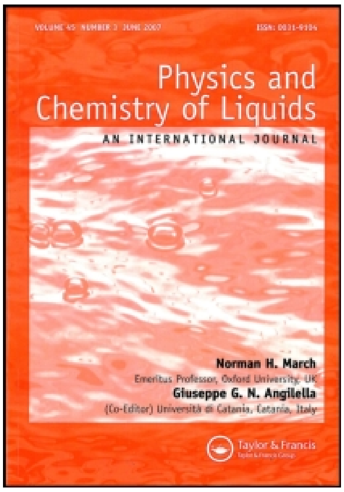


Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Investigation of NMR shielding tensors in 1,3 dipolar cycloadditions: solvents dielectric effect

M. Monajjemi[a]; E. Rajaeian[b]; F. Mollaamin[c]; F. Naderi[a]; S. Saki[ab]
[a] Department of Chemistry, Science & Research Branch, Islamic Azad University, Tehran, Iran [b] Department of Biology, Arak Branch, Islamic Azad University, Tehran, Iran [c] Department of Chemistry, Qom Branch, Islamic Azad University, Tehran, Iran

To cite this Article Monajjemi, M. , Rajaeian, E. , Mollaamin, F. , Naderi, F. and Saki, S.(2008) 'Investigation of NMR shielding tensors in 1,3 dipolar cycloadditions: solvents dielectric effect', Physics and Chemistry of Liquids, 46: 3, 299 — 306

To link to this Article: DOI: 10.1080/00319100601124369

URL: http://dx.doi.org/10.1080/00319100601124369

Physics and Chemistry of Liquids
Vol. 46, No. 3, June 2008, 299–306

Investigation of NMR shielding tensors in 1,3 dipolar cycloadditions: solvents dielectric effect

M. MONAJJEMI*†, E. RAJAEIAN‡, F. MOLLAAMIN§,
F. NADERI† and S. SAKI†‡

†Department of Chemistry, Science & Research Branch, Islamic Azad University,
PO Box 14155-775, Tehran, Iran
‡Department of Biology, Arak Branch, Islamic Azad University, Tehran, Iran
§Department of Chemistry, Qom Branch, Islamic Azad University, Tehran, Iran

(*Received 21 August 2006; in final form 17 November 2006*)

In this article, NMR shielding is investigated in the reactions of 1,3 dipolar cycloaddition of benzonitrile oxide with acrylonitrile, which have been recently studied [E. Rajaeian, M. Monajjem, Cholami, *J. Chem. Res.*, **s**, 279, (2002); E. Rajaeian, M. Monajjem, Cholami, *J. Chem. Res.*, **s**, 91, (2003)]. We reported ^{15}N and ^{17}O tensors for benzonitrile oxide and two products in reactions in gas phase and several various solvents and compared the effect of dielectric constant on tensors of the materials mentioned above. Also diffuse and polarizable function effects in basis set are investigated.

Keywords: NMR; Chemical shielding tensor; 1,3 Dipolar cycloaddition

1. Introduction

At present, quantum chemistry is almost universally applicable to the interpretation of physical and chemical properties of various compounds. Recent improvements in *ab initio* quantum chemical methodologies, when combined with similar improvements in a computer hardware, have recently permitted the first successful predictions of the ^{15}N, ^{13}C and ^{19}F nuclear magnetic resonance spectra of materials in solution, [3,4] and have led to methods for refining existing solution structures [5]. Successful interpretation of nuclear magnetic resonance (NMR) data requires an accurate knowledge of the chemical shifts anisotropy (CSA) [6–9].

The calculation of NMR parameters using semi-empirical and *ab initio* techniques has become a major and powerful tool in the investigation to look at how variations in the molecular structure occurs. The ability to quickly evaluate and correlate the magnitude and orientation of the chemical shielding anisotropy tensor with variations

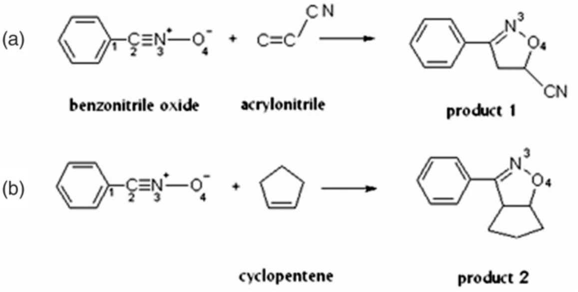
---

*Corresponding author. Email: m_monajjemi@yahoo.com

ISSN 0031-9104 print/ISSN 1029-0451 online
DOI: 10.1080/00319100601124369

in bond length, bond angles and local coordination and nearest neighbor interactions has seen a number of recent applications in the investigation of molecular structure [10–14].

