

Solvent Polarity and Excitation Wavelength Dependence of the Dual Fluorescence in *N,N*-Diethyl-4-Nitrosoaniline

Nizamudin A. Hussien · Ahmed M. Mohammed ·
M. Tessema · F. B. Dejene · Mesfin Redi-Abshiro

Received: 11 July 2011 / Accepted: 13 September 2011 / Published online: 22 September 2011
© Springer Science+Business Media, LLC 2011

Abstract Dual fluorescence in *N,N*-Diethyl-4-nitrosoaniline (DENA) has been studied employing absorption, excitation and emission spectroscopic techniques and computational methods. The absorption and fluorescence spectra of DENA were measured in solvents of various polarities at room temperature. The emission spectra of DENA were found to exhibit a single emission band in non polar solvent (cyclohexane) and in a highly polar solvent (acetonitrile). In the contrary, two emission bands were observed in medium polar solvents (tetrahydrofuran, 1,2-dichloroethane and dichloromethane) whereby the short (local excited; LE) and long (charge transfer; CT) emission maxima correspond to the emission maxima of the compound observed in cyclohexane and acetonitrile solutions, respectively. Moreover, the two emission bands have shown strong excitation wavelength dependence, and area normalization resulted in an iso-emissive point. The two emission maxima were in addition found to correspond to two excitation maxima in 3D fluorescence spectra. Further, two minima were obtained in potential energy surface calculation of DENA. From the experimental and computational results it was concluded that the dual fluorescence may be attributed to the presence of two different ground state structural conformers of DENA in equilibrium that are stabilized through solute-solvent interaction.

Keywords Dual fluorescence · DENA · Solvent polarity dependence · Excitation wavelength dependence

Introduction

Fluorescent compounds in general possess a single fluorescence band for a particular absorption. However, a number of organic donor-acceptor substituted compounds show dual fluorescence in polar solvents. Beside the normal fluorescence from the solvent relaxed primary excited state, a second, strong red-shifted emission from charge transfer state is observed for these compounds [1]. Parallel to this, the intensity of the first band becomes weaker and is not even observed in high polar solvents [2]. This phenomenon was first discovered by Lippert et al. [3] while studying the photophysical behavior of 4-(*N,N*-Dimethylamino)-benzonitrile (DMABN) and its derivatives in different solvents. This unusual dual fluorescence property of DMABN has successively been observed in several other electron donor-acceptor compounds [4].

Dual fluorescence could be due to a single species that undergoes an excited state reaction; excited-state intramolecular charge transfer [5–17] or the existence of two isomers of that compound in the ground state [21, 22]. However, most of the attempts so far, were concerned with the excited state structural rearrangements [1, 2]. Consequently, several models have been proposed to interpret the nature of the local excited (LE) and charge transfer (CT) states and to explain the mechanism of dual fluorescence. Twisted Intramolecular Charge Transfer (TICT) [6–10], Planar Intramolecular Charge Transfer (PICT), [11–14] Wagging Intramolecular Charge Transfer (WICT) [15] and Rehybridization Intramolecular Charge Transfer (RICT) [16, 17] are some of them. From these, TICT is supported

N. A. Hussien · A. M. Mohammed · M. Tessema ·
M. Redi-Abshiro (✉)
Department of Chemistry, Addis Ababa University,
P.O. Box 1176, Addis Ababa, Ethiopia
e-mail: mesfinr@chem.aau.edu.et

F. B. Dejene
Department of Physics, University of the Free State,
P.O.Box 339, Bloemfontein 9300, South Africa

by several theoretical studies. There are also significant numbers of studies, which show that TICT model does not hold for all dual fluorescing systems [18, 19]. On the other hand, the RICT and WICT models are seen to be frequently rejected, while the PICT model is favored by some studies [2, 20]. However, no direct experimental proof of each model has been obtained up to now [19] and the mechanism of formation of the excited state charge transfer is still under debate.

