R= C_4H_9	δH2 R= C_8H_{17}	X^-
1	HOAc	0.62	1.09	0.60	8.583	8.611	8.620	SbF_6^-
					8.650	8.639	8.702	PF_6^-
					[a]	8.767	[a]	BF_4^-
2	MeOH	0.60	0.98	0.62	8.804	8.817	8.800	SbF_6^-
					8.782	8.776	8.817	PF_6^-
					8.856	8.880	[a]	BF_4^-
3	Acetone	0.72	0.07	0.48	9.001	9.015	8.987	SbF_6^-
					8.924	8.953	9.012	PF_6^-
					8.999	9.009	[a]	BF_4^-
4	DMSO	1.00	0.00	0.76	9.157	9.169	9.175	SbF_6^-
					9.136	9.152	9.170	PF_6^-
					9.123	9.131	[a]	BF_4^-
5	DMF	0.88	0.00	0.69	9.300	9.316	9.319	SbF_6^-
					9.240	9.268	9.334	PF_6^-
					9.257	9.248	[a]	BF_4^-
6	$CDCl_3$	0.76	0.34	0.00	[a]	[a]	8.460	SbF_6^-
					[a]	[a]	8.588	PF_6^-
					[a]	[a]	[a]	BF_4^-
7	NM	0.85	0.23	0.30	8.525	8.516	8.735	SbF_6^-
					8.518	[a]	[a]	PF_6^-
					[a]	[a]	[a]	BF_4^-
8	CD_2Cl_2	0.80	0.22	0.00	8.395	8.409	[a]	SbF_6^-
					[a]	8.501	[a]	PF_6^-
					8.886	8.897	[a]	BF_4^-
9	*i*-PrOH	0.46	0.78	0.90	9.001	8.819	9.067	SbF_6^-
					8.912	8.832	9.139	PF_6^-
					9.027	8.998	[a]	BF_4^-
10	EtOH	0.54	0.86	0.77	8.819	8.866	9.045	SbF_6^-
					8.878	8.839	9.076	PF_6^-
					8.993	9.017	[a]	BF_4^-

[a] Insoluble or partially soluble in the deuterated solvent. HOAc, Acetic acid; MeOH, methanol; DMSO, dimethyl sulfoxide; DMF, dimethyl formamide; NM, nitromethane; *i*-PrOH, *iso*-propanol; EtOH, ethanol.

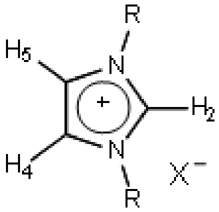

Figure 1. Structure of imidazolium salts considered in this study.
R = C_2H_5, C_4H_9 and C_8H_{17}; and X = SbF_6, PF_6 and BF_4.

It is obvious from Table 1 that the chemical shift changes are solvent dependent. For example, the H2 chemical shift values for 1,3-diethylimidazolium hexafluoro-antimonate vary between 8.395 ppm in CD_2Cl_2 and 9.300 ppm DMF. Table 2 shows the coefficients and statistics for the MLR equations in which the chemical shift change for H2 and the solvatochromic parameters (shown in Table 1) were considered. A larger data set would have been desired, but owing to the limited solubility of these compounds in a wide variety of deuterated solvents, our study was restricted to the solvents shown in Table 1. Even with this limited data set, a standard deviation of <0.15 and 0.966> R >0.906 were obtained for these relationships. For the MLR equations, the solvent dipolarity/polarizability effect was not of statistical significance and as a result was excluded in these correlations. This observation is reasonable because it is known that ionic liquids are relatively polar compounds,[14] and as a result they do not require significant stabilization via this mode from the solvent.