The calculations also provide valuable information for exploring the experimental NMR chemical shifts with the molecular geometry and environment [15,16]. Also NMR chemical shifts are quite sensitive to intermolecular interactions. In this work, we obtained the ^{15}N and ^{17}O chemical shifts principal values in two available methods and in several media for two 1,3 dipolar cycloadditions of benzonitrile oxide with acrylonitrile and cyclopentene (scheme 1). Also diffuse and polarizable functions effects in basis sets are investigated on NMR shielding tensors.



Scheme 1.

2. Theoretical background

Chemical shielding refers to the phenomenon associated with the secondary magnetic field created by the induced motions of the electrons surrounding the nuclei when in the presence of an applied magnetic field. The energy of a magnetic moment, μ, in a magnetic field, B, is:

$$E = -\mu(1-\sigma)B.$$

Where the shielding, σ, is the differential resonance shift due to the induced motion of the electrons. The chemical shielding is characterized by a real 3×3 Cartesian matrix [18]. A 3×3 matrix can also represent the chemical shift tensor and in a special coordinate system called the principle axis system (PAS) it is diagonal:

$$\begin{pmatrix} \sigma_{xx} & 0 & 0 \\ 0 & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}.$$

With, σ_{xx}, σ_{yy} and σ_{zz} as the three principle components. The isotropic shielding values, defined as:

$$\sigma_{iso} = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}).$$

In liquids, where there is a rapid isotropic tumbling motion, all possible orientations are experienced on an NMR time scale and the resonance frequency is an "average" of the different fields experienced by the nucleus given by σ_{iso}.

There are other partial alignment effects on NMR spectra. The chemical shielding of nuclei in most molecular groups varies with orientation in a magnetic field due to the anisotropy of the group's electronic distribution.

An asymmetry in the magnetic susceptibility of a chemical group leads, in the presence of an external magnetic field, to electrostatic currents in the group. These currents are the source of additional magnetic fields – and thus chemical shifts – at atoms surrounding the asymmetric group [19].

This form of the chemical shift tensor can be augmented by defining some other useful terms such as:

$$\text{CSA} = \frac{3}{2}(\sigma_{zz} - \sigma_{\text{iso}}).$$

That CSA is chemical shift anisotropic shielding value [19].

3. Computational methods

Chemical shift calculation and geometry optimization were performed with the Gaussian 98 suite of program [17]. Our computational model consists of two parts:

(1) Geometries for benzonitrile oxide (BNO), product 1 (P1) and product 2 (P2) were fully optimized by restricted Hartree Fock (RHF) with 6-31G (d) and 6-31++G (d,p) levels.
(2) The chemical shift tensors of ^{15}N and ^{17}O were calculated by two methods: the gauge-independent atomic orbital (GIAO) and continuous set of gauge transformations (CSGT).

In this article, we compare two reactions of cycloadditions which have various reactants.

4. Results and discussion

We have reported our results for BNO and its products in table 1. Our results have been calculated at the optimized geometry of the molecules using HF/6-31G (d), HF/6-31++ (d,p) levels in the gas phase and four solvents by different dielectric constants. We first consider the principal components of the ^{15}N, ^{17}O isotopes of the chemical shifts for BNO, P1 and P2 at GIAO and CSGT methods. With this model, we have referred to the preliminary isotropic and anisotropic tests.

Thus, it is apparent that for a more accurate prediction of solvent effects on shielding, it is necessary to consider specific solute–solvent interactions by introducing one or several molecules in the calculations. In this article, solvent shifts are given relative to the value in BNO, P1 and P2 and we have obtained different values for the gas-phase shifts and solvents of water, acetone, chloroform and heptane.

Interestingly, the NMR calculations display the solvent changes for chemical shielding arising only from polarization of the electronic structure of the molecule by

Table 1. ^{15}N & ^{17}O principal values of the chemical shifts by HF/6-31G (d), HF/6-31++G (d,p) and GIAO/CSGT methods.