Recently, the dual fluorescence property of DMABN was discussed from the perspective of ground state structural isomers [21, 22]. In this work, the effect of the alkyl chain extension on the solvent dependency of the dual fluorescence was investigated, and similar explanation pattern was followed, i.e. existence of two stable ground state species of DENA was examined. The absorption, excitation and emission spectra of DENA in various solvents were studied. Computational methods were applied to verify the experimental results.

Experimental Details

For spectroscopic measurements DENA solutions were prepared in cyclohexane (GC grade, Riedel-de Haen, Germany), Tetrahydrofuran (HPLC grade, Lancaster, England), Dichloromethane (LR, TLS, England), 1,2-Dichloroethane (GC grade, Sigma-Aldrich, Germany), Acetonitrile (HPLC grade, Sigma-Aldrich, Switzerland), Carbontetrachloride (GC grade, Riedel-de Haen, Germany), Butanol (GC grade, BDH, England), and 1-pentanol (Sigma-Aldrich, Germany). The concentrations of the solutions were kept low in order to obtain optical densities of less than 1 and 0.1 for absorption and fluorescence measurements, respectively.

The absorption spectra were recorded on UV-Visible spectrophotometer (Spectronic Genesis, 2PC, USA) with a resolution of 1 nm. Fluorescence measurements were performed with a spectrofluorometer (Fluoromax4, Jobin Yvon, USA). Solvent blanks were subtracted from the spectra before analysis. The excitation spectra are all corrected to compensate for the intensity of the light source.

To identify the two stable structural conformers computational techniques were used. All calculations, structural and potential energy surface and frequency were performed using the GAUSSIAN 03 W program package [25]. The ground state geometry optimizations were performed at the DFT/B3LYP and MP2 levels as implemented in the program package using 6–31 G(d) basis sets. The self-consistent reaction field theory (SCI-PCM model) [26] as implemented in the Gaussian 03 W has been used to determine the frequency in acetonitrile and cyclohexane at B3LYP level of theory using 6–31 G* basis sets.

The potential energy surface (PES) scan was done along the twist coordinate at the donor site. We have used rotational angle θ (shown in Scheme 1) to get the twisting of the donor ($-NEt_2$). The angle was θ varied from 0 to 180° with a step of 1°. It is defined by $(\theta_1 + \theta_2)/2$, where θ_1 represents the dihedral angle 3–4–9–10 and θ_2 the dihedral angle 5–4–9–12.

Result and Discussion

Fluorescence Spectra in Medium of Non-Polar Solvent

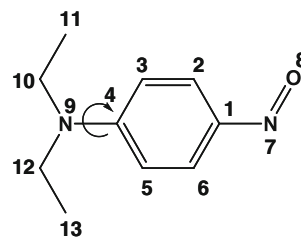
In cyclohexane solution of the compound only a single emission from the LE state is observed. The occurrence of dual fluorescence could not be discovered (Fig. 1). The emission band maximum was found to be independent of the excitation wavelengths.

The excitation spectra of the compound also showed only one band, and the band shape did not change irrespective of the emission (observation) wavelength (Fig. 2). Moreover, the excitation and emission bands look mirror image to each other, suggesting the existence of a single electronic transition corresponding to a single exciting species in the ground state.

In order to further verify the excitation and emission bands are correlated, 3D spectra were recorded. The 3D spectra (Fig. 3) contour exhibited a single maximum at 281 nm and 306 nm corresponding to the excitation and emission wavelength maxima, respectively, which further confirmed the existence of only one stable species in the ground state.