Table 2. Coefficients and Statistics for the MLR for the Individual sets;

$\Delta\delta = s\pi^* \quad + \quad a\alpha + b\beta + c$

Salt	a(±)	b(±)	c(±)	N	R	SD
1) R=C_2H_5; X=SbF_6	-0.44(0.09)	1.02(0.15)	8.47(0.09)	9	0.947	0.11
2) R=C_4H_9; X=SbF_6	-0.44(0.12)	0.94(0.20)	8.51(0.12)	9	0.906	0.15
3) R=C_8H_{17}; X=SbF_6	-0.39(0.07)	0.92(0.11)	8.58(0.07)	9	0.966	0.15
4) R=C_2H_5; X=PF_6	-0.37(0.09)	0.99(0.23)	8.43(0.15)	8	0.919	0.11
5) R=C_4H_9; X=PF6	-0.42(0.08)	0.72(0.14)	8.65(0.09)	8	0.945	0.10
6) R=C_8H_{17}; X=PF_6	-0.35(0.07)	0.79(0.12)	8.68(0.08)	8	0.957	0.09
7) R=C_2H_5; X=BF_4	-0.25(0.07)	0.34(0.10)	8.92(0.07)	7	0.907	0.07
8) R=C_4H_9; X=BF_4	-0.28(0.06)	0.33(0.1)	8.94(0.06)	8	0.921	0.07

Hydrogen bond donor acidity (HBDA): The solvent properties that are of statistical significance are the solvents' acidity (α) and basicity (β). It is known that the interaction of ionic liquids with acidic solvents occurs primarily via solute-solvent interaction involving the anions.[14] Both [bmim] [BF_4] and [bmim]

[PF_6] are known to have the ability to form H-bonds to acidic sites.[15] From Table 2, the relative magnitudes of the "a" coefficients are smaller than those of the "b" coefficients. The indication is that the solvation effect via the solvents' acidity property is not as significant, compared to the solvation effect via the hydrogen bond acceptor basicity mode, which is discussed in the next section. Even though variation in the nature of the anions contributes to differences in their solvation (interaction *a* in Figure 2), as reflected by the slight differences in magnitudes of the "a" coefficients, the dominant role is not played by this mode.

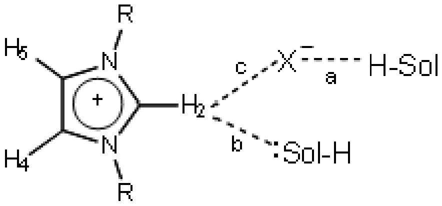

Figure 2. Solvation of imidazolium salts, R and X^- represent the alkyl groups and anions shown in Table 1, respectively. H-Sol represents the solvent.

Hydrogen bond acceptor basicity (HBAB): From Table 2, the coefficients for solvent hydrogen bond basicity are larger than those of the hydrogen bond donor acidity contribution, except for entries 7 and 8, which will be discussed later. The ability of imidazolium-derived ionic liquids to form hydrogen bonds with a substrate is dictated primarily by the acidic hydrogens of the imidazolium cation; it has been shown that 1-*n*-ethyl-3-methylimidazolium (EMI^+) salts are capable of forming hydrogen bonds to basic solutes.[16] Since H2 is bonded to a carbon of the imidazolium cation that is situated between two electronegative nitrogen atoms, it has the greatest potential to hydrogen bond with solvents. Owing to the acidity of H2, there is an interaction involving the counter anions (interaction *c* in Figure 2), and we have shown that the strength of this interaction is dictated by the nature of the anion; the interaction is strongest with the harder BF_4^- anion, compared to the softer SbF_6^- and PF_6^- anions.[17,18] Owing to the acidity of H2, imidazolium-derived ionic liquids when used as solvents to carry out reactions that require basic conditions often yield undesired side products.[19] This type ionic liquid/solvent interaction (interaction *b* in Figure 2) contributes to the stabilization of these type ionic liquids. Since the magnitudes of the coefficients for the salts with different alkyl groups are relatively the same, the indication is that there is not much discrimination due to different alkyl groups bonded to the imidazolium cation.

