
F.L. SUPIAN, T.H. RICHARDSON*, M. DEASY, F. KELLEHER, J.P. WARD & V. MCKEE

ABSTRACT

A study of surface pressure - area (Π-A) isotherms, surface potential (ΔV) and effective dipole moment (μ⊥) of two calix[4]arenes, 5,11,17,23-tetra-tert-butyl-25,27-diethoxycarbonyl methyleneoxy-26,28,dihydroxycalix[4]arene (calixarene I) and 5,17-(3-nitrobenzylideneamino)-11,23-di-tert-butyl-25,27-diethoxycarbonyl methyleneoxy-26,28,dihydroxycalix[4]arene (calixarene II) LB films which have the same lower rim but different upper rim has been carried out. This work used a NIMA Surface Potential (S-POT) sensor attached to an LB trough. Space filling model or Corey, Pauling and Koltun (CPK) precision molecular models have been used to estimate the size and the flexibility of both calix[4]arenes, which has been confirmed by X-Ray analysis in one case. The Π-A-isotherms confirmed that both of the calix[4]arenes form a monolayer film and the orientations of the plane of the calix ring are parallel with the air-water interface. The value of limiting area, (Alim) increases as a result of adding Fe3+ salt in the water subphase. For I, the value increases from 1.28 nm2 to 1.44 nm2 while for II, it increases from 1.70 nm2 to 1.86 nm2. ΔV measurements were performed on a water subphase containing Fe3+ salt in the concentration range 0 – 1.25 × 10–1 mM. ΔV of the compressed monolayer films increased with increasing Fe3+ concentration indicating the presence of Fe3+ salt bound within the calix[4]arenes. Using the ΔV values, the effective dipole moment has been found using the Helmholtz equation.

Keywords: Π-A isotherm, calix[4]arenes, effective dipole moment; LB; surface potential

INTRODUCTION

Basket-shaped macromolecules known as calixarenes have proved popular building blocks for the development of highly specific synthetic receptors particularly for ionic guest species (Gutsche 1998; Casnati & Ungaro 2000). They are attractive candidates for use in novel sensing materials since their properties are often modified via such binding interactions. Calix[n]arenes are macrocyclic compounds in which phenolic units are linked via methylene bridging groups at their ortho positions.
The spectacular development of these well defined macromolecular systems in recent years is related to the ease with which the upper (aryl) and lower (phenolic) rims have been modified in a stereocontrolled and regiocontrolled manner, coupled with the wide range of cationic and neutral and guests they have been found to bind. The smallest in the series is where four phenolic units make up the macrocyclic backbone \((n = 4)\). This offers a highly rigid platform on which to attach functional groups with potential to act as pre-organised binding sites for selective complexation, hence they have been widely studied in the field of molecular recognition, transportation and separation (Creaven et al. 2009). Langmuir-Blodgett (LB) films formed by calixarenes can be used to explore these functions.

The chemical structures of the two calix[4]arenes used in this study are shown in Figure 1. They are similar in cavity size and conformation, but differ in their substituents at the wider or upper rim. I is the known distal di-derivatised calix[4]arene compound bearing terminal ester groups at the narrow lower rim of the calixarene scaffold, where binding in solution normally occurs with alkali metal guests (Collins & McKervey 1989). The relatively rigid cone structure at this narrow rim often precludes strong binding to larger metal ions. The wider (upper rim) bears lipophilic tert-butyl groups with no ionophoric activity. II is a new calix[4]arene derivative synthesised by this group with the same functional groups at the lower rim, but with more diverse binding sites at the wider rim, to facilitate binding to the larger transition metals. Fe\(^{3+}\) is a physiologically important metal cation and plays a catalytic role in many processes such as oxygen metabolism and electron transfer (Aisen et al. 1999; Eisenstein 2000). A deficiency or excess can contribute to serious disease (Andrews & Engl 1999; Touati 2000; Cairo & Pietrangelo 2000; Beutler et al. 2001) hence detection of Fe\(^{3+}\) is of great importance. There have been only a few Fe\(^{3+}\) chemosensors reported to date (Zhang et al. 2009; Zhang & Fan 2009).

