Characterization of a Solvatochromic Fluorophore: 1-(2,2-Dicyanovinyl)-2,5-Dimethoxybenzene (DCN-2,5-DMOB)[1]

John R. Traver,[2] Gretchen M. Rehberg,[3] and Brian Wesley Williams[3,4]

Absorption spectra and steady-state fluorescence emission spectra for 1-(2,2-dicyanovinyl)-2,5-dimethoxybenzene in five solvents were determined. Although the absorption spectra demonstrate little solvatochromism, emission peaks show a red shift of roughly 90 nm between cyclohexane and methanol or acetonitrile, which appears to indicate charge transfer associated with a relaxed, as opposed to a vertical, excited state. Semiempirical gas phase AM1 calculations on this compound and the related unsubstituted 2,2-dicyanovinyl benzene indicate a dihedral twist of roughly 35° between the phenyl and the dicyanovinyl planes for both molecules in their ground states, as well as substantial polarity associated with the ground states of these compounds.

INTRODUCTION

Organic compounds having a charge transfer character are of both theoretical and practical interest. Theoretically, investigation of such molecules can promote a better understanding of mechanisms or theories of electron transport in biological or chemical systems. Practically, such molecules often have unique conductive or optical properties and, hence, may serve as interesting materials for electronic, nonlinear optical, or sensor devices. Most simply, since such molecules often demonstrate changes in their absorption and emission spectra with changing solvation (*solvatochromism*), they may also serve as spectral probes of different chemical or biological environments. Here, we wish to report some results on one such organic compound, 1-(2,2-di-

cyano)-2,5-dimethoxybenzene (DCN-2,5-DMOB) (Fig. 1). This molecule possesses a substituted aromatic electron donor connected through pi conjugation to a vinyl dicyano acceptor. Previous reports on the solvatochromic response of molecules with aromatic donors and conjugated vinyl dicyano electron acceptors include those on the unsubstituted dicyanovinyl benzene
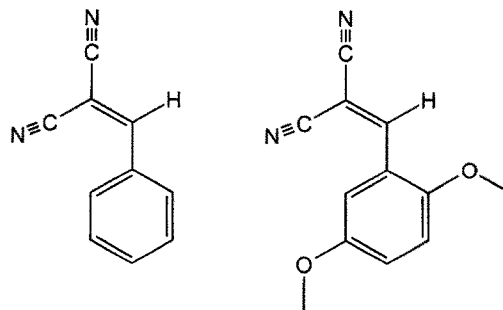

Fig. 1. 2,2 Dicyanovinylbenzene (DCNB), left, and 1-(2,2-dicyanovinyl)-2,5-dimethoxybenzene (DCN-2,5-DMOB), right. The cyano groups lie above the plane of the benzene ring, with the plane defined by the dicyanovinyl group making a dihedral angle of 35° with respect to the benzene plane.
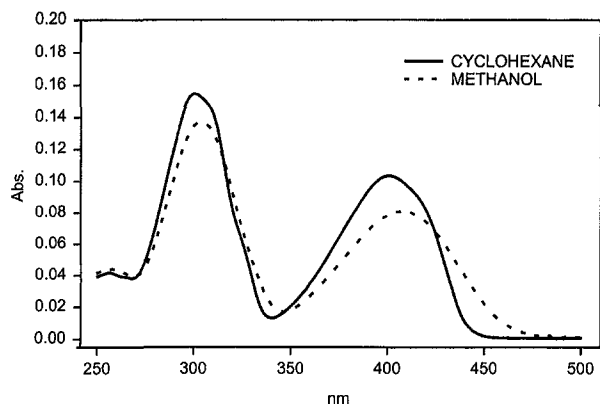
Fig. 2. Absorption spectra for DCN-2,5-DMOB in cyclohexane and methanol.

Table I. Absorption and Emission Data for DCN-2,5-DMOB in Several Solvents[a]

Solvent	Polarity (F)	Abs. Peak (nm)	Ext. Coeff. (10^3 M^{-1} cm^{-1})	Em. Peak (nm)
Cyclohexane	−0.0065	401	10.32	452
Ethyl acetate	0.4902	405	9.49	513
Acetone	0.7909	406	8.55	533
Methanol	0.8552	407	8.05	543
Acetonitrile	0.8636	407	8.28	542

[a]Absorption spectra were taken at a concentration of 1×10^{-5} M; emission spectra at a concentration of 3×10^{-6} M with excitation at the absorption maxima shown for each solvent.