From Table 2, the coefficients for the solvents' hydrogen bond acceptor basicity contribution show differences as a function of the anion, the SbF_6^- and PF_6^- salts exhibit similar magnitudes, whereas the magnitudes for the BF_4^- salts are different. The implication is that greater solvation by this mode (interaction *b* in Figure 2) occurs for the SbF_6^- and PF_6^- salts, compared to the BF_4^- salts. This observation is consistent with our prior results, which show that solvation via this mode is more effective with softer anions, compared to that involving the harder BF_4^- anion.[18] For solvents however, that are not good hydrogen bond acceptors and have low dielectric constants, such as $CDCl_3$ and CD_2Cl_2, most of the imidazolium cations are expected to be associated with the anions.

In conclusion, solvation effects on imidazolium salts that contain alkyl side chains in the 1 and 3 positions of the imidazolium cation have been analyzed using multi-linear regression equations. The major solvation contributions are from the solvents' hydrogen bond donor acidity effect and hydrogen bond acceptor basicity effects, with the latter effect being more significant. For imidazolium BF_4^- salts, it was observed that the relative strength of the H-bond interaction between H2 and the solvent is weaker than that of the SbF_6^- and PF_6^- salts. For imidazolium salts with different alkyl groups in the 1 and 3 positions, there is not much discrimination for the solvation of these salts. These results confirm previous observations that RTILs exist as polymeric hydrogen bonded supramolecules and the introduction of other molecules, such as a solvent, disrupts that hydrogen bond network to form a network of solvated ions.[20]

EXPERIMENTAL

The synthesis, purification and characterization of all alkyl substituted imidazolium hexafluoroantimonate, hexafluorophosphate and tetrafluoroborate salts of this study are described elsewhere.[18] All NMR solutions were prepared in a dry- atmosphere glovebox, and the residual solvent for each sample was used as internal standard for the NMR data shown in Table 1. The concentration of all salts was 0.45 ±0.01 mol L^{-1}. The ^1H NMR spectra were recorded on a Varian Gemini 500 MHz FT-NMR spectrometer. The Minitab multi-linear regression analysis computer program was used to obtain the correlation equations shown in Table 2.[21]

ACKNOWLEDGEMENTS

We are grateful to the Robert A. Welch Foundation (T-1460) for their financial support of this research.

REFERENCES (AND NOTES)

1. For review see: T. Welton, *Chem. Rev.*, 1999, **99**, 2071; J. Dupont, R. F. de Souza, and P. A. Z. Suarez, *Chem. Rev.*, 2002, **102**, 3667; P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, Germany, 2003; R. D. Rogers, K. R. Seddon, and S. Volkov, *Green Industrial Applications of Ionic Liquids*, Kluwer Academic, Dordrecht, 2002; C. Baudequin, J. Baudoux, J. Levillain, D. Cahard, A. C. Gaumontb, and J. C. Plaqueventa, *Tetrahedron: Asymmetry*, 2003, **14**, 3081; M. Freemantle, *Chem. Eng. News*, 2004, **82**, 44.