Calix[4]arenes have been successfully employed in ion selective electrodes (Cadogan et al. 1989; O’Connor et al. 1992; Diamond & McKervey 1996; Zeng et al. 2000; Lu et al. 2004; Lu et al. 2002; Lu et al. 2003). Difficulties associated with electrode modification can result in lower sensitivities being achieved, than is required for the determination of low levels of ionic species present in some real samples (Zhang et al. 2009).

In recent years, there has been an increase in the level of interest in the generation of ultrathin organic films, encapsulating ionophoric macromolecules, using techniques such as Langmuir-Blodgett (LB), as a way of overcoming such problems (Wang et al. 2009; Nabok et al. 1997).

The advantage of using the LB technique lies in the fact that sequential layers of ultrathin films can be formed, with controlled thickness and order on the molecular scale (Fanucci et al. 2001; Wu et al. 2001). Calixarenes form stable Langmuir films at air-water interface due to their amphiphilic structure (Lonetti et al. 2005). A way to understand the behaviour of Langmuir monolayers at the air-water interface is through the surface potential measurement (\(\Delta V\)) (Taylor & Bayes 1999). Based on the \(\Delta V\) values, the effective dipole moment \((\mu)\) of molecules at the interface can be calculated using the Helmholtz equation (Korchowiec et al. 2007). In this work, determination of the Langmuir properties of two calixarenes containing very different upper rims (one a conjugated push-pull electron system, the other a small-dipole system) is reported and the associated changes resulting from the addition of an Fe\(^{3+}\) analyte.

The synthesis of double-armed calixarenes with ionophoric ligating groups is well known, both with simple alkyl halides, RX or those with further functionality, for example XCH\(_2\)COOR. Hence, I was prepared in three steps as follows. \(p\text{-tert-Butylcalix[8]arene}\) (cyclic octamer) was first prepared by the modified Munch procedure (Gutsche et al. 1981; Munch & Gutsche 1990) from \(p\text{-tert}-\)butylphenol and paraformaldehyde in the presence

of KOH and was isolated as a white powder, in 70% yield. This was then subjected to molecular mitosis (Gutsche et al. 1985; Schmitt et al. 1997) to form \( p\)-tert-butylicalix[4]arene (cyclic tetramer). Sodium hydroxide was the base of choice due to the template effect between the cavity size of the tetramer and the size of the Na\(^+\) cation, which induced formation of the tetramer in a 71% yield. The reaction of \( p\)-tert-butylicalix[4]arene with ethyl bromoacetate, under conventional conditions for AC alkylation (\( K_2 CO_3 \) as base in acetonitrile as solvent) (Arnaud-Neu et al. 1989) resulted in the expected A,C-dialkyl derivative I with terminal ester groups.

The upper rim derived Calix-Schiff II was synthesized from I by the synthetic route shown in Figure 2. The distal di-derivatised calixarene I was subjected to nitrodealkylation, according to the literature procedure by W. Verboom et al. 1992.

Reduction of the nitro calix[4]arene IA to the calix[4]arene diamine IB was achieved by hydrogenation, at 2 atm. of pressure, in ethanol in the presence of Raney-Nickel in

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**Figure 2.** Reaction Conditions: (i) HCHO, KOH, xylene; (ii) NaOH, Ph\(_3\)O; (iii) BrCH\(_2\)COOEt, \( K_2 CO_3 \), CH\(_2\)CN; (iv) HNO\(_3\), CH\(_3\)COOH, CH\(_2\)Cl\(_2\); (v) H\(_2\) (2 atm.), Ra/Ni, EtOH; (vi) 3-nitrobenzaldehyde, EtOH
almost quantitative yield (99%). The $^1$H NMR spectrum displayed a broad singlet at 6.30 ppm, which exchanged with D$_2$O for the NH$_2$ group at the upper rim. An upfield shift was noted for the aromatic protons which resonated at 7.01 ppm and 6.95 ppm. The tert-butyl protons also shifted downfield to 1.24 ppm. A quartet at 4.29 ppm and triplet at 1.32 ppm were observed for the ester protons. The $^{13}$C NMR spectrum showed an upfield shift for the ArC$_{-}$OH to 151.7 ppm and peaks for the ester CH$_3$ and ester CH$_2$ were observed at 61.2 ppm and 14.2 ppm, respectively. The IR spectrum showed an absorbance for the NH and phenolic OH at 3310 cm$^{-1}$ while the ester carbonyl group absorbed at 1746 cm$^{-1}$. No signals were apparent for the NO$_2$ group indicating successful reduction to the diamine.

