

Processable low band gap π -conjugated polymer, poly(isothianaphthene)

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Low band gap conducting polymer poly(isothianaphthene) (PITN), which is usually considered to be insoluble and cannot be processed into film, has been prepared by dehydrogenation from its precursor polymer, poly(1,3-dihydroisothianaphthene), with sulfuryl chloride. It is found that the intermediate towards PITN is structure **2**. Through propagation of structure **2**, a quinoid type conjugated poly(isothianaphthene) is obtained. The structure defects are benzyl chloride bonds and chlorine-doped species, which can induce aggregation of PITN in the solution. A stable PITN dispersion can be obtained by precise control of the reaction conditions together with the use of pyridine as an agent for termination of the reaction and for solvation to prevent PITN from further aggregation. The resulting PITN dispersion can be cast into film.

(Keyword: low band gap; poly(isothianaphthene); sulfuryl chloride)

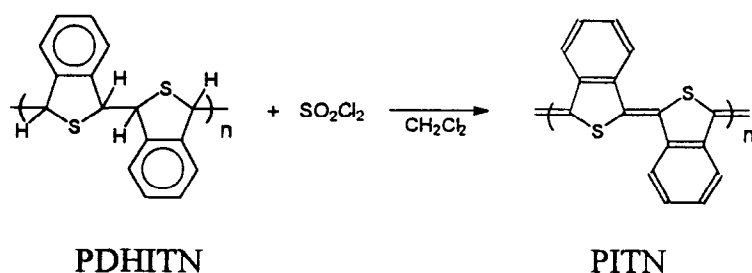
Low band gap polymers are important conjugated conducting polymers and have drawn great attention for their much higher conductivity in the neutral state ($10^{-2} \text{ S cm}^{-1}$) than other conjugated polymers (10^{-9} – $10^{-14} \text{ S cm}^{-1}$), for their colourless transparency after doping¹, and their non-linear optical properties². The low band gap polymers that have been found so far include poly(isothianaphthene)s (PITNs) **1** (1.0 eV)^{3,4}, poly(2,3-dihexylthieno[3,4-b]pyrazine) (0.95 eV)⁵, poly(arene methine)s (0.69–1.47 eV)^{6,7}, poly(cyclopentadienophene)s (0.8–1.2 eV)^{8–10}, ladder-type oligomers (1.2–1.6 eV)^{11,12}, tetrathiafulvalene oligomers¹³ and zwitterionic planar conjugated pyrrole-derived oligomers (1.1 eV)¹⁴, which have band gaps lower than 1.5 eV. Among these polymers, PITN is the most studied and its film prepared electrochemically^{14,15} exhibits a high contrast and reversible colour change from blue at the neutral state to nearly transparent light greenish-yellow at the doped state. All of the low band gap polymers mentioned above are insoluble except the oligomers and poly(2,3-dihexylthieno[3,4-b]pyrazine).

The PITNs can be prepared via polymerization of the monomers electrochemically, to obtain films deposited on the electrode surface, and chemically, using FeCl_3^{16} as an oxidant to obtain powdery products. They can also be prepared chemically via a precursor route using $\text{SO}_2\text{Cl}_2^{17}$ as dehydrogenation agent to remove the hydrogen from main chains of the precursor polymer, poly(1,3-dihydroisothianaphthene) (PDHITN), in solution. The resulting PITN is powdery. The PITN prepared by the methods mentioned above is all insoluble and non-processable. Introducing a long chain alkyl substituent ($\text{C}_{10}\text{H}_{21}$) on the carbon 5 of the aromatic ring allows PITN to become soluble and processable⁵. However, the resulting PITN derivative has an increased band gap of 1.4 eV (λ_{max} at 512 nm).

