

# Oligomeric bis(1,3-indandiylidene)azines: preparation, electrochemical and spectroscopic properties, and implications for the use of polyazines as conducting materials

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Four oligomeric azines of the general structure  $\text{Fl}=\text{N}(\text{N}=\text{C}_9\text{H}_4=\text{N})_n\text{N}=\text{Fl}$ , where Fl represents the 9-fluorenylidene group,  $\text{C}_9\text{H}_4$  the 1,3-indandiylidene unit, and  $n$  has the values 1 to 4, have been prepared and characterised. Their electrochemical reduction has been studied by cyclic voltammetry and the results compared with the behaviour of fluorenone azine. Two reversible peaks have been observed for each of the compounds and the peak potentials observed show an unusual alternation in their values as  $n$  increases. Vibrational spectra have been recorded for all five compounds. The strong Raman lines associated with the collective stretching of the C–C bonds involved in  $\pi$ -delocalisation [ $\mathcal{R}$  (ya) modes] have been studied. The effect of chain length on the frequency and intensity of this mode is the reverse of that found, for example, with polyacetylene. This suggests that, while polyazines are unlikely to produce materials of very high electrical conductivity, they may be candidates as materials for electroluminescence purposes in the fabrication of organic light-emitting diodes.

In the search for organic conducting materials, conducting polymers have attracted much attention and research effort. The common feature of such materials is continuous  $\pi$ -conjugation along the main polymer chain, with structures falling into two main categories: (i) purely hydrocarbon structures such as polyacetylene and poly-*p*-phenylenevinylene; and (ii) polymers based on heterocyclic repeat units such as polypyrrole and polythiophene. All can be doped so as to produce materials of high electrical conductivity (of the order of  $10^2 \text{ S cm}^{-1}$ ). In polypyrrole and related structures in the undoped condition, the heteroatoms can be regarded as being attached to, rather than a part of, the main polymer chain; on doping, however, the heteroatom participates more directly in the through  $\pi$ -conjugation (as indeed it does in polyaniline). Moreover, unlike the situation in polyacetylene, a one bond shift of the  $\pi$ -bonds along the chain does not lead to an identical structure. Such structural non-degeneracy is also found in polyazines,  $-\text{N}=\text{C}(\text{R})-\text{C}(\text{R})=\text{N}-$ , but now the heteroatoms all lie in the main conjugated sequence in all states.

There has been sporadic interest in polyazines in recent years. Compared with polyacetylene, the corresponding polyazine,  $-(\text{CH}=\text{N}-\text{N}=\text{CH})_n-$ , has been predicted to have a band gap larger by a factor of about two.<sup>1a</sup> Euler and co-workers<sup>1b</sup> reported on polyazines prepared by acidic treatment of butane-2,3-dione dihydrazone, and showed that they appeared to adopt planar structures with the double bonds *trans*. Iodine doping afforded electrically conducting material with modest specific conductivity (up to  $1.3 \text{ S cm}^{-1}$ ). Recent interest has centred on the nature of the charge carriers in doped polyazines which are diamagnetic; nitrenium ion centres have been proposed,<sup>2</sup> but this interpretation has been challenged on the basis of molecular orbital calculations.<sup>3</sup> Our interest has been in the production of polyazines by electropolymerisation of bis(diazo)-compounds; early work was concerned with polyazines of the indenofluorene series,<sup>4</sup> but we have recently turned our attention to polymers from 1,3-bis(diazo)indane and 1,3-bis(diazo)indan-2-one.<sup>5</sup> In support of this work we now report on the synthesis of a series of polyazine oligomers (bearing fluoren-9-ylidene end-groups) **1** related to the expected products from 1,3-bis(diazo)indane electropolymerisation. Electrochemical and vibrational spectroscopic measurements

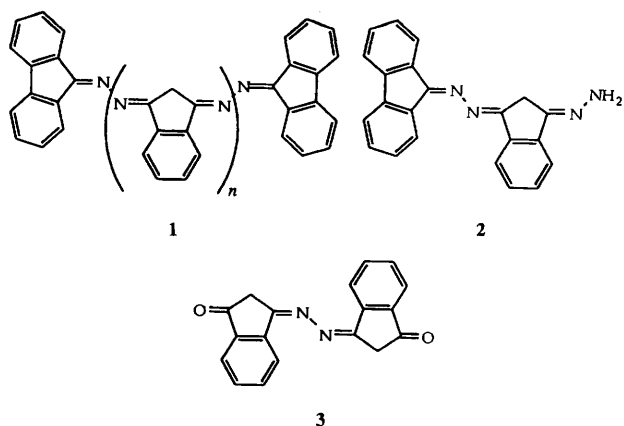
have been made on these compounds and these, particularly the latter, permit some conclusions to be reached about the suitability of polyazines for use as conducting materials.