(DCNB)[1] and 4-dimethylamino phenyl[2] compounds. Fluorescence was not observed from DCNB in several solvents, and low quantum yields were reported for the 4-dimethylamino phenyl in several different solvents at room temperature. Unlike these derivatives, an earlier brief report[3] on a series of dimethoxy-substituted phenyls indicated that the 2,5 derivative had a quantum yield in ethanol greater than that reported for the 4-dimethylamino derivative in several solvents,[2] as well as the greatest bathochromic shift in absorption of all the derivatives considered. As neither solvatochromic effects nor the extent of charge transfer appears to have been systematically investigated for any of these dimethoxy derivatives, we undertook investigation of solvatochromism in DCN-2,5-DMOB.

EXPERIMENTAL PROCEDURES

DCN-2,5-DMOB was prepared from 2,5-dimethoxybenzaldehyde and malonitrile using the $ZnCl_2$-catalyzed

Knoevenagel condensation described by Rao and Venkataratnam.[4] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.23 (1H, s), 7.66 (1H, d, $J = 3.0$), 7.09 (1H, dd, $J = 3.0$, 9.2), 6.86 (1H, d, $J = 9.2$), 3.81 (3H, s), 3.75 (3H, s). Absorption spectra for this compound were collected on Varian Cary 2300 UV-VIS-NIR and Hewlett-Packard 8452A spectrophotometers, at concentrations of 1×10^{-5} M in each of the solvents reported. Steady-state technical emission spectra were collected on a Perkin–Elmer LS-50 spectrofluorimeter in 1-cm quartz cuvettes at solution concentrations of 3×10^{-6} M, using a red-sensitive Hammamatsu R-955 photomultiplier, excitation for each solvent at the absorption maxima determined for that solvent, and excitation and emission bandpasses of 5.0 nm. The technical emission spectra were corrected for photomultiplier response by comparison with the fluorescence emission of the compound N,N-dimethyl-3-nitroaniline (Aldrich) and the use of published standard emission data for this compound[5] Reported absorption and emission peak values represent the weighted averages of experimental intensities within 90% of the highest experimental values observed, with the exception of the cyclohexane emission spectra, where a 95% value was used. All solvents used were of spectral grade or better and showed no fluoresence or unexpected absorbance under the conditions of measurement.

EXPERIMENTAL AND THEORETICAL RESULTS

Absorption Spectra

Representative absorption spectra for DCN-2,5-DMOB between 250 and 500 nm in cyclohexane and methanol are shown in Fig. 2. Peak maxima near 300–310 and 400–410 nm were observed in all five solvents examined. A previously reported spectrum for DCNB in cyclohexane shows a broad band centered at 300 nm, with no indication of absorption near 400 nm[1] Additionally, a reference spectrum[6] for 1,4-dimethoxybenzene in methanol shows a peak at approximately 290 nm but also no indication of any peak near 400 nm. Together, these data indicate that the presence of the 400-nm absorption peak requires both dimethoxy and dicyanovinyl substitution on the phenyl group, in that it cannot be accounted for by either substitution individually. Peak wavelengths and associated extinction coefficients for the 400-nm band absorption in all solvents are reported in Table I.
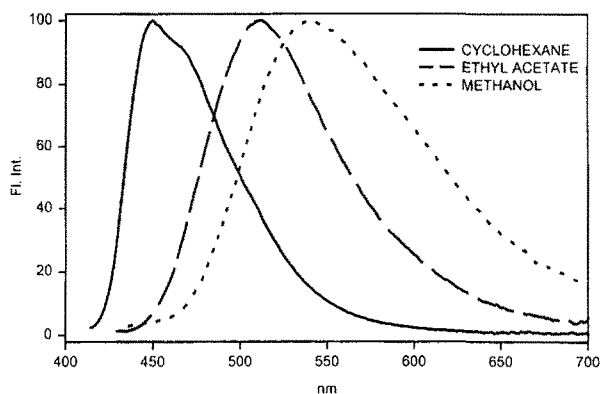
Fig. 3. Corrected, normalized steady-state emission spectra for DCN-2,5-DMOB in cyclohexane, ethyl acetate, and methanol. Excitation wavelengths correspond to the absorption maxima for each solvent.