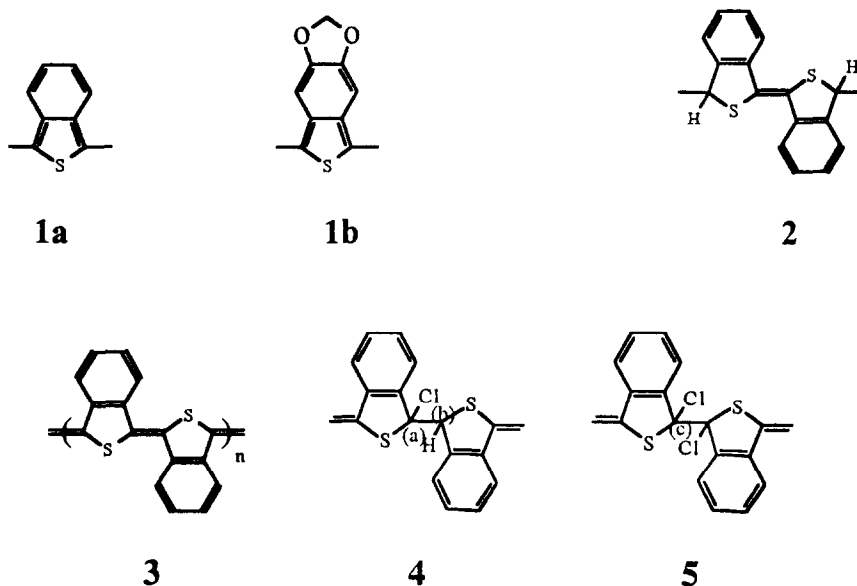
PITN is expected to be insoluble and non-processable due to its highly coplanar quinoid structure **3** according to the quantum-chemical calculation¹⁸. This work reports a method for the preparation of processable PITN dispersion, which can be cast into films having a conductivity of $10^{-1} \text{ S cm}^{-1}$ and electrochromic properties with high contrast. Our approach to preparing PITN film involves the dehydrogenation of PDHITN in dichloromethane solution followed by addition of pyridine, which serves as a dehydrogenation-terminating, undoping and stabilizing agent. The resulting PITN in the solution is unexpectedly stable. It is expected that this method is also applicable for preparations of PITN derivatives, such as **1b**.

The reaction procedure is described below. PDHITN was prepared in accordance with the method of Wudl *et al.*³ by cationic polymerization of ITN monomer (100 mg per 5 ml solvent) with $\text{BF}_3 \cdot \text{OEt}_2$ as catalyst (0.3 μl per 100 mg of ITN) in anhydrous dichloromethane at -78°C for 30 min. The PDHITN in dichloromethane was subjected to dehydrogenation by addition of SO_2Cl_2 in order to obtain PITN (Scheme 1). The concentrations of PDHITN and SO_2Cl_2 were controlled at the level of 1 mg PDHITN in 1 ml solvent and 1 equivalent SO_2Cl_2 . The reaction was allowed to proceed for about 3 min at room temperature, and then terminated by addition of pyridine with a volume ratio to solvent of 1/20. The resulting solution has a dark blue colour and is stable at room temperature for about 2 days. Gel permeation chromatography (g.p.c.) analysis on the resulting stable solution with chloroform as eluent gives a sharp peak with elution time which is lower than that of the polystyrene standard at the upper limit, 2.7×10^7 . However, the weight- and number-average molecular weights of its precursor polymer, PDHITN, are only 2.0×10^5 and 7.8×10^4 , respectively. This result would indicate that aggregation of the PITN in the solution occurs and that the PITN appeared as microgels

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Scheme 1



Scheme 1

in the solution. Such microgels have a diameter smaller than $0.25 \mu\text{m}$, since they can pass through a $0.25 \mu\text{m}$ filter during the preparation of testing samples for g.p.c.

Higher concentrations of PDHITN and SO_2Cl_2 and longer reaction time would result in precipitation of PITN even though pyridine is added; addition of a strong base (i.e. triethylamine) as terminating agent would also lead to precipitation of PITN. The critical conditions for obtaining the stable PITN solution are the concentrations of PDHITN and SO_2Cl_2 as well as the reaction time and addition of a suitable base.