		HF/6-31G(d)				HF/6-31G++(d,p)				
		N		O		N		O		
Structure	Method	σ_{iso}	CSA	σ_{iso}	CSA	σ_{iso}	CSA	σ_{iso}	CSA	Medium
Benzonitrile	GIAO	52.02	170.51	207.88	85.68	53.68	172.31	213.59	90.62	Gas
		51.21	171.68	202.90	91.42	52.79	173.56	207.87	97.03	Heptane
		49.93	173.03	195.80	98.82	51.47	175.01	199.70	105.47	Chloroform
		48.77	174.08	189.33	105.22	50.17	176.14	191.91	112.97	Acetone
		48.29	174.37	186.95	107.37	49.74	176.46	189.42	115.27	Water
	CSGT	44.71	177.59	197.76	92.94	48.01	178.64	206.74	93.09	Gas
		43.95	178.73	192.62	98.65	47.13	179.83	200.95	99.40	Heptane
		42.72	180.02	185.33	106.02	45.84	181.22	192.71	107.73	Chloroform
		41.61	181.03	178.69	112.39	44.16	182.60	184.87	115.13	Acetone
		41.15	181.31	178.69	112.39	44.16	182.60	182.37	117.41	Water
Product 1	GIAO	−110.73	314.87	178.25	104.40	−109.73	313.44	176.35	106.83	Gas
		–110.97	313.58	177.72	105.28	−109.96	310.29	175.73	107.47	Heptane
		–111.28	311.85	177.08	106.31	−110.27	308.90	174.93	108.07	Chloroform
		–111.45	310.69	176.56	106.84	−110.57	307.81	174.31	108.44	Acetone
		–111.52	310.27	176.40	107.06	−110.57	307.51	174.13	108.53	Water
	CSGT	−110.73	314.87	162.11	88.73	−119.52	307.60	162.16	95.18	Gas
		–110.97	313.58	161.53	90.02	−119.76	306.45	161.65	96.19	Heptane
		–111.28	311.85	160.83	91.42	−120.07	305.05	160.98	97.23	Chloroform
		–111.45	310.69	160.24	92.10	−120.29	303.93	160.45	97.90	Acetone
		–111.52	310.27	160.02	92.38	−120.35	303.62	160.3	98.07	Water
Product 2	GIAO	−99.79	266.92	185.47	47.51	−100.42	268.24	157.58	48.90	Gas
		–101.76	272.02	161.47	47.53	−100.55	267.84	157.00	49.65	Heptane
		–100.91	271.51	165.95	48.19	−100.67	267.23	156.43	50.53	Chloroform
		–102.03	271.07	160.48	48.85	−100.77	266.91	156.06	50.89	Acetone
		–102.03	271.07	160.48	48.85	−100.80	268.35	155.95	51.05	Water
	CSGT	−109.41	261.73	146.48	39.45	−110.04	263.02	145.59	40.65	Gas
		–114.82	269.83	148.62	35.82	−110.16	262.61	145.03	41.34	Heptane
		–114.95	269.29	148.09	36.38	−110.24	262.02	144.47	41.99	Chloroform
		–115.07	268.87	147.60	36.96	−110.34	261.67	144.11	42.34	Acetone
		–115.07	268.87	147.60	36.96	−110.37	261.60	144.00	42.50	Water

the surrounding dielectric medium. Changes make these small differences quite visible in our calculated isotropic chemical shielding, σ_{iso}, and CSA constants. The anisotropic magnetic in solution causes such molecules to adopt a small degree of alignment in a magnetic field. Given its well-defined solution structure, is an ideal candidate for a reliable measurement of total magnetic susceptibility anisotropy.

Oxygen at position 4 and nitrogen at position 3 by GIAO, CSGT methods and 6-31G(d), 6-31++G(d,p) basis sets indicate that the variations especially in σ_{iso} and CSA that can explain for products of P1 and P2 by the atom's position in our molecules. Therefore, P2 could then be a more controllable and cooperative alternative than P1 for exploiting the strength and directionality in solvent medium. The parameters of the various CSA–NMR tensors are summarized in table 1. For products ^{15}N, ^{17}O CSA tensors in the molecular frame, we have used the different groups of –CN and $-C_5H_8$ in P1 and P2, respectively. The values of the CSA interaction in P2 have given high value in shift because of $-C_5H_8$ group. Also we have prepared