These data indicate little solvatochromism for DCN-2,5-DMOB in this absorption band. Absorption or excitation bands associated with charge transfer often demonstrate red shifts with increasing solvent polarity, rationalized on the basis of increasing stabilization of a more polar Franck–Condon excited state relative to a less polar ground state. However, the lack of solvatochromic response observed for DCN-2,5-DMOB is consistent with the response of several other aromatic electron donors conjugated to vinyl dicyano electron acceptors which also lack pronounced solvatochromic shifts in absorption.[1] From ^{13}C NMR data, Katritzky *et al.* have suggested that, for these aromatic compounds, the ground state also has substantial polarity and that this solute polarity can be affected by changes in solvent polarity. Hence, any expected decrease in absorption energy brought about by stabilization of a polar excited state with increasing solvent polarity would be mitigated by concurrent stabilization of a polar ground state, leaving net absorption energies less affected by different solvents.

Extinction coefficients for the 400-nm band of DCM-2,5-DMOB are much smaller than those reported for the 425-nm band of 4-dimethylamino phenyl donor in a series of solvents (50 × 10^3 M^{-1} cm^{-1})[2] or the 300-nm band of DCNB in tetrahydrofuran (20.4 × 10^3 M^{-1} cm^{-1}).[1] For unsubstituted aromatic donors, Katritzky *et al.*[1] have previously rationalized the decreased extinction coefficient observed for 9-dicyanovinyl anthracene versus DCNB on the basis of steric hindrance, leading to an increased dihedral angle between planes defined by the aromatic and dicyano groups. As DCN-2,5-DMOB has a smaller extinction coefficient than unsubstituted phenyl, this explanation might suggest that the

steric effect of 2-methoxy substitution is to increase the dihedral angle between the aromatic donor and the dicyano vinyl acceptor. This possibility, along with a desire to understand the electronic properties of these compounds, motivated semiempirical computational studies on both DCN-2,5-DMOB and DCNB (see below).

Fluorescence Emission Spectra

Corrected, normalized emission spectra for DCN-2,5-DMOB in cyclohexane, ethyl acetate, and methanol are shown in Fig. 3, with the emission peak wavelengths for all five solvents given in Table I. Unlike absorption, a substantial solvatochromic red shift is observed in emission, with an overall magnitude of roughly 90 nm among these solvents. The emission spectrum for cyclohexane possesses a shoulder, unlike the more polar solvents with broad, structureless bands. Similar differences between emission spectra taken of the solvatochromic fluorophores Nile Red and 1-PDMPO in polar and nonpolar solvents have also been observed,[7,8] with the structure in nonpolar solvents attributed to different vibronic bands.

Exact quantum yields or lifetimes were not determined in the present study. Nevertheless, some qualitative comments can be made as to the relative intensities of DCN-2,5-DMOB emission in the different solvents and in comparison to emission from the 4-dimethylamino phenyl derivative. (The latter fluorophore was synthesized in a fashion similar to that for DCN-2,5-DMOB, and its emission measured using similar instrumental conditions). Overall, DCN-2,5-DMOB demonstrated easily measurable fluorescence in all the solvents, with observed emission much greater than that found for the more widely investigated 4-dimethylamino phenyl derivative. Uncorrected emission peak intensities for DCN-2,5-DMOB in methanol were roughly half of those for cyclohexane. The remaining solvents had relatively equal intensities among themselves, totaling roughly 80% of the cyclohexane intensity. In the same solvent, uncorrected emission peak intensities from DCN-2,5-DMOB were consistently 5 to 10 times greater than emission peak intensities observed for the 4-dimethylamino phenyl measured at three times the concentration (10^{-5} M). These qualitative trends appear to be consistent with reported quantum yields of 0.06 for DCN-2,5-DMOB in ethanol compared to 1 × 10^{-3} for the 4-dimethylamino phenyl in methanol.[2,3]