In the PDHITN system, the active hydrogen is a sterically hindered benzylic hydrogen, so the elimination reaction is preferred to the substitution reaction, leading to the formation of tetrasubstituted alkenes in between two neighbouring units (structure 2). This intermediate structure is identified by examining the structure of the product prepared at the reduced concentration of SO_2Cl_2 (0.25 equivalent) so that the dehydrogenation reaction is incomplete. Its i.r. absorption spectrum shows the generation of new peaks at 1680 cm^{-1} (stretching absorption peak of tetrasubstituted alkenes¹⁹), indicating that structure 2 does appear during the reaction period. Its u.v.-vis-n.i.r. spectrum together with that of the case with 0.5 equivalent SO_2Cl_2 (Figure 1, curves a, d) shows the presence of the absorption peak at 489 nm ($\pi-\pi^*$) of structure 2. The assignment is made based on the absorption peak of dialkylsulfide stibene (diphenyl

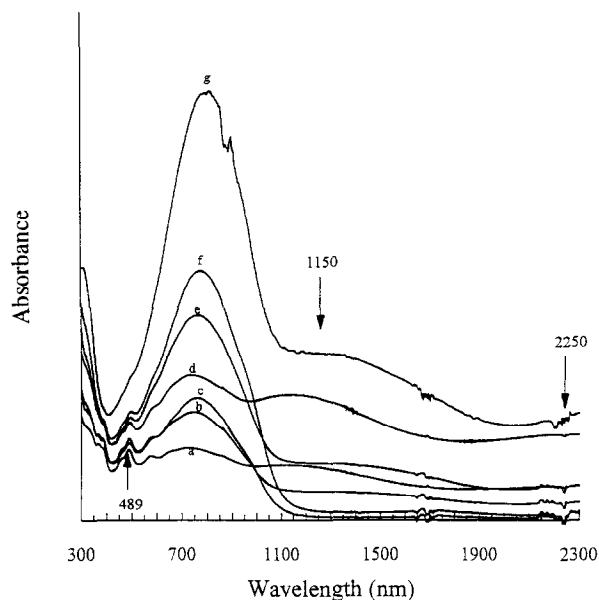


Figure 1 U.v.-vis-n.i.r. spectra of PITN solutions after dchydrogenation of PDHITN with various contents of SO_2Cl_2 : (a) 0.25 eq., (b) 0.25 eq. with pyridine, (c) 0.25 eq. with triethylamine, (d) 0.50 eq., (e) 0.50 eq. with pyridine, (f) 0.50 eq. with triethylamine, (g) 1.0 eq. with pyridine

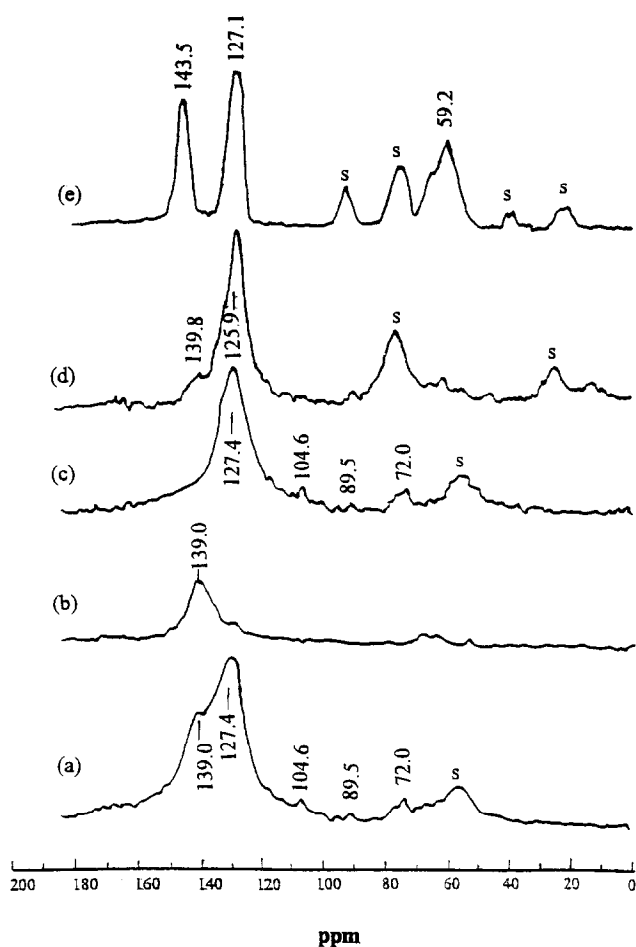


Figure 2 Solid state ^{13}C n.m.r. spectra: (a) PITN without neutralization; (b) non-protonated carbon absorption curve of PITN without neutralization by INEPT method; (c) protonated carbon absorption curve by subtracting (b) from (a); (d) neutral PITN; (e) PDHITN ('s' means side band)