Fluorescence Spectra in Medium of Polar Solvents

In the medium polar solvents different result was obtained. For example, the emission spectra of DENA in THF (tetrahydrofuran) contains two emission bands ('dual fluorescence') centered at $\lambda_{em}=310$ nm and 355 nm (Fig. 4). The emission bands were found to be highly dependent on the excitation wavelengths. As the excitation wavelength varied the ratio of the intensity of LE to CT



Scheme 1 Chemical structure of *N,N*-Diethyl-4-nitrosoaniline (DENA)

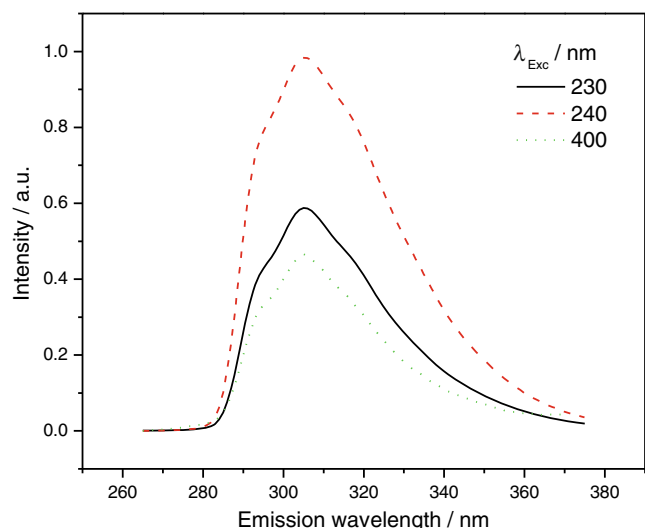


Fig. 1 Emission spectra of DENA in cyclohexane at different excitation wavelengths

bands (I_{LE}/I_{CT}) changed significantly. This phenomenon is in violation of the Kasha rule, which states that for a single electronic transition the band shape of the emission spectrum shape should stay the same regardless of the excitation wavelength; i.e. the emission band intensity-ratio should not be dependent on the excitation wavelength. Thus, the observed wavelength dependence may indicate the presence of two species in the ground state, as the existence of two electronic transitions may be excluded.

To further demonstrate the wavelength dependence, the emission spectra of the compound in the short (260 to 270 nm) and long (>298 nm) excitation wavelength regions were considered separately. In λ_{exc} between 260 to 270 nm

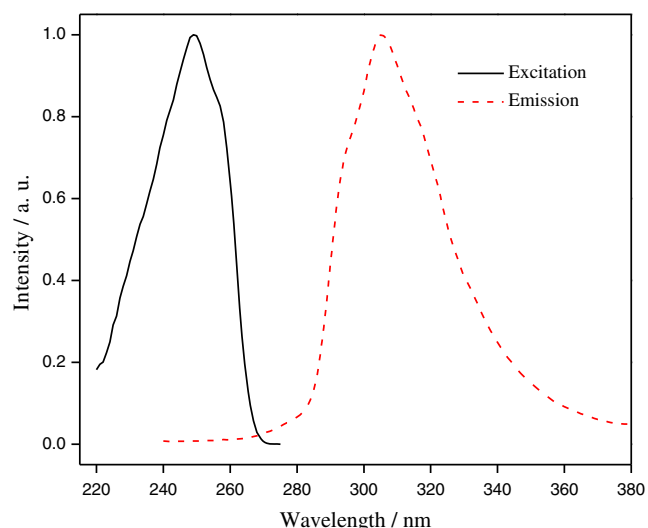


Fig. 2 Normalized corrected excitation and emission spectra of DENA in cyclohexane