When both emission and absorption data are available for a solvatochromic compound, a conventional type of analysis is to the consider the Stokes' shift as some function of the bulk solvent polarity. Such analysis
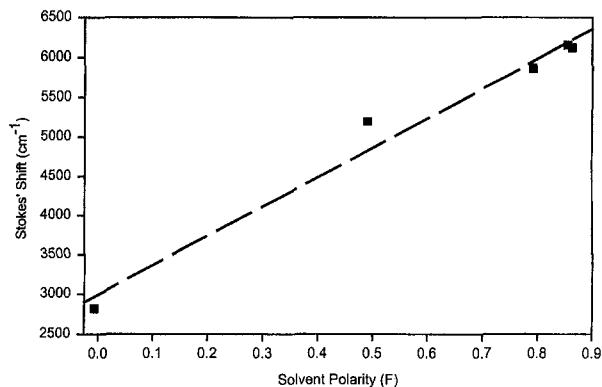
Fig. 4. Lippert plot of Stokes' shift versus the solvent polarity parameter F (see text). The dashed line represents a linear regression fit to the solvatochromic data.

is motivated by simple theoretical models which suggest a linear relationship between Stokes' shift and solvent polarity parameters; the slopes of such plots are then related to the dipole moment difference between the ground and the excited states. Among the usual assumptions in such models is that the ground and excited states have fixed dipole moments independent of the solvent and that excitation and emission are vertical processes. In a study of the validity of different polarity functions for this type of analysis, Koutek[9] recommended the use of the solvent polarity function F defined by

$$F = \left[\frac{2n^2 + 1}{n^2 + 2}\right]\left[\frac{(D - 1)}{(D + 2)} - \frac{(n^2 - 1)}{(n^2 + 2)}\right] \quad (1)$$

where D is the static dielectric constant and n is the refractive index. In Fig. 4, we have plotted the Stokes' shift observed for the five solvents measured versus this solvent polarity function F and carried out a linear regression fit to these data. The slope of the fitted line was found to be 3740 cm^{-1}. Analysis of these data using the conventional expression,[9]

$$\nu_{abs} - \nu_{em} = \frac{2\Delta\mu^2}{hca^3} F + \text{const.} \quad (2)$$

where $\nu_{abs} - \nu_{em}$ is the Stokes' shift between absorption and emission for each solvent, $\Delta\mu$ is the dipole moment difference between the ground and the excited states, a is the cavity radius of the solute within the solvent, F is the solvent polarity function, h is Planck's constant, and c is the speed of light, gives the dipole moment difference as

$$\Delta\mu = (3.3325 \times 10^{-32} \, C - \text{meters})[a^3 s]^{1/2} \quad (3)$$

where s is the slope of a plot of Stokes' shift versus the

solvent polarity parameter for each solvent (cm^{-1}) and the cavity radius a is given in Å. Estimation of the molecular volume and of intramolecular distances using molecular modeling (see below) suggest that a reasonable value for the cavity radius of DCN-2,5-DMOB is about 4 Å. With these parameters, and assuming a 10% relative error in the values for both the slope and the cavity radius, the experimental Stokes' shift data analyzed in a conventional fashion indicate a dipole moment difference of about 4.9 ± 1.0 D between the ground and the excited states.

Normally, a dipole moment change of this magnitude might be expected to lead to solvatochromic shifts in absorption as well as emission, yet only limited shifts in the absorption spectra were observed for DCN-2,5-DMOB. The simplest explanation for the available experimental spectra appears to be that the vertical Franck–Condon excited state produced immediately after excitation has a dipole moment which differs little from the ground state and that the dipole moment change associated with emission is therefore substantially dependent on an excited-state relaxation process involving changes in the molecular geometry. This would be consistent with some twisted intramolecular charge transfer (TICT) process. The presence of an excited-state relaxation process, which well accounts for the solvatochromism observed in emission, however, does not of itself entirely rule out the suggestion (experimentally supported by ^{13}C NMR data[11]) that absorption spectra may be influenced by effects related to a ground state dependent on the polarity of the solvent. Both of these effects tend to invalidate the assumption of a constant value for the ground state dipole moment: the ground state reached after emission from a relaxed excited state may differ substantially from the relaxed ground state undergoing absorption, and/or the relaxed ground state dipole moment may change with solvent polarity. Our conclusion from the conventional analysis of the steady-state spectroscopic data is that the magnitude of the dipole moment difference obtained is certainly consistent with charge transfer associated with changes in the molecular geometry following the initial excitation. However, because the conventional analysis assumes a constant dipole moment value for the ground state, the exact dipole moment difference obtained through this analysis may not be entirely correct.