The attachment of N-ligating groups through imine bond formation has been successful at the upper and lower rim of calixarenes. This has resulted in the formation of calixarene-Schiff base receptors which have shown potential for cation recognition, particularly with transition metals (Creaven et al. 2008).

Therefore the calixarene diamine IB was heated to reflux temperature in ethanol with a 5 molar excess of 3-nitrobenzaldehyde. A yellow precipitate was isolated after cooling which was recrystallised from chloroform/ether); the nitrophenyl ArC$_{-}$NH$_2$ showing a signal for water also being present. The inclusion of solvent is a common occurrence. The mass spectral analysis for [M+1]$_{\text{H}}$ was calculated to 1005.4, which was in agreement with the observed value.

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**EXPERIMENTAL PROCEDURES**

**CALIXARENE SYNTHESIS AND COMPOUND DATA**

**Preparation of 5,11,17,23-tetra-tert-butyl-25,27-diehoxycarbonyl methyleneoxy-26,28,dihydroxycalix[4]arene [I]** The calixarene diester derivative (I) was prepared in 81% yield following a procedure similar to that described by McKervey et al., m.p.: 172 – 174ºC (lit.$^{19}$ 182 – 184ºC); R$_f$: 0.21 (70% DCM/petroleum ether); $\nu_{\text{max}}$/cm$^{-1}$ (KBr): 3427 (polymeric OH str.), 2962, 2902, 2864 (C-H str.), 1751 (C=O), 1750 (C-OH str.), 3310 (phenolic OH & NH), 1746 (C=O); $\delta_{\text{H}}$/ppm (75 MHz, CDCl$_3$): 7.07 (2H, s, phenolic OH), 7.02 (4H, s, ArCH$_2$), 6.82 (4H, s, ArCH$_2$), 4.72 (4H, s, -O-C$_3$H$_7$-CO$_2$CH$_3$), 4.45 (4H, d, ArCH$_2$-Ar, $J$ = 12.0 Hz), 4.30 (4H, q, CH$_2$CH$_2$CH$_3$, $J$ = 7.0 Hz), 3.32 (4H, d, methylene, $J$ = 12.0 Hz), 1.33 (6H, t, CH$_3$CH$_2$, $J$ = 7.0 Hz), 1.30 & 1.26 (2 x 18H, s, tert-butyl); $\delta_{\text{C}}$/ppm (75 MHz, CDCl$_3$): 169.2 (ester C=O), 150.7 (ArC$_{-}$OH), 150.3 (ArC$_{-}$OR), 147.1, 141.5 (ArC$_{-}$-tert-butyl), 132.5, 128.0 (ArC$_{-}$), 125.7, 125.1 (ArCH$_2$), 72.4 (Ar-OCH$_2$), 61.2 (ester -CH$_2$CO), 33.9, 33.7 (C$_q$-tert-butyl), 31.8 (Ar-CH$_2$-Ar), 31.6, 31.0 (tert-butyl CH$_3$), 14.2 (ester -CH$_3$CH$_2$).