2. S. Park and R. J. Kazlauskas, *J. Org. Chem*., 2001, **66**, 8395; C. Chiappe and D. Pieraccini, *J. Phys. Org. Chem.,* 2005, **18**, 275; M. Freemantle, *Chem. Eng. News,* 1998, **76**, 32.
3. P. Wasserscheid and W. Keim, *Angew. Chem. Int. Ed.,* 2000, **39**, 3772; S. T. Handy, *Chem. Eur. J.,* 2003, **9**, 2938; R. Sheldon, *Chem. Commun*., 2001, 2399; I. Meracz and T. Oh, *Tetrahedron Lett*., 2003, **44**, 6465; S. T. Handy and M. OKello, *Tetrahedron Lett*., 2003, **45**, 8399; S. V. Dzyuba and R. A. Bartsch, *Tetrahedron Lett*., 2002, **43**, 4657; J.-C. Xiao and J. M. Shreeve, *J. Org. Chem*., 2005, **70**, 3072; X. Xu, S. R. S. S. Kotti, J. Liu, J. F. Cannon, A. D. Headley, and G. Li, *Org. Lett*., 2004, **6**, 4881; S. R. S. S. Kotti, X. Xu, Y. Wang, A. D. Headley, and G. Li, *Tetrahedron Lett*., 2004, **45**, 7209; G. W. Kabalka, B. Venkataiah, and B. C. Das, *Synlett*, 2003, **12**, 2194; G. W. Kabalka, B. Venkataiah, and G. Dong, *Tetrahedron Lett*., 2003, **44**, 4673; H. Zhao and S. V. Malhotra, *Biotechology Letters*, 2002, **24**, 1257; H. Zhao and S.V. Malhotra, *Aldrichimica Acta*, 2002, **35**, 75; K. K. Laali and V. J. Gettwert, *J. Org. Chem*., 2001, **66**, 35; J. H. Davis and J. K. J. Forrester, *Tetrahedron Lett*., 1998, **39**, 8955.
4. T. Welton, *Chem Rev*., 1999, **99**, 2071; P. Wasserschied and W. Keim, *Aangew. Chem. Int. Ed*., 2000, **39**, 3772; J. E. Brennecke and E. Maginn, *J. Al. Ch. E*., 2001, **47**, 2384 ; D. W. Kim, C. E. Song, and D. Y. Chi, *J. Am. Chem. Soc*., 2002**, 124**, 10278.
5. M. Freemantle, *Chem. Eng. News*, 1998, **30**, 32.
6. C. L. Hussey, *Pure & Appl. Chem*., 1998**, 60,** 1763.
7. B. Ni, A. D. Headley, and G. Li, *J. Org. Chem*. 2005, **70**, 10600; J. Ding and D. W. Armstrong, *Chirality*, 2005, **17,** 281; J. Ding, V. Desikan, X. Han, T. L. Xiao, and R. Ding, *Org. Lett*., 2005, **7,** 335; X. Xu, S. R. S. S. Kotti, J. Liu, J. F. Cannon, A. D. Headley, and G. Li, *Org. Lett*., 2004, **6**, 4877; R. S. S. Kotti, X. Xu, Y. Wang, A. D. Headley, and G. Li, *Tetrahedron Lett*., 2004, **45**, 7209; D. Chen, C. Timmons, J. Liu, A. D. Headley, and G. Li, *Eur. J. Org. Chem*., 2004, **15**, 3330; R. S. S. Kotti, X. Xu, G. Li, and A. D. Headley, *Tetrahedron Lett.,* 2004, **45**, 1427.
8. J. Shorter, *Correlation Analysis of Organic Reactivity,* Research Studies Press: New York, 1982; C. Hansch, *Acc. Chem. Res*, 1969, **2,** 232; I. A. Koppel and V. A. Palm, In *Advances in Linear Free Energy Relationships*, ed. by N. B. Chapman and J. Shorter, Plenum Press, London, 1972; M. Charton *Prog. Phys. Org. Chem*., 1981, **13,** 119; W. F. Reynolds, *Prog. Phys. Org. Chem*., 1983, **14,** 165.
9. G. N. Burkhart, *Nature (London)*, 1935, **17***,* 684; L. P. Hammett, *Chem. Rev*., 1935, **17**, 125; L. P. Hammett, *J. Am. Chem. Soc*., 1937, **59**, 96; C. D. Johnson, *The Hammett Equation*, Cambridge University Press, England, 1973; O. Exner, In *Correlation Analysis of Chemical Data,* ed. By J. Shorter, Plenum Press, New York, 1988.
10. M. J. Kamlet, R. M. Doherty, M. H. Abraham, and R. W. Taft, *Quant, Struct.-Act. Relat*., 1988, **7**, 71; M. Mishima, R. T. McIver, R. W. Jr. Taft, F. G. Bordwell, and W. N. Olstead, *J. Am. Chem. Soc*., 1984, **106**, 2717.