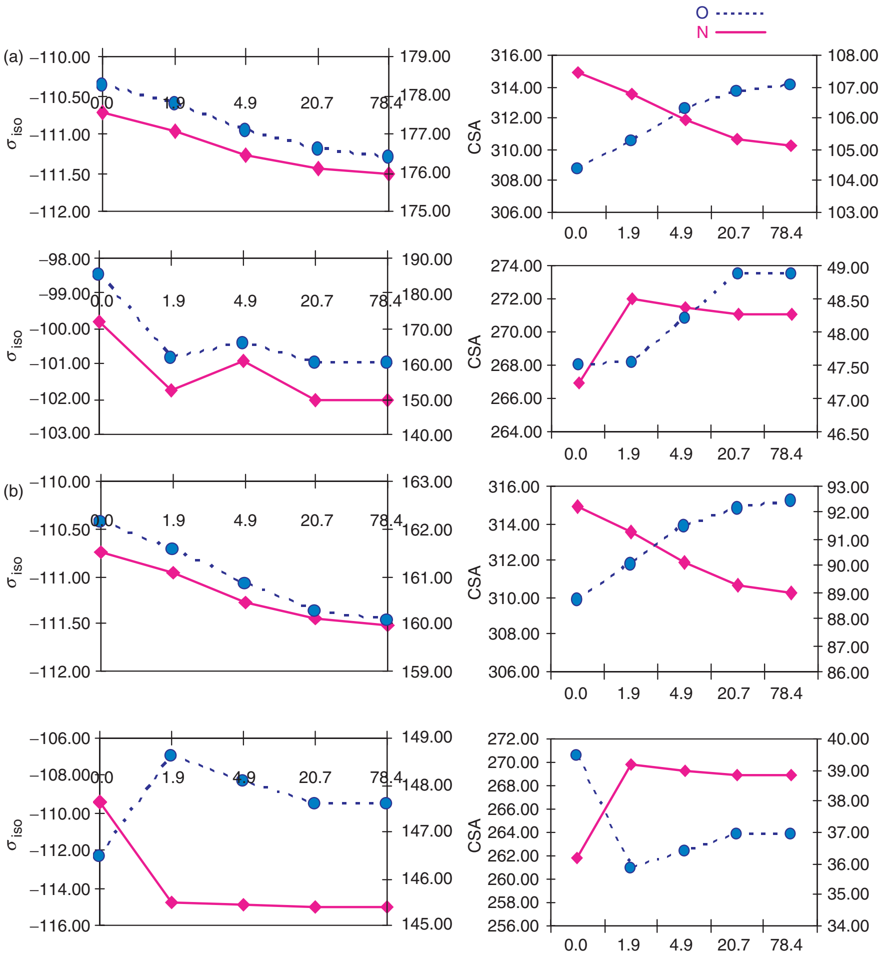


Figure 1. The shielding tensor elements *vs*. dielectric constants, calculated by HF/6-31G (d) and (a) GIAO method (b) CSGT method.

figures 1 and 2 for comparison of results in table 1 and investigation effect in calculation methods on nuclear magnetic resonance properties. These results have represented ^{17}O CSA tensor stronger than ^{15}N isotope.

NMR determination of ^{15}N, ^{17}O couplings in oriented samples imply the essential nature of these products in variant media. Therefore, dielectric constant influences oxygen and nitrogen charges, dipole moment to be changed and consequently tensors to shift on maximum values. Our results indicate that this maximum in the solvent shifts arise from the opposing effects of the direct polarization of the electronic structure of the solvated molecules. The charges of nitrogen and oxygen atoms in these structures vary insignificantly due to solvation, but the analysis of the atomic charges in molecules under study reveals a considerable increase in the negative charge of the oxygen atoms due to the interaction with solvent molecules. When these are going from gas-phase to the solvent-optimized geometry of P1 and P2, deshielding of oxygen and nitrogen atoms causes that tensor to shift to high values (table 2). Also, calculation at the HF/6-31G (d)