## Results and discussion

### Synthesis of the oligomeric azines

In general azine linkages were formed by acetic acid catalysed condensation of hydrazones, either by self-condensation or with the appropriate carbonyl compound, according to well established precedents.<sup>6</sup> In order to provide stable end groups for the oligomers, and because we envisaged (mistakenly as it turned out in this case) carbanion-induced polymerisation of bis(diazo)-compounds as a general route to polyazines on the basis of a model reaction of fluorenyl anion with azibenzil, fluoren-9-ylidene moieties were attached at both chain ends.<sup>7</sup> Thus the general structure of the target molecules was as in **1**, with values of  $n$  from 1 to 4. Fluoren-9-one azine (*i.e.* **1** with  $n = 0$ ) was used for purposes of comparison.

A key step in the synthesis of the series of oligomers was the reaction of 1,3-bis(hydrazono)indane with a two-fold excess of fluoren-9-one in refluxing ethanol containing a few drops of acetic acid. As well as the expected production of **1** ( $n = 1$ ) in moderate yield, a substantial amount of the 1:1 condensation product **2** was obtained. Self-condensation of **2** then afforded **1** ( $n = 2$ ) in acceptable yield. Furthermore, treatment of **2** with half an equivalent of indane-1,3-dione afforded the next member of the series of oligomers, *i.e.* **1** ( $n = 3$ ). The final member of the series **1** ( $n = 4$ ) was obtained by condensation of indane-1,3-dione azine **3**, obtained from the parent dione by reaction with the stoichiometric quantity of hydrazine hydrate, with two molar equivalents of **2**. The reaction in this case proved to be rather slow under the standard conditions using acetic acid as catalyst, and it proved necessary to add a few drops of concentrated sulfuric acid to carry the reaction to completion in excellent yield. All the oligomeric azines were yellow crystalline compounds of low solubility in common organic solvents; purification was in most cases achieved by Soxhlet extraction of the compound from the crude product using ethanol as the solvent—the pure compound crystallising from this solvent.



**Table 1** Peak reduction and reoxidation potentials (V vs. SCE)<sup>a</sup> for the oligomers **1**

<i>n</i>	$-E_{R1}$	$-E_{O1}$	$-E_{R2}$	$-E_{O2}$
0	0.48	0.42	0.85	0.79
1	0.73	0.68	1.01	0.89
2	0.39	0.32	0.77	0.69
3	0.72	0.66	0.99	0.90
4	0.79	0.73	1.06	0.92

<sup>a</sup> In DMSO containing 0.1 M Bu<sub>4</sub>NBF<sub>4</sub>; potential scan rate 200 mV s<sup>-1</sup>.

### Cyclic voltammetric studies

The electrochemical reduction of all the oligomeric azines including fluorenone azine was examined by cyclic voltammetry at a platinum electrode in dimethyl sulfoxide solution containing tetrabutylammonium tetrafluoroborate (0.1 mol dm<sup>-3</sup>) as supporting electrolyte. Current-potential curves were normally recorded at a potential scan rate of 200 mV s<sup>-1</sup> and the first scan was compared in each case with the steady state voltammogram obtained after five complete pre-sweeps; for all compounds there was little difference between the two voltammograms. Compounds **1** (*n* = 3) and **1** (*n* = 4) gave voltammograms that appeared somewhat distorted compared with the responses from the other compounds. This could indicate adsorption at the electrode, but might indicate the presence of small amounts of a second compound reduced at somewhat less cathodic potentials. In all cases two reversible reduction waves were observed; peak potentials are in Table 1.

Comparison with the cyclic voltammograms under similar conditions for the black polymeric products from decomposition of 1,3-bis(diazo)indane, either at a platinum cathode or by treatment with tetraethylammonium hydroxide, shows that the present oligomers are all reduced at much less negative potentials than the polymers. We interpret this as being a consequence of the presence in the oligomers of two fluorenylidene units which are capable of accommodating additional electrons in their central cyclopentadienyliene group to give formally relatively stable 6π-electron structures.