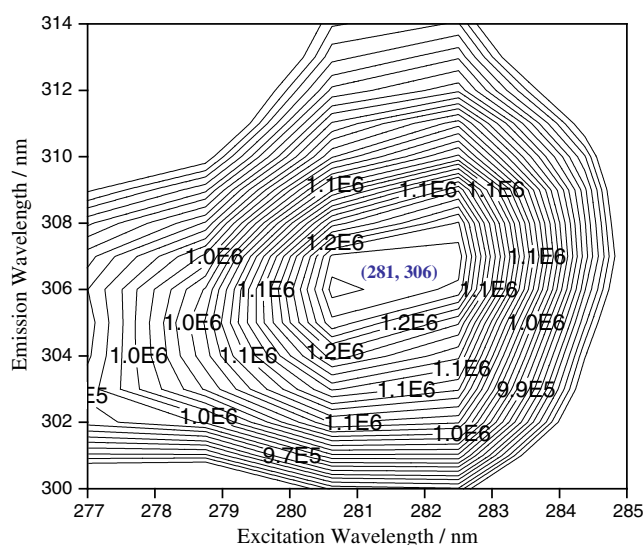


Fig. 3 3D emission spectra contour map of DENA in cyclohexane

only one emission band (LE) with maximum intensity at 310 nm is observed (Fig. 5), whereas, in $\lambda_{exc} > 298$ nm only the CT state emission centered at 355 nm is monitored (Fig. 6). The observation of two different emission spectra as a function of excitation wavelength suggests two excitation spectral regions, i.e. the existence of two electronic transitions, further supplement the suggestion that there exist two species in the ground state.

Excitation spectra were also recorded at emission (observation) wavelengths $\lambda_{em} = 310$ nm and $\lambda_{em} = 355$ nm, and two excitation spectra were observed with intensity maxima at 287 nm and 300 nm corresponding to the shorter and longer emission wavelengths, respectively. The 3D emission spectra of DENA in THF also exhibited two maxima centered in the contours map (Fig. 7). The first maximum appeared at excitation wavelength of 287 nm and

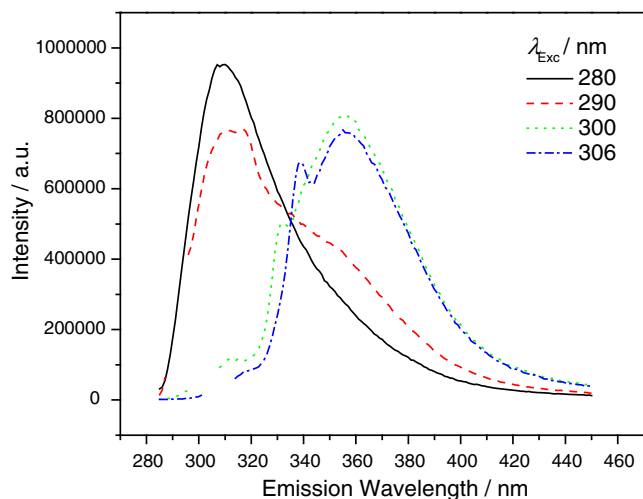


Fig. 4 Emission spectra of DENA in THF

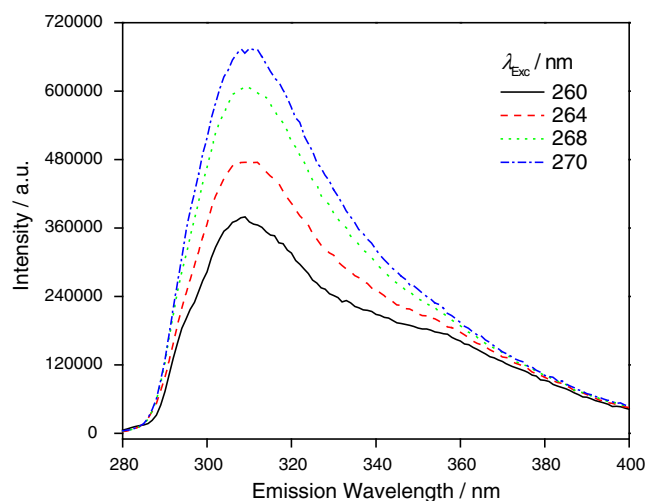


Fig. 5 Emission spectra of DENA in THF at blue edge of excitation wavelength range

the corresponding emission wavelength of 310 nm, whereas, the second maximum was centered at 300 and 355 nm excitation and emission wavelengths, respectively.

The emission and excitation spectra of DENA in THF together with the 3D emission spectra substantiate the suggestion that two absorptive species exciting at different wavelengths are responsible for the observed apparent dual fluorescence.