dialkylsulfide alkene) and the use of empirical rule of enone and dienone absorptions^{20,21}. The λ_{max} of structure **2** can be estimated as 473 nm, which is obtained from $[303 \text{ nm} + (85 \times 2)]$; the first term in the bracket is the λ_{max} of stilbene and 85 nm in the second term is the increment of one SR group. This estimated value is close to the experimental value, 489 nm, which leads us to make such an assignment. The absorption intensity of the PITN subchains at 724–734 nm increases as the content of SO_2Cl_2 increases from 0.25 (curve a) to 0.5 equivalents (curve d), indicating the increase of the extent of dehydrogenation. The PITN subchains so produced are of structure **3**, since the quinoid structure has lower energy than the aromatic structure¹⁸ and no rearrangement is required in the propagation of structure **2** during the dehydrogenation step. However, during the dehydrogenation reaction, substitution of the hydrogen by chlorine cannot be avoided and thus can result in a formation of benzylic chloride bonds, which are randomly dispersed in the backbone of PITN. The presence of benzylic chloride bonds can be observed from the solid state ^{13}C n.m.r. spectrum of this PITN (without neutralization with pyridine) (Figure 2, curve a). Further examination of this PITN product with insensitive nucleus enhancement by polarization technique

(INEPT) for non-protonated (quaternary) carbon was also carried out and the spectrum is shown as curve b. By subtracting spectrum b from a, the protonated (tertiary) carbon absorption spectrum is obtained (curve c). The chemical shifts of the protonated and non-protonated aromatic carbons appear at 127.4 and 139.0 ppm, respectively. Comparing curve c with the absorption spectrum of the neutral PITN (curve d), several additional minor peaks appear in curve c. Three of them, at 104.6, 89.5 and 72 ppm, are of particular interest, and must be contributed from tertiary carbons. For the precursor PDHITN, the peak at 59.2 ppm (Figure 2, curve e) can be assigned to benzylic carbon²², which is to be used as a reference, in conjunction with the empirical rule of n.m.r. shift (which is an empirical correlation of n.m.r. shift by substituent effects upon replacement of hydrogen by various substituents in linear and branched alkanes²³). These minor n.m.r. peaks can be assigned to various carbon atoms (a, b, c) indicated in structures **4** and **5**: 104.6 ppm (carbon c), 89.5 ppm (carbon a) and 72 ppm (carbon b). These peaks are very weak in comparison to the tertiary and quaternary aromatic carbons. These aromatic form structures can be considered as conjugation defects in the backbone of PITN. The amounts of structures **4** and **5** are very minor, since the X-ray photoelectron spectrum of doped PITN (i.e. PITN without neutralization with organic base) shows a very small chlorine peak.

As the content of SO_2Cl_2 increases to 1.0 equivalent, the u.v.–vis.–n.i.r. spectrum of the resulting solution (Figure 1, curve g) shows a λ_{max} at 794 nm contributed from structure **3**, which is higher than those with 0.25 and 0.5 equivalents SO_2Cl_2 by 70 nm and 60 nm, respectively. This indicates an increase in conjugation length after the increase in extent of dehydrogenation.

As the resulting solutions with 0.25 and 0.5 equivalents SO_2Cl_2 are added with the strong base, triethylamine, the λ_{max} of u.v.–vis.–n.i.r. absorption due to π – π^* transition (Figure 1, curves c and f) show a red-shift toward 760 and 768 nm, respectively, and a disappearance of the absorptions at 1150 and 2250 nm (due to polaron/bipolaron resulting from HCl doping). This indicates that the strong base can eliminate the benzyl chloride bond, resulting in an increase of conjugation length, and completely neutralize the sample. The undoped PITN in the solution is only stable for about 1 h and cannot be cast into film. For the case with 1 equivalent SO_2Cl_2 , precipitation of PITN occurs immediately. This is because triethylamine can attack the benzylic chloride bond through substitution nucleophilic bimolecular reaction ($\text{S}_{\text{N}}2$) for its strong basicity.