Theoretical Results

Questions relating to possible conformational differences between DCNB and DCN-2,5-DMOB, the polarity of the ground state of DCN-2,5-DMOB, and the

Table II. AM1 Semiempirical Results for Vertical Excited States of Gas Phase DCNB and DCN-2,5-DMOB

	Abs. Wavelength (nm)	Configuration	Weight	Rel. Osc. Strength
DCNB	331.5	HOMO -> LUMO	0.768	7.81
		HOMO-1 -> LUMO +1	0.117	
		HOMO-2 -> LUMO +2	0.039	
		HOMO -> LUMO +2	0.030	
DCN-2,5-DMOB	367.5	HOMO -> LUMO	0.652	4.19
		HOMO-1 -> LUMO +1	0.089	
		HOMO -> LUMO +2	0.087	
		HOMO -> LUMO +1	0.059	
		HOMO-2 -> LUMO +1	0.051	
		HOMO-1 -> LUMO +2	0.046	

interpretation of steady-state spectral data prompted us to undertake semiempirical AM1 theoretical calculations on gas phase DCN-2,5-DMOB and DCNB. These calculations represent an initial attempt to understand the electronic structure of these two molecules through theory. While the structure and experimental data for DCN-2,5-DMOB, like DCNB, suggest the possibility of twisted intramolecular charge transfer (TICT), this point was not examined in detail. Also, no attempt was made explicitly to model or account for solvation effects in these calculations, in part because this is an active area for computational chemical research, and simple models quantitatively accounting for solvatochromism are still under development. This may seem somewhat inconsistent with experimental work centered on solvatochromic effects. However, comparison between theoretical results and experiment offers a means of interpreting experimental results as well as a way to test the reliability of the simplest theoretical models.

Investigation of the ground-state geometry of DCN-2,5-DMOB began by first considering the geometry of DCNB. Two earlier reports differ in their conclusions about the ground state geometry. The semiempirical MNDO studies reported by Moustafa et al.[10] conclude that DCNB, as well as several p-substituted derivatives, are planar. However, Katritzky et al.[1] reported that a semiempirical AM1 calculation indicated a dihedral angle of 37° between the dicyano and the phenyl planes and note that this agreed with experimental crystal structure values. To help resolve this question, geometry optimization of the DCN using AM1 as implemented in the SPARTAN computational chemistry package[11] was carried out. Initiated with several starting geometries, the results indicated a lower energy for the twisted geometry, agreeing with Katritzky et al.

Conformational searches using the AM1-SPARTAN package were also carried out for DCN-2,5-DMOB at several starting geometries. These calculations generally found minimum energy conformations to exist where the dimethoxy substituents are located in the phenyl plane but oriented away from the sigma bond connecting the dicyano and phenyl planes, the vinyl hydrogen is located on the same side of the molecule as the 2-methoxy substituent, and the plane containing the dicyano carbons makes a dihedral angle of approximately 35 or −35° with respect to the plane of the phenyl ring. These final geometries are essentially mirror images of each other and are consistent with an attempt to minimize stearic interaction between the 2-methoxy and the dicyano substituents. (The geometries shown in Fig. 1 represent an arbitrary choice of one of these two mirror image conformers.) These results suggest that the 2-methoxy substitution has little effect on the dihedral angle between the aromatic and the dicyano vinyl planes, at least in the gas phase, in that the minimum AM1 geometry found for DCMB can be superimposed almost exactly upon the DCN-2,5-DMOB conformers.

Following the calculation of Hartree–Fock (HF) molecular orbitals at these geometries, singly excited configuration interaction (CIS) calculations involving the 10 occupied and 10 unoccupied orbitals bracketing the highest occupied and lowest unoccupied (HOMO and LUMO) HF orbitals were then performed. Based on this calculation, dipole moment values for the ground and vertical excited states of DCNB and DCN-2,5-DMOB, as well as gas phase absorption wavelength values and relative oscillator strengths, were determined (Table II). Ground-state values of 4.52 and 7.09 D, respectively, were found for DCNB and DCN-2,5-DMOB. The ground-state value of 4.52 D for DCNB agrees with

that reported by Katritzky et al.,[1] but as these authors note, this is roughly 1 D lower than the reported experimental values of 5.44 and 5.28 D. This result suggests that the value of 7.09 D found for DCN-2,5-DMOB may also be too low, although no experimental data are available. The relatively high ground-state dipole moment value found for gas phase DCN-2,5-DMOB seems consistent with the suggestion of Katritzky et al.[1] that the ground state of dicyano-substituted aromatics are highly polar; this calculation does not, of course, address the question of whether the ground-state dipole moment might be changing with increasing solution polarity.