**Preparation of 5,17-dinitro-11,23-di-tert-butyl-25,27-diehoxycarbonyl methyleneoxy-26,28-dihydroxycalix[4]arene [I]A** Nitro de-alkylation of the diethyl ester calixarene I was achieved following the literature procedure (Eisenstein 2000) using nitric acid in a mixture of acetic acid and dichloromethane. Recrystallisation from methanol afforded a yellow solid (4.32 g, 21%). M.p.: 197-199 ºC (lit.$^{20}$ 198-200ºC); R$_f$: 0.42 (70% DCM/Pet. ether); $\nu_{\text{max}}$/cm$^{-1}$ (KBr): 3289 (phenolic OH), 2967: 2868 (aliphatic CH), 1727 (C=O), 1510: 1336 (NO$_2$); $\delta_{\text{H}}$/ppm (300 MHz, CDCl$_3$): 9.84 (s, 2H, phenolic OH), 7.96 (s, 4H, ArCH$_2$), 7.03 (s, 4H, ArCH$_2$), 4.72 (4H, -OCH$_2$CO), 4.51 (d, 4H, Ar-CH$_2$-Ar), 4.32 (q, 4H, ester CH$_2$), 3.44 (d, 4H, Ar-CH$_2$-Ar), 1.36 (t, 6H, ester CH$_2$), 1.09 (s, 18H, tert-butyl); $\delta_{\text{C}}$/ppm (75 MHz, CDCl$_3$): 168.6 (C=O), 158.8 (C$_q$-Ar-OH), 151.8 (ArC$_{-}$OR), 144.8 (C$_q$-Ar-tert-butyl), 141.8 (C$_q$-Ar-NO$_2$), 131.1 (ArC$_{-}$), 128.9 (ArC$_{-}$), 126.8, 125.4 (ArCH$_2$), 73.5 (-OCH$_2$CO), 60.8 (ester CH$_3$), 33.9 (C$_q$-tert-butyl), 31.7 (Ar-CH$_2$-Ar), 29.9 (tert-butyl CH$_3$), 14.0 (ester CH$_3$).

**Preparation of 5,17-diamino-11,23-di-tert-butyl-25,27-diehoxycarbonyl methyleneoxy-26,28-dihydroxycalix[4]arene [IB]** To a suspension of dinitro calixarene IA (2 g, 2.4 mmol) in ethanol (200 mL) was added a catalytic amount of Raney-Nickel. The mixture was placed on a hydrogenator for 2 hours (2 atm) then filtered through a bed of celite. The solution was moved in vacuo to leave compound IB as a pink solid (1.97 g, 99%), m.p.: 175 – 177ºC; R$_f$: 0.75 (DCM/Pet. Ether); $\nu_{\text{max}}$/cm$^{-1}$ (KBr): 3310 (phenolic OH & NH), 1746 (C=O); $\delta_{\text{H}}$/ppm (300 MHz, CDCl$_3$): 7.12 (s, 2H, phenolic OH), 7.01 (s, 4H, ArCH$_2$), 6.95 (s, 4H, ArCH$_2$), 6.30 (s, 4H, NH$_2$), 4.82 (s, 4H, -OCH$_2$CO), 4.52 (d, 4H, Ar-CH$_2$-Ar), 4.29 (q, tert-butyl).
Preparation of 5,17-(3-nitrobenzylideneamino)-11,23-dihydroxycalix[4]arene [II] To a solution of calixarene diamine IB (1.0 g, 1.2 mmol) in ethanol (75 mL) was added m-nitrobenzaldehyde (1.0 g, 6 mmol), and the solution was heated at reflux temperature for 16 hours. After cooling, the solid residue was recovered by vacuum filtration and recrystallised from chloroform/methanol to give a yellow solid (0.80 g, 67%). M.p.: 242 – 244ºC; Rf = 0.48 (30% EtOAc/Pet. Ether); cPK PRecISIoN MoLecULAR MoDeLS

**X-RAY EXPERIMENT**

Diffraction data for Calix-Schiff II were collected at 150(2)K on a Bruker Apex II CCD diffractometer. The structure was solved by direct methods (Sheldrick et al. 2005) and refined on F² using all the reflections (Sheldrick 2008). All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms were inserted at calculated positions using a riding model. C₆H₁₁NO₃, monoclinic, C₂, a = 25.174(3), b = 10.8910(15), c = 10.0060(14) Å, β = 112.315(2)º, V = 2537.9(6) Å³, T = 150(2)K, λ = 0.17073 Å, Z = 2, 10963 reflections measured, 2637 unique (Rint = 0.0391), wR2 = 0.1544 (all data), R1 = 0.0542 (I > 2σI).