During the dehydrogenation process, the side reaction of chlorination substitution always takes place simultaneously, which induces aggregation. However, as a weak base is added, in our case pyridine, partial undoping and solvation by pyridine occur simultaneously. Since the weak base, pyridine, does not attack the benzylic chloride bond, precipitation of PITN can be prevented. For the cases with 0.25 and 0.5 equivalents SO_2Cl_2 , their u.v.–vis.–n.i.r. spectra (Figure 1, curves b and e) show an absorption due to π – π^* transition with λ_{max} at 747 and 757 nm, which are higher than those without addition of pyridine by 23 nm. However, very weak absorption bands at 1150 and 2250 nm still appear, indicating that the undoping by

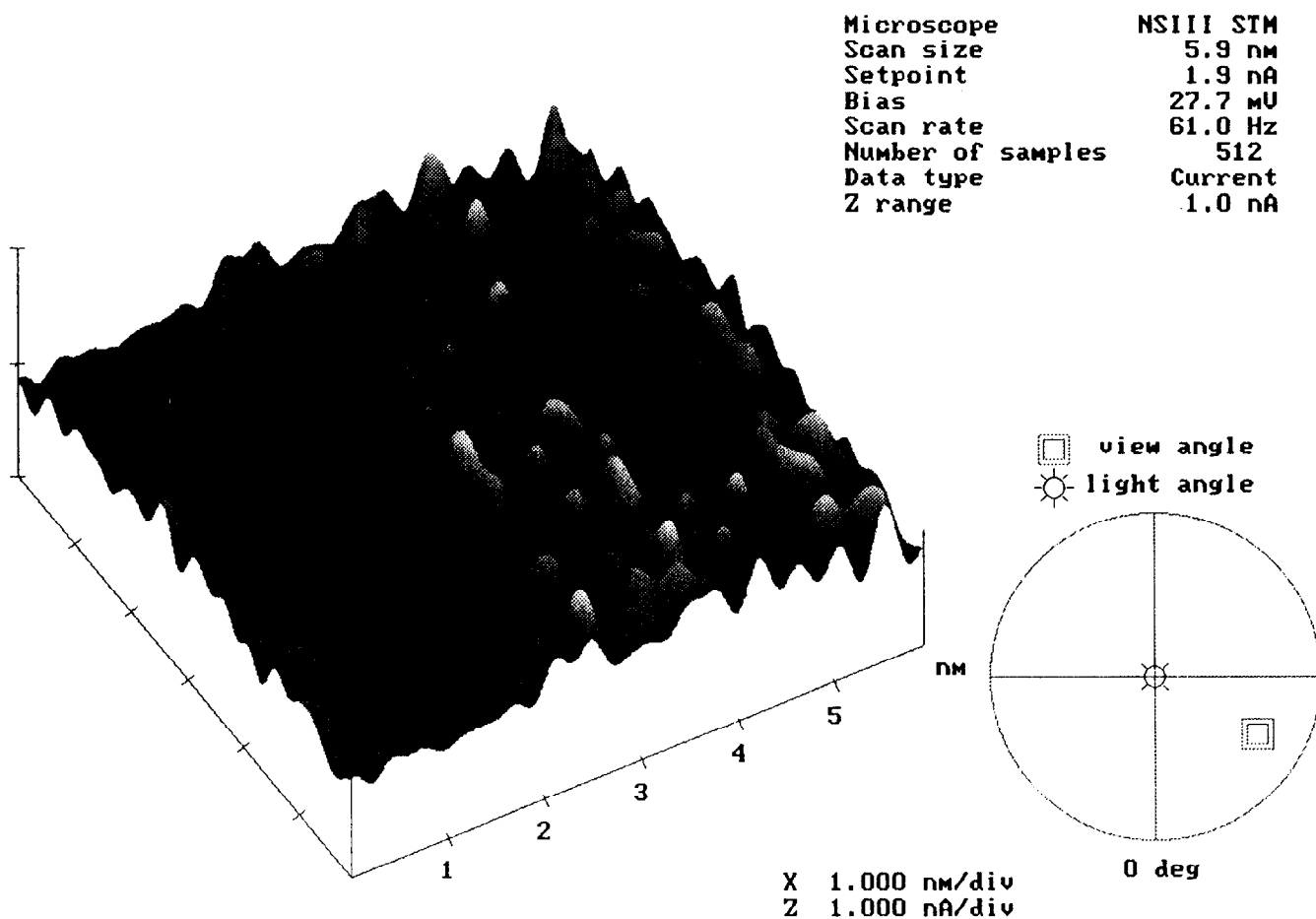


Figure 3 STM micrograph of the PITN film coated on graphite

pyridine is not complete. By the addition of pyridine, these PITN dispersions can be stable for about 2 to 4 weeks at room temperature and that with 1.0 equivalent SO_2Cl_2 can be stable for about 2 days. All of these PITN dispersions can be cast into films.