Interpretation of the gas phase theoretical results for the vertical excited states for both DCNB and DCN-2,5-DMOB is somewhat more difficult. The lowest energy allowed gas phase absorption wavelengths calculated are in reasonable agreement with values observed for each compound in nonpolar solvents; the ratio of the calculated relative oscillator strengths of the two transitions is also consistent with the ratio of the experimental extinction coefficients observed. However, the vertical excited-state dipole moments values obtained (7.94 and 12.04 D for DCNB and DCN-2,5-DMOB, respectively) represent substantial increases over the values obtained for the ground states. Such substantial changes in dipole moment might be expected to result in solvatochromism in the absorption spectra, yet this was not observed experimentally. At a minimum, this difference between theory and experiment seems to suggest that gas phase calculations at this level on aromatic dicyano compounds may not give an accurate representation of vertical excited-state dipole moment values in the presence of solvent.

CONCLUSIONS

DCN-2,5-DMOB is a solvatochromic fluorophore demonstrating a total magnitude of emission red shift with increasing solvent polarity roughly comparable to that observed with the better-studied fluorophores Nile Red and PRODAN. Compared to the structurally related DCNB and 4-dimethylamino phenyl compounds, this emission is relatively intense and easily observed at micromolar solution concentrations. Dimethoxy substitution on the phenyl in DCN-2,5-DMOB causes a 100-nm red shift in the absorption wavelength of the first absorption band in solution compared to DCNB. While the fluorescence emission spectra demonstrate substantial solvatochromism, the absorption spectra demonstrate little. The simplest explanation of the spectral data appears to be that, in solution, emission occurs from a relaxed,

rather than a vertical excited, state which has undergone substantial charge transfer associated with some change in the molecular geometry.

Resolving the details of exactly how charge transfer takes place in DCN-2,5-DMOB will obviously require additional study. Dynamic fluorescence studies of the emission from DCN-2,5-DMOB and related compounds should help to resolve questions related to relaxation of the vertical excited state. The synthesis and investigation of structural analogs of dicyano aromatics with greater rigidity about the single bond connecting aromatic donors to the dicyano acceptors would represent a different approach to this question. Finally, future higher-level theoretical calculations incorporating solvation effects might also help resolve the present difficulties between theory and experiment for the vertical excited state. The thorough investigation of aromatic dicyano compounds with respect to the mechanism of charge transfer appears to offer several avenues for investigation.

REFERENCES

1. A. R. Katritzky, D. Zhu, and K. S. Schanze (1991) J. Phys. Chem. 95, 5737–5742.
2. R. O. Loutfy and K. Y. Law (1980) J. Phys. Chem. 84, 2803–2808.
3. K. Y. Chu, J. Griffiths, and D. Ward (1981) J. Chem. Res. Soc. 300–301.
4. P. S. Rao and R. V. Venkataratnam (1991) Tetrahedron Lett. 32, 5821–5822.
5. K.-H. Hellewege (ed.) (1967), Luminescence of organic substances, in Atomic and Molecular Physics, Vol. 3, Landolt-Börnstein, New Series II, Springer-Verlag, Berlin, p. 228.
6. Sadtler Research Laboratories, Inc. Spectral Collection, UV 17874.
7. A. K. Dutta, K. Kamada, and K. I. Ohta (1996) Photochem. Photobiol. 93, 57–64.
8. T. A. Brugel and B. W. Williams (1993) J. Fluoresc. 3, 69–76.
9. B. Koutek (1978) Coll. Czech. Chem. Comm. 43, 2368–2386.
10. H. Moustafa, M. Hamed, S. El-Taher, and R. Hilal (1994) Ber. Bunsenges. Phys. Chem. 98, 1015–1021. H. Moustafa, S. El-Taher, M. Hamed, and R. Hilal (1994) Int. J. Quant. Chem. 49, 805–816.
11. SPARTAN Version 4.0, Wavefunction, Inc., 18401 Von Karman Avenue, No. 370, Irvine, CA 92715 USA. Calculations were performed on a Silicon Graphics Indigo^2 workstation.