One of the more interesting features of the results in Table 1 is the apparent alternation of peak potentials between extremes some 300 mV apart as the first few indane units are introduced between the fluorenylidene ends. The effect seems to disappear after the third indane unit is inserted. The observations are quite unexpected, since the formal extension of conjugation in the polyazine chain would be expected to lead to a progressive decrease in the lowest unoccupied molecular orbital (LUMO) energy of the system [and a progressive increase in the highest occupied molecular orbital (HOMO) energy]; such changes are evident in simple Hückel calculations on the main polyazine chain corresponding to the compounds studied here. Apart from expecting to find progressively decreasing values of  $-E_R$ , bathochromic shifts in the UV-VIS absorption maxima are to be expected and this is also not found; the oligomers with *n* = 1 to 4 showed longest wavelength absorptions at 354 ± 2 nm. A

number of complicating factors are present in these molecules, however: (i) the oligomers all have fluorenylidene end-groups, the ability of which to stabilise negative charge may be of overriding importance in determining  $E_R$ ; (ii) there is a possibility of *E*- and *Z*-configurations about the C=N bonds and of *s-cis*- and *s-trans*-conformations (or even non-planar geometries; see below) at each of the azine linkages, which could alter the average distance apart of the end-groups.

In the context of (ii), it may be significant that fluorenone azine and the oligomer with *n* = 2 which have low values of  $-E_{R1}$  also have larger potential separations between the first and second reduction peaks than the other compounds. These could both reflect closer proximity of the fluorenylidene groups.

### Vibrational spectroscopy

The interpretation of the vibrational spectra of polyconjugated molecules requires particular attention because of the existence of a network of π-electrons delocalised probably over a large molecular domain. The delocalisation gives rise to very peculiar spectroscopic features which have required the development of new theoretical concepts.<sup>8-10</sup> In this discussion we base our interpretation on the theory of the effective conjugation coordinate (ECC)<sup>8-11</sup> which has permitted a common understanding of the vibrational spectra (infrared and Raman) of these complex molecules.

**Infrared spectra.** Spectra are shown in Fig. 1. According to ECC theory, the frequencies of the absorption lines in the infrared spectra should be practically independent of the chain length,<sup>8-10,12</sup> while, with the help of relative intensities, it is possible to distinguish bands associated with vibrations localised at either end of the molecular chain (designated T = 'terminal') from those associated with vibrations, either collective or localised, on the inner units (labelled B = 'bulk').<sup>12</sup>

As expected, most of the relevant infrared transitions for the series of compounds studied in this investigation have the same frequencies. Of particular interest are the stretching modes of the aromatic rings, which occur as a sharp doublet at 1624 and 1598 cm<sup>-1</sup> for the end-groups and as a strong band at 1628 cm<sup>-1</sup> for the units of the bulk. The C-H out of plane motions of the fluorenylidene groups (three modes are expected) are the origin of the strong triplet at 789, 725 and 647 cm<sup>-1</sup>. This decreases in intensity approximately linearly relative to the strong doublet at 760 and 731 cm<sup>-1</sup> which we associate with the out of plane motions localised in the α- and β-positions of the indane units and this is taken to justify the assignment of the T and B modes.

Next we consider the frequencies and intensities of the C-H stretching modes. From correlative spectroscopy the structured absorption peak at approximately 3055 cm<sup>-1</sup> has to be associated with the stretching of the sp<sup>2</sup>-C-H groups of the aromatic rings. The CH<sub>2</sub> group of each indanediylidene unit of the bulk should show out-of-phase and in-phase stretching signals near 2900 cm<sup>-1</sup>. A weak, broad and ill-defined absorption is indeed observed at this frequency. From intensity spectroscopy<sup>13-16</sup> it is known that the intensity of aromatic C-H stretching absorptions is generally weaker than that of aliphatic C-H stretching because the effective atomic charge on the hydrogen atom is larger and more positive for the aromatic case. The paradigm is the value of the ratio of the intensities of the C-H stretching absorptions in ethane (sp<sup>3</sup>; 2850 darks) to benzene (sp<sup>2</sup>; 1912 darks): *R* = 2.8 per C-H bond. This should be compared with *R* = 0.79 in cyclopentadiene,<sup>18</sup> 0.45 in β,β'-methano-α,α'-dithienyl<sup>17</sup> and the immeasurably small values observed for the oligomers **1** in the present investigation. The observation provides experimental evidence for a large, positive charge on the CH<sub>2</sub>-groups of the indanediylidene units, thus indicating that hyperconjugation takes place between the CH<sub>2</sub> group and the aromatic rings.<sup>18</sup> The CH<sub>2</sub>-group has injected charge into the ring, thus making its H atoms much more positive.<sup>19</sup> The reactivity of the CH<sub>2</sub>-groups finds an