**X-RAY EXPERIMENT**

**Surface Potential and Effective Dipole Moment Measurements**

The NIMA surface potential probe has a precision of ±1 mV together with the LB trough (Figure 3). It connects directly to the existing NIMA Interface Unit. While the LB software measures the surface pressure at the air-water interface, the ΔV sensor measures the potential difference above and below the film. Changes in surface pressure are only detected once a closely packed monolayer begins to form, whereas ΔV often increases as soon as the molecules are spread onto the water surface. During compression, as the orientation of the molecules change, the alignment of molecular dipoles causes a large change in the surface potential (NIMA 2009).

A net potential or Volta potential arises when the molecules are aligned at a surface and a double layer of charges exists. ΔV is hence the change in the Volta potential between the clean water surface and the monolayer coated surface. From the ΔV, the molecular orientation and dipole per molecule can be calculated. (Langmuir Films or Insoluble Monolayers at the Air Water Interface 2009).

From the ΔV values, μ of molecules at the interface can be calculated using either equation (1) or (2). Equation (1) is from the Helmholtz equation:

\[
\Delta V = \frac{\mu}{\varepsilon \varphi A}
\]  

(1)
where $A$ is the area per molecule, $\varepsilon_0$ is the vacuum permittivity ($8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$), $\varepsilon$ is the relative permittivity of the monolayer (here, it is assumed to be 1) (Korchowiec et al. 2007).

The same values also can be obtained from equation (2):

$$\mu_\perp = \Delta V A (2.65 \times 10^{-2}).$$

where $A$ is the area per molecule in $\text{Å}^2$, and $2.65 \times 10^{-2} \text{ C m}^{-1} \text{ V}^{-1}$ is a constant arising from converting the dipole moment into Debye units ($(1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m})$ Osvaldo et al. 1997).

**RESULTS AND DISCUSSIONS**

**X-RAY RESULTS**

Crystals of Calix-Schiff II, suitable for an X-ray diffraction study, were obtained from chloroform/methanol. The X-ray crystal structure of II is shown below (Figure 4).

The molecule lies on a 2-fold axis and adopts a distorted cone conformation in the solid state. The conformation of II is defined by the angles which the aromatic rings make with the plane of the four methylene carbon atoms which link them, viz 75.59(8)$^\circ$ and 43.33(9)$^\circ$ for the rings carrying the Schiff base and the tert-buty1 groups, respectively. There is an intramolecular O-H…O hydrogen bond between the the phenolic O-H group and a proximal ethereal oxygen (O3-H3…O5 0.2692(4) nm. The molecules are stacked one inside the other, with the stacks running parallel to the b axis as shown in Figure 5.

**CPK PRECISION MOLECULAR MODELS**

CPK modelling reveals a projected area per molecule for I and II ranging from 1.21- 1.96 nm$^2$ and 1.44- 1.96 nm$^2$ respectively if the assumption is made that the lower rim groups make contact with the water surface and the upper rim groups protrude orthogonally from the plane of the surface.

**LB: Π-A isotherm** From the isotherm, the limiting area ($A_{lim}$) values are slightly different for of the two
calix[4]arene. The limiting area of both films increases upon the additional of Fe$^{3+}$ salt in subphase, indicating that the Fe$^{3+}$ ions have been incorporated into the calixarene layer, most probably within the lower rim region since there would be a strong interaction between the triply charged cation and the oxygen lone electron pairs.

The size for both calix[4]arenes using the CPK modelling ranges from 1.1 nm to maximum 2.5 nm while from the experimental values, $A_{\text{lim}}$ (Figure 7), the values are estimated to be around 1.28 nm to 1.40 nm and 1.70 nm to 1.78 nm for I and II respectively (Table 1). By comparing the modelled values using CPK modelling with the limiting area, conclusion can be drawn that the calixarenes are orientated such that the plane of the calix ring is parallel to the water surface (Lonetti et al. 2005). Figure 8 shows the possible orientations of the calixarene molecules.