11. R. W. Taft, In *Steric Effects in Organic Chemistry*, ed. by M. S.Newman, Wiley and Sons: New York, 1956; M. J. Kamlet, R. W. Taft, and J.-L. M. Abboud, *J. Am. Chem. Soc.*, 1977, **92**, 8325; R. W. Taft, J.-M. L. Abboud, F. Anvia, M. Berthelot, M. Fujio, J.-F. Gal, A. D. Headley, W. G. Henderson, I. Koppel, J. H. Qian, M. Mishima, M. Taagepera, and S. Uiji, *J. Am. Chem. Soc.*, 1988, **110**, 1797; R. W. Taft, J.-M. L. Abboud, M. J. Kamlet, and M. H. Abraham, *J. Sol. Chem.*, 1985, **14**, 153.
12. M. J. Kamlet, R. W. Taft, G. R. Famini, and R. M. Doherty, *Acta Chem. Scand.*, 1987, **41**, 589.
13. M. J. Kamlet, J. L. M. Abboud, and R. W. Taft, *Prog. Phys. Org. Chem.*, 1981, **13**, 485; D. E. Leahy, P. W. Carr, R. S. Pearlman, W. R. Taft, and M. J. Kamlet, *Chromatographia*, 1986, **21**, 473; J.-L. M. Abboud, G. Guiheneuf, M. Essfar, R. W. Taft, and M. J. Kamlet. *J. Phys. Chem.*, 1984, **88**, 4414.
14. C. Chiappe and D. Pieraccini. *J. Phys. Org. Chem.*, 2005, **18**, 275; J. van de Broeke, M. Stam, M. Lutz, H. Kooijman, A. L. Spek, B.-J. Deelman, and G. van Koten. *Eur. J. Inorg. Chem.*, 2003, **26**, 2798; A. J. Charmichael and K. R. Seddon, *J. Phys. Org. Chem.*, 2000, **13**, 591; S. V. Dzyuba and R. A. Bartsch, *Tetrahedron Lett.*, 2002, **43**, 4657.
15. L. Crowhurst, P. R. Mawdsley, J. M. Perez-Arlandis, P. A. Salter, and T. Welton, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2790.
16. J. S. Wilkes and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1992, 965; S. Tait and R. A. Osteryoung, *Inorg. Chem.*, 1984, **23**, 4352; A. K. Abdul-Sada, A. M. Greenway, P. B. Hitchcock, T. J. Mohammed, K. R. Seddon, and J. A. Zora, *J. Chem. Soc., Chem. Commun.*, 1986, 1753; J.-F. Huang, P.-Y. Chen, I.-W. Sun, and S. P. Wang, *Spectroscopy Let.*, 2001, **34**, 591; J. Fuller, R. T. Carlin, H. C. De Long, and D. Haworth, *J. Chem. Soc., Chem. Commun.*, 1994, 299; C. J. Dymek, Jr., D. A. Grossie, A. V. Fratini, and W. W. Adams, *J. Mol. Struct.*, 1989, **213**, 25.
17. A. D. Headley and N. M. Jackson. *J. Phys. Org. Chem.*, 2002, **15**, 52.
18. A. D. Headley, S. R. S. S. Kotti, J. Nam, and K. Li, *J. Phys. Org. Chem.*, 2005, **18**, 1018.
19. V. K. Aggarwal, I. Emme, and A. Mereu, *Chem. Commun.*, 2002, 1612.
20. J. Dupont, *J. Braz. Chem. Soc.*, 2004, **15**, 341. (b) A. Mele, G. Romano, M. Giannone, E. Ragg, G. Fronza, G. Raos, and V. Marcon. *Angew. Chem. Int. Ed.*, 2006, **45**, 1123. (c) A. Mele, C. D. Tran, and S. H. De Paoli Lacerada, *Angew. Chem. Int. Ed.*, 2003, **42**, 4364.
21. The program is marketed by Minitab, State College, PA, USA.