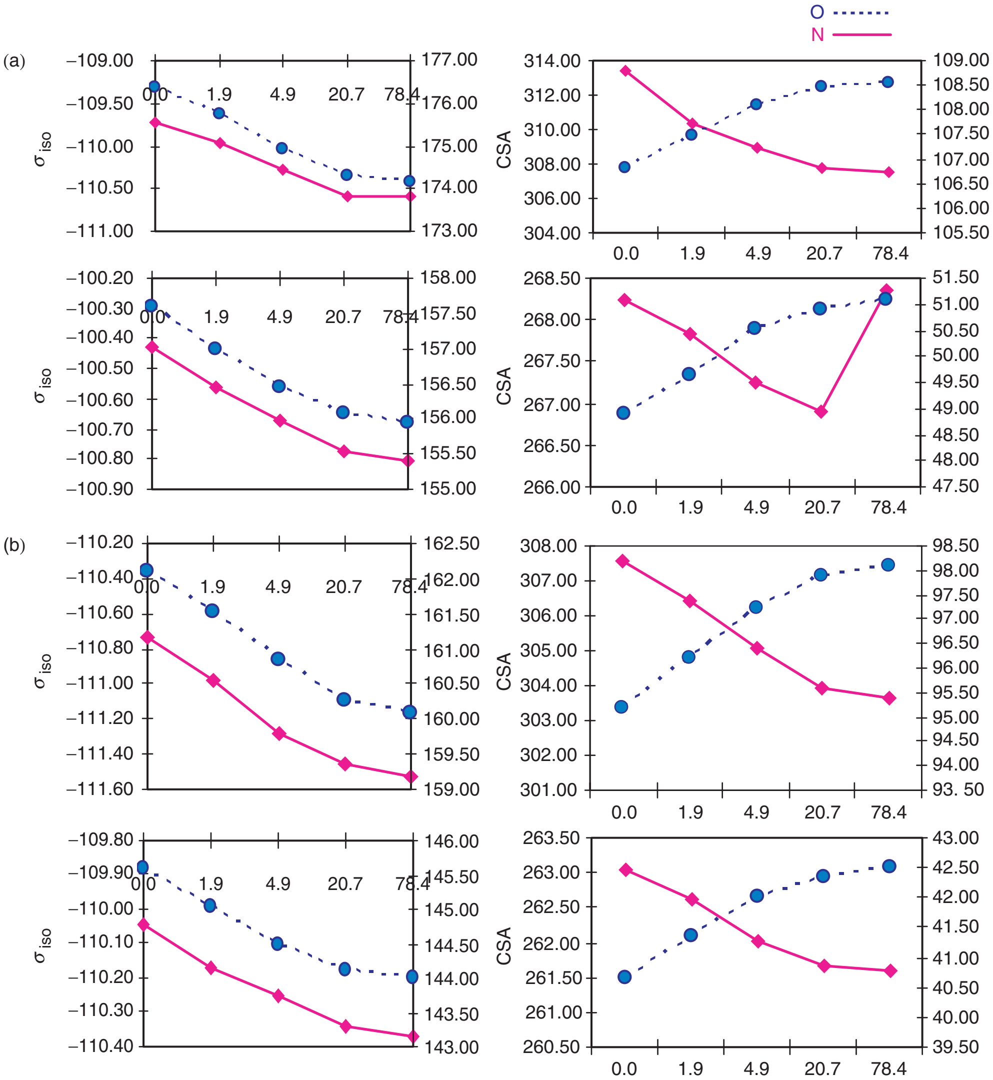


Figure 2. The shielding tensor elements *vs*. dielectric constants, calculated by HF/6-31++G (d,p) and (a) GIAO method (b) CSGT method.

and CSGT method has shown that molecular geometries and shielding properties are better than the other method, HF/6-31++ (d, p), for reactions.

5. Summary and conclusions

The present work provides a nitrogen and oxygen brief assessment of the theoretical model in describing influence of solvent on nuclear magnetic shielding. In this case, ^{15}N, ^{17}O chemical shift values and dipolar interaction tensors have been determined, and are reported for BNO and its products (P1, P2). The above mentioned parameters

Table 2. N_3 and O_4 in BNO, product 1 and 2 at various solvents by HF/6-31(d) and CSGT method.