Similar studies on the compound in solution of another medium polar solvent, DCM (dichloromethane), were conducted, and similar spectral features and excitation as well as emission wavelength dependency were observed. The emission spectra of DENA in DCM at different excitation wavelengths showed two emission bands at 383 nm and 424 nm and, as could be expected from a relatively more polar nature of DCM, the solvatochromic shift in DCM was larger than in THF.

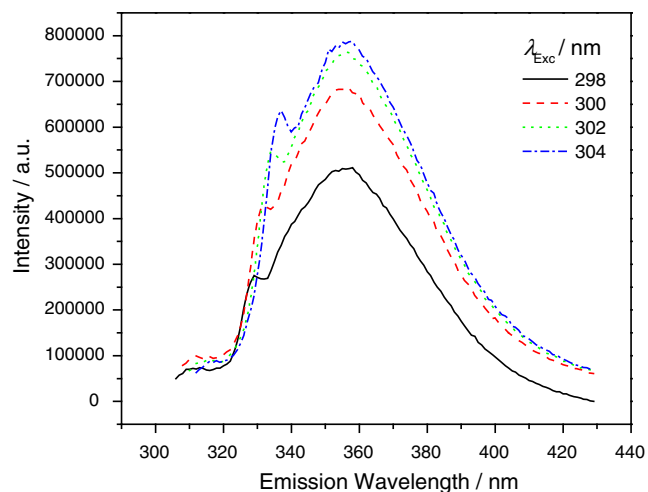


Fig. 6 Emission spectra of DENA in THF at the red edge of excitation wavelength range

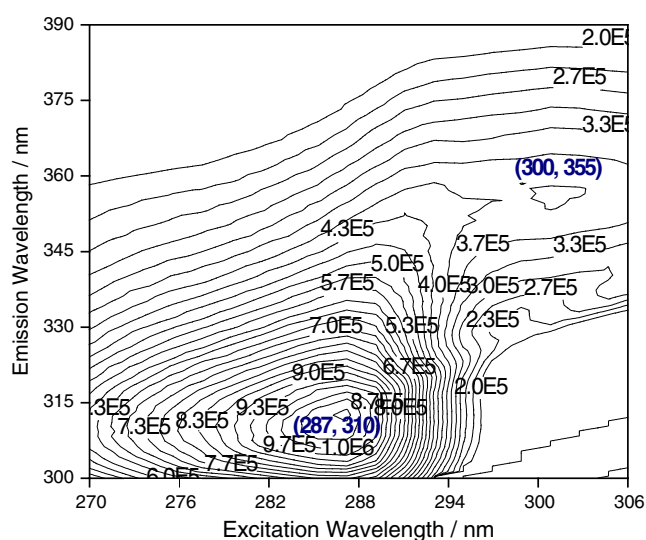


Fig. 7 3D emission spectra of DENA in THF

Solvatochromic Shift and Excited State Dipole Moment

Investigation of the solvatochromic shift in the electronic spectra of molecules provides important information on the interactions occurring in the solutions. To understand the effect of solvent polarity on the absorption spectrum, the solvatochromic shift of the compound in cyclohexane, tetrahydrofuran, dichloromethane, 1,2-dichloroethane and acetonitrile of different polarities were studied.

The bathochromic shift observed with an increase in solvent polarity depends on the difference in permanent dipole moments of the ground and excited state, and this is in accordance with the theory of dielectric polarization. According to this theory, the larger the dipole moment difference between the ground and the excited state, the larger will be the solvent induced spectral shift [23]. A shift to longer wavelength generally shows an increase in the permanent dipole moment of the excited state than the ground state. Quantitative treatment of the dipole difference may be done using Lippert-Mataga equation (Eq. 1) and the slope of the plot of stocks shifts versus Lipperts solvent polarity parameters for LE and CT states band maximum [24].

$$\tilde{\nu}_a - \tilde{\nu}_f = \frac{2(\mu_e - \mu_g)^2}{4\pi\epsilon_0 h c a^3} \left(\frac{\epsilon_r - 1}{2\epsilon_r + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) + constant$$

where $\tilde{\nu}_a$ is absorption maximum, $\tilde{\nu}_f$ is emission maximum, h is the Planck's constant, c is the speed of light in vacuum, a is the Onsager radius of the cavity in which the fluorophore reside, n is the refractive index of the solvent, ϵ_r is the dielectric constant of the solvent, and μ_g and μ_e are ground and excited state dipole moments, respectively.