**Figure 5.** Stacking arrangement of II

**Figure 6.** CPK modelling for I (left) and II (right); Front view

**Surface Potential ($\Delta V$) and Effective Dipole Moment of Molecules at the Interface ($\mu_{\perp}$).**

Figure 9 depicts the $\Delta V$-A versus area per molecule relationship for II on a pure water subphase. The relationship can be seen at the onset of the surface potential occurs at slightly larger area for the ion-doped subphase, as is also the maximum $\mu_{\perp}$ reached. This suggests that the inclusion of the Fe$^{3+}$ ions is contributing to the overall measured potential.

Table 2 presents the individual potential values for both materials along with the effective dipole moments over the Fe$^{3+}$ concentration range studied. These data are

**Figure 7.** $\Pi$-A isotherm for I; the limiting area increased from (a) water subphase to (b) Fe$^{3+}$ salt ($1.25 \times 10^{-2}$mM)
TABLE 1. Limiting area and possible orientation of I and II in water subphase and Fe$^{3+}$ subphase

<table>
<thead>
<tr>
<th>Subphase</th>
<th>Concentration (1.00 × 10$^{-2}$ mM)</th>
<th>I A$_{lim}$ (nm$^2$)</th>
<th>Orientation</th>
<th>I A$_{lim}$ (nm$^2$)</th>
<th>Orientation</th>
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<tbody>
<tr>
<td>1 Water</td>
<td>0</td>
<td>1.28</td>
<td>II</td>
<td>1.70</td>
<td>II</td>
</tr>
<tr>
<td>2 Fe$^{3+}$ salt</td>
<td>1.25</td>
<td>1.30</td>
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<td>II</td>
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<tr>
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<td>1.78</td>
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FIGURE 8. Possible orientation of the molecules at water-air interface; (a) parallel orientation (ǁ), where a line underneath shows where the air/water interface, (b) perpendicular (⊥) orientation.

FIGURE 9. (a) Surface potential and (b) effective dipole moment for II
plotted in Figure 10 as a function of concentration. For both calixarenes, $\Delta V$ gradually rises up to $\approx 0.04$ mM, before stabilising for higher concentrations. This suggests that the potential rises monotonically as increasing number of Fe$^{3+}$ ions are incorporated into the calixarene monolayer, but once the maximum amount of ions have been complexed, no further increase in $\Delta V$ is possible.

As expected, $\mu_\perp$ of the complex (Figure 11) increases rapidly to a maximum value at a concentration of $\approx 0.04$ mM (Taylor et al. 1992).

The $\mu_\perp$ measured for II is significantly larger than that for I. This is because the presence of the conjugated electron system terminated in the nitro group in II compared to the simple methyl group in material I lead to a strong dipole that is aligned orthogonally with respect to the plane of the water surface. The $\mu_\perp$ calculations have used $\varepsilon = 1$ for both materials; as most researchers assume that for ultra-thin films since the thickness of the air gap between the monolayer and the vibrating electrode is very large compared to the thickness of the monolayer itself.

The Langmuir properties of two calixarenes containing very different upper rims (calixarene II which is a conjugated push-pull electron system, and calixarene I which is a small-dipole system) have been investigated. II-A isotherms and $\Delta V$ plots have revealed that Fe$^{3+}$ ions

<table>
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<tr>
<th>Subphase</th>
<th>Concentration ($1.00 \times 10^{-2}$ mM)</th>
<th>$\Delta V_{\text{max}}$ (mV)</th>
<th>$\mu_{\perp \text{max}}$ (D)</th>
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<tbody>
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$\Delta V_{\text{max}}$, and effective dipole moment of molecules at the interface ($\mu_\perp$)

**CONCLUSION**

FIGURE 10. Surface potential maximum, $\Delta V_{\text{max}}$ versus concentration for I and II added with Fe$^{3+}$ salts
Figure 11. Effective dipole moment, $\mu_{\perp \text{max}}$ versus concentration for I and II added with Fe$^{3+}$ salts.

ACKNOWLEDGEMENTS

F.L.S. wishes to acknowledge the Universiti Pendidikan Sultan Idris (UPSI) and Government of Malaysia for the award of a scholarship which enabled her to undertake this work. J.P.W. wishes to thank the Postgraduate R&D Skills Programme, and ITT-Dublin’s PhD Continuation Fund for grant support.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 746610. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

REFERENCES