Structure	Oxygen charge	Nitrogen charge	Dipole moment	Medium
Benzonitrile	−0.5777	0.0797	6.1141	Gas
	–0.5786	0.0739	6.2114	Heptane
	–0.5792	0.0664	6.3262	Chloroform
	–0.5794	0.0601	6.4182	Acetone
	–0.5794	0.0579	6.4464	Water
Product 1	−0.1354	−0.4907	4.1832	Gas
	–0.1345	−0.4900	4.3443	Heptane
	–0.1334	−0.4894	4.5002	Chloroform
	–0.1328	−0.4892	4.6027	Acetone
	–0.1327	−0.4891	4.632	Water
Product 2	−0.0039	−0.4616	3.8301	Gas
	–0.5302	−0.1522	3.7512	Heptane
	–0.5305	−0.1524	3.7626	Chloroform
	–0.5309	−0.1526	3.7723	Acetone
	–0.5309	−0.1526	3.7723	Water

have been computed at HF/6-31G (d), HF/6-31++ (d, p) levels of theory by GIAO and CSGT algorithms. Comparing computational calculation of the NMR shielding evidences these results:

(1) The eigenvalues of the P1 and P2 (two different products of benzonitrile) ^{15}N, ^{17}O tensors, σ_{iso} give high shift due to *ab initio* methods.
(2) The position of N and O atoms in compounds and connection of two different groups to products make changes in components of CSA tensors.
(3) ^{15}N, ^{17}O CSA tensors have been shifted to high field and ^{17}O CSA has stronger anisotropy by HF/6-31G (d) and CSGT method.
(4) It has been demonstrated that dipolar chemical shift NMR calculations can give valuable information about the structure of small molecular groups.
(5) Investigations of contribution to the total solvent effect show that the intensity of the reaction field determines shielding variation more than solute geometry does. This can serve as a significant consideration when performing a large number of calculations to investigate solvent effects on nuclear magnetic shielding.

References

[1] E. Rajaeian, M. Monajjemi, M.R. Cholami. *J. Chem. Res.*, **s**, 279 (2002).
[2] E. Rajaeian, M. Monajjemi, M.R. Cholami. *J. Chem. Res.*, **s**, 91 (2003).
[3] A.C. De Dios, E. Oldfield. *Sol. State NMR*, **6**, 101 (1996).
[4] E. Old field. *J. Biomol. NMR*, **5**, 217 (1995).
[5] J.G. Pearson, J.F. Wang, J.L. Markely, H. Le, E. Old field. *J. Am. Chem. Soc.*, **117**, 8823 (1995).
[6] D. Fushman, D. Cowburn. *J. Am. Chem. Soc.*, **120**, 7109 (1998); J. Byed, C. Redfield. *J. Am. Chem. Soc.*, **120**, 9692 (1998).
[7] D. Fushman, N. Tjandra, D. Cowburn. *J. Am. Chem. Soc.*, **120**, 10947 (1998).
[8] D. Fushman, D. Cowburn. *J. Biomol., NMR*, **103**, 139 (1999).
[9] K. Pervushin, R. Riek, G. Wider, K. Wuthrich. *Proc. Natl. Acad. Sci.*, USA, **94**, 12366 (1997); R. Riek, G. Wider, K. Pervushin, K. Wuthrich. *Proc. Natl. Acad. Sci.*, USA, **96**, 4918 (1999).
[10] U. Sternerg, F. Pietrowski, W. Priess. *Chemie Neue Folge.*, **168**, 115 (1990).

[11] P. Losso, *et al. J. Non. Cryst. Sol.*, **13**, 265 (1992).
[12] T.M. Alam. *Sandia Natl. Labs*, **98**, 2053 (1998).
[13] A. Marquez, J.F. Sanz, J.A. Odriozola. *J. Non. Cryst. Sol.*, **263**, 189 (2000).
[14] G.D. Cody, B. Mysen, G. Saghi-Szabo. *J.A. Geochima et Coschimica Acta*, **65**, 2395 (2001).
[15] M.S. Solum, K. Altman, M. Strohmeier, D.A. Berges, Y. Zhang, J.C. Facelli, R.J. Pugmire, D.M. Grant. *J. Am. Chem. Soc.*, **119**, 9804 (1997).
[16] D.M. Grant, F. Liu, R.J. Iuliucci, C.G. Phung, J.C. Facelli, D.W. Alderman. *Acta Crystallogr.*, **B 51**, 450 (1995).
[17] M.J. Frisch, *et al. Gaussian 98*, *Revision* A.9, Gaussian, Inc., Pittsburgh PA (1998).
[18] T.H. Sefzik, D. Turco, R.J. Luliucci, J.C. Facelli. *J. Phys. Chem.*, **109A**, 1180 (2005).
[19] D. Sitkoff, D.A. Case. *J. Am. Chem. Soc.*, **119**, 12262 (1997).