Table 1 The energies of the minima in gas phase and in solution

Medium	Isomer 1 (6°)	Isomer 2 (127°)	Energy difference (a.u.)	Energy difference (eV)
Gas	-574.14515468	-574.13269472	0.01245996	0.3390
	-572.28788329 ^a	-572.27652172 ^a	0.01136157 ^a	0.3092 ^a
Acetonitrile	-574.15594401	-574.14120012	0.01474389	0.4012
THF	-574.15414208	-574.13978797	0.01435411	0.3906
Cyclohexane	-574.14944332	-574.13608177	0.01336155	0.3636

^aResults obtained by using MP2/6-31 G*

The slope obtained from absorption maxima was quantitatively comparable with that obtained from LE emission maxima, indicating that the ground state is mainly composed of the species that gives rise to the LE emission. On the other hand, the slope obtained for the CT state emission maxima was about seven times larger than that of the slope from LE state emission maxima, suggesting there is appreciable difference in dipole moment between the excited states of the two conformers, which is consistent with the large CT character of the second emission [22].

From the slope, the value of Onsager cavity radius and the ground state dipole moment ($\mu_g=7.0$ D) obtained from computational calculation, the dipole difference between the excited and ground states were found to be 5.25 D and 12.77 D for the LE and CT states, respectively. Considering the ground state dipole moment of both conformers to be comparable, the excited state dipole moment of both structures are thus, $\mu_e(\text{LE})=12.25$ D and $\mu_e(\text{CT})=19.77$ D. The large difference in dipole moment for the CT state $\Delta\mu(\text{CT})=12.25$ D is due to charge redistribution in the excited state by the process of charge transfer from the electron rich diethyl amino donor moiety to the nitrobenzene acceptor moiety.

These findings together with the results of emission and excitation spectra discussed earlier, strongly support the hypothesis that there exist two structural conformers in equilibrium in the ground state that both fluoresce when excited with proper radiation. Similar observation was reported [21].

Computational Results

In order to explain the experimental findings in more detail, computational techniques were applied. The PES was determined by defining the reaction coordinate as the dihedral angle between the plane of diethyl amino group and that of the benzene ring. The energy of the ground electronic state increases along the twisting coordinate and the results predict two minima at 6° and 127° dihedral angles of the structures of DENA resulting in two relatively stable conformers.

The rotational activation energy barrier (defined to be the energy difference in energy between the two conformers) to the 127° conformation (conformer 1) of DENA from its equilibrium (6°) structure (conformer 2) in the

solution state are listed in Table 1. All stable conformations were calculated, but only the most stable conformers were discussed.

The energy barrier in acetonitrile is greater than that of cyclohexane indicating that conformer 1 is more stabilized in polar solvents. Also, the rotational energy barrier is greater than the thermal energy ($kT\sim 0.026$ eV at room temperature) indicating that the two structures coexist at room temperature. Therefore, the theoretical results, further supports the presence of two ground state species.

Further, thermodynamics properties were calculated and displayed in Table 2. The results suggest that conformer 1 is more stable in acetonitrile and conformer 2 in cyclohexane, again supporting the results obtained above.

A comparison of the present experimental and theoretical studies on DENA indicates that the dual emission observed originates from the two different conformations of the same molecule.

Conclusion

In this work, the dual fluorescence in *N,N*-Diethyl-4-nitrosoaniline (DENA) has been studied on the basis of absorption, excitation and emission spectroscopy and computational techniques, with the aim of determining the origin of dual fluorescence in DENA.