The film from the case with 1 equivalent SO_2Cl_2 and termination by pyridine has a conductivity of 0.1 S cm^{-1} (measured using the four-probe method) and also exhibits electrochromic properties with high contrast from blue (in the undoped state) to pale yellow-green (in the doped state). The micrograph of the film coated on a graphite surface determined from scanning tunneling microscopy (STM) (Figure 3) shows that the molecular chains align in a considerably ordered fashion to give a high quality film. Furthermore, the micrograph also shows that the repeat units align in all-*trans* conformation with a length of dimer unit of 7.5 \AA , which is in agreement with the theoretical value of 7.6 \AA determined from MNDO.

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References

- 1 Yashima, H., Kobayashi, M., Lee, K.-B., Chung, D., Heeger, A. J. and Wudl, F. *J. Electrochem. Soc.: Electrochem. Sci. Technol.* 1987, **134**, 46
- 2 Lakshmikantham, M. V., Lorey, D., Kelly, C. S., Wu, X.-L., Parakka, J. P., Metzger, R. M. and Cava, M. P. *Adv. Mater.* 1993, **5**, 773

- 3 Wudl, F., Kobayashi, M. and Heeger, A. J. *J. Org. Chem.* 1984, **49**, 3382
- 4 Wudl, F. and Heeger, A. J. US Patent 4,795,242, 1989
- 5 Pomerantz, M., Gill, B. C., Harding, L. O., Tseng, J. J. and Pomerantz, W. J. *Synth. Met.* 1993, **55**, 960
- 6 Hanack, M., Mangold, K.-M., Röhrig, U. and Mössmer, C. M. *Synth. Met.* 1993, **60**, 199
- 7 Jenekhe, S. A. US Patent 4,717,762, 1991
- 8 Quattrocchi, C., Lazzaroni, R. and Bredas, J. L. *Macromolecules* 1993, **26**, 1260
- 9 Ferraris, J. P. and Lambert, T. L. *J. Chem. Soc., Chem. Commun.* 1991, 1268
- 10 Ferraris, J. P. and Lambert, T. L. *J. Chem. Soc., Chem. Commun.* 1991, 752
- 11 Müllen, K. *Synth. Met.* 1991, **41-43**, 777
- 12 Bohnen, A., Räder, H. J. and Müllen, K. *Synth. Met.* 1992, **47**, 37
- 13 Weger, R., Beye, N., Fanghanel, E., Scherer, U., Wirschem, R. and Müllen, K. *Synth. Met.* 1993, **53**, 353
- 14 Brockmann, T. W. and Tour, J. M. *J. Am. Chem. Soc.* 1994, **116**, 7435
- 15 Chandrasekhar, P., Masulaitis, A. M. and Gumbs, R. W. *Synth. Met.* 1990, **36**, 303
- 16 Jen, K.-Y. and Elsenbaumer, R. *Synth. Mat.* 1986, **16**, 379
- 17 Rose, T. L. and Liberto, M. C. *Synth. Met.* 1989, **31**, 395
- 18 Lee, Y. S. and Kertesz M. *Int. J. Quantum Chem.: Quantum Chem. Symp.* 1987, **21**, 163
- 19 Socrates G. 'Infrared Characteristic Group Frequencies', John Wiley, Chichester, 1980, p. 83
- 20 Fieser, L. M. and Fieser, M. 'Natural Products Related to Phenanthrene', Reinhold, New York, 1949, p. 18
- 21 Fieser, L. M. and Fieser, M. 'Steroids', Reinhold, New York, 1959
- 22 Silverstein, R. M., Bassler, G. C. and Morrill, T. C. 'Spectrometric Identification of Organic Compounds' 5th edn, John Wiley, New York, 1991, p. 263
- 23 Wehrli, F. W. Marchand, A. P. and Wehrli, S. 'Interpretation of Carbon-13 NMR Spectra', 2nd edn, John Wiley, 1989, p. 52