The fluorescence spectrum of DENA was found to exhibit dual fluorescence in medium polar solvents, and strong excitation wavelength dependence was observed. The results from the potential energy surface scan indicated two minima which confirms the presence of two different conformations of the same molecule in the ground state that lead to two closer lying excited state; locally excited (LE) and charge transfer (CT), and thereby results in the dual fluorescence of the compound.

Table 2 Thermodynamic quantities computed in gas phase and in solution

	Gas	Acetonitrile	Cyclohexane
$\Delta H/\text{eV}$	0.2938	0.3517	0.3426
$\Delta G/\text{eV}$	0.2769	0.3337	0.2217

On the basis of these experimental and computational results, we suggested that the existence of two different conformers of DENA in the ground state, which are in equilibrium as the cause of dual fluorescence in DENA.

Acknowledgments The authors would like to thank Prof. Wondemagegn Mammo, Department of Chemistry, Addis Ababa University, for providing us access to the fluorescence measurements facilities available to him.

References

1. Parusel ABJ, Köhler G, Nooijen M (1999) *J Phys Chem A* 103:4056–4064
2. Schamschule R, Parusel ABJ, Köhler G (1998) *Internet J Chem* 1–5
3. Lippert E, Lüder W, Boos H (1962) In: Mangini A (ed) *Advances in Molecular spectroscopy*. Oxford, Pergamon
4. Sukumaran M (2005) Ph D. Dissertation Submitted to Berlin University
5. Lirong L, Jiang Y (2000) *Sci China B* 43:3
6. Retting W, Bliss B, Dirnberger K (1999) *Chem Phys Lett* 305:8–14
7. Rotkiewicz K, Grellmann KH, Grabowski ZR (1973) *Chem Phys Lett* 19:315–318
8. Serrano-Andrés L, Merchán M, Roos BO, Lindh R (1995) *J Am Chem Soc* 117:3189–3204
9. Grabowski ZR, Rotkiewicz K, Siemiarczuk A (1979) *J Lumin* 18:420
10. Singh RB, Mahanta S, Kar S, Guchhait N (2007) *Chem Phys* 342:33–42
11. Zachariasse KA, von der Haan T, Hebecker A, Linhos U, Kuhnle W (1993) *Pure Appl Chem* 65:1745–1750
12. Il'ichev YV, Kuhnle W, Zachariasse KA (1998) *J Phys Chem A* 102:5670–5680
13. Yoshihara T, Druzhinin SI, Zachariasse KA (2004) *J Am Chem Soc* 126:8535–8539
14. Mennucci B, Toniolo A, Tomasi J (2000) *J Am Chem Soc* 122:10621–10630
15. Gorse A-D, Persquer M (1995) *J Phys Chem* 99:4039
16. Sobolewski AL, Domcke W (1996) *Chem Phys Lett* 250:428
17. Sobolewski AL, Domcke W (1996) *Chem Phys Lett* 259:119
18. Dobkowski J, Wojcik J, Kozminski W, Kołos R, Waluk J, Michl J (2002) *J Am Chem Soc* 124:2407
19. Jodicke CJ, Luthi HP (2003) *J Am Chem Soc* 125:252–264
20. Parusel ABJ (2000) *Phy Chem Chem Phys* 2:5545–5552
21. Tesfay A, Ahmed MM, Mesfin RA (2010) *J Fluor* 20:1241–1248
22. Thiagarajan V, Selvaraju C, Malar EJP, Ramamurthy P (2004) *ChemPhysChem* 5:1200–1209
23. Lee C, Yang W, Parr RG (1998) *Phys Rev B* 37:785
24. Ainavarapu Sri Rama Koti (2002) Ph.D Theses submitted to Tata Institute of Fundamental Research Mumbai
25. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA Jr, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, 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 JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, and Pople JA, 2003. Gaussian 03, Revision B.01. Gaussian, Inc., Pittsburgh
26. Foresman JB, Keith TA, Wiberg KB, Snoonian J, Frisch MJ (1996) *J Phys Chem* 100:16098