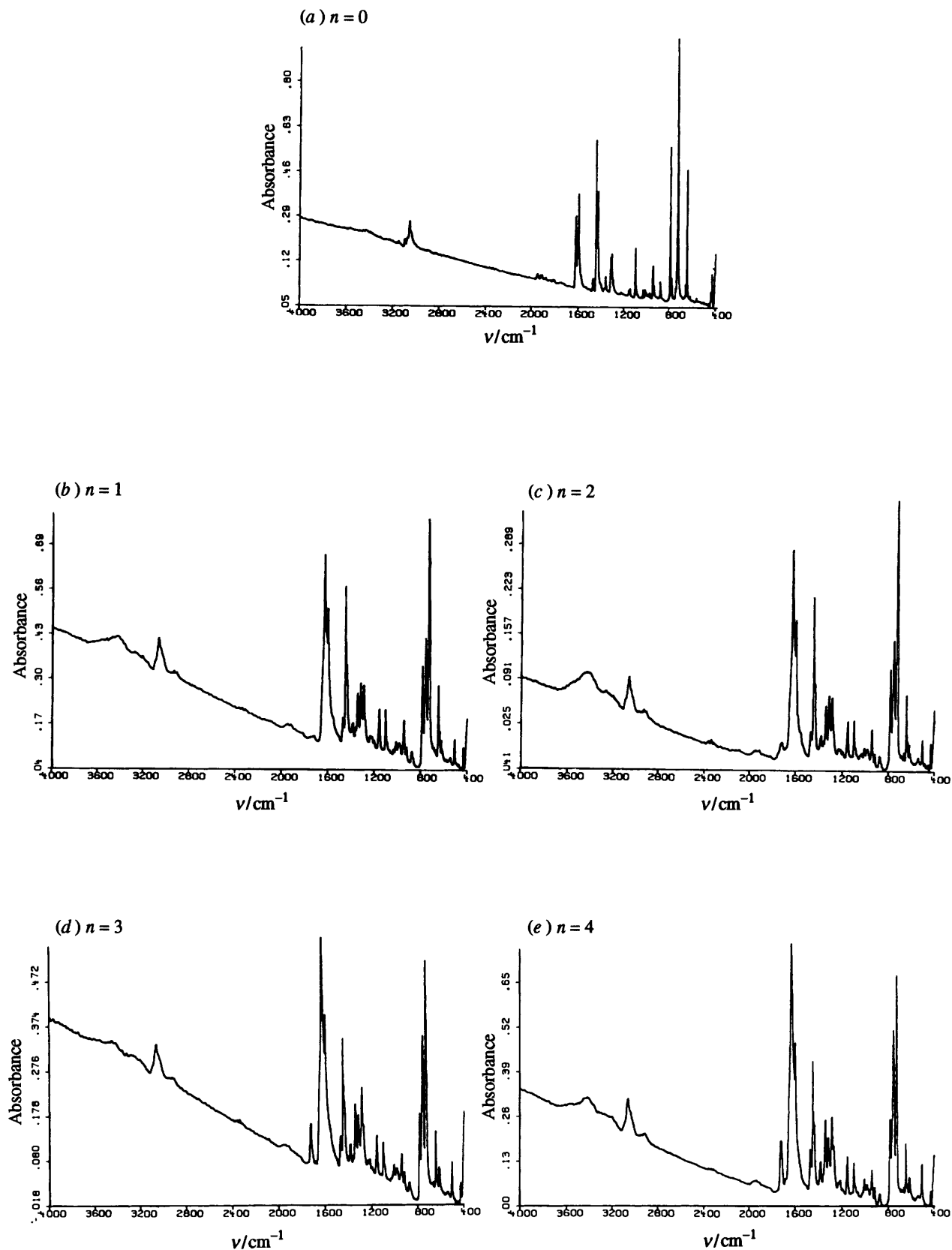


Fig. 1 Infrared spectra of the oligomers 1. The number of indanediylidene units is given by  $n$ .

explanation from vibrational intensity spectroscopy. From the frequency and intensity measurements, the length of the aromatic C–H bond (absorbing near  $3051\text{ cm}^{-1}$ ) is *ca.*  $1.085\text{ \AA}$  and the fixed charge on the H atom is *ca.*  $+0.13\text{ e}$ .<sup>17</sup>

**Raman spectra.** The spectra are in Fig. 2. For unknown experimental reasons, the quality of the Raman spectra recorded is acceptable for oligomers 1 with  $n = 0$  and 4, but is

much less satisfactory for oligomers with  $n = 1, 2$  and 3. Nevertheless useful and interesting conclusions can still be reached.

ECC theory<sup>8-11</sup> indicates that when  $\pi$ -bonds can be delocalised along a delocalisation path which extends throughout an oligomeric or polymeric chain, at least one totally symmetric (TS) normal mode, involving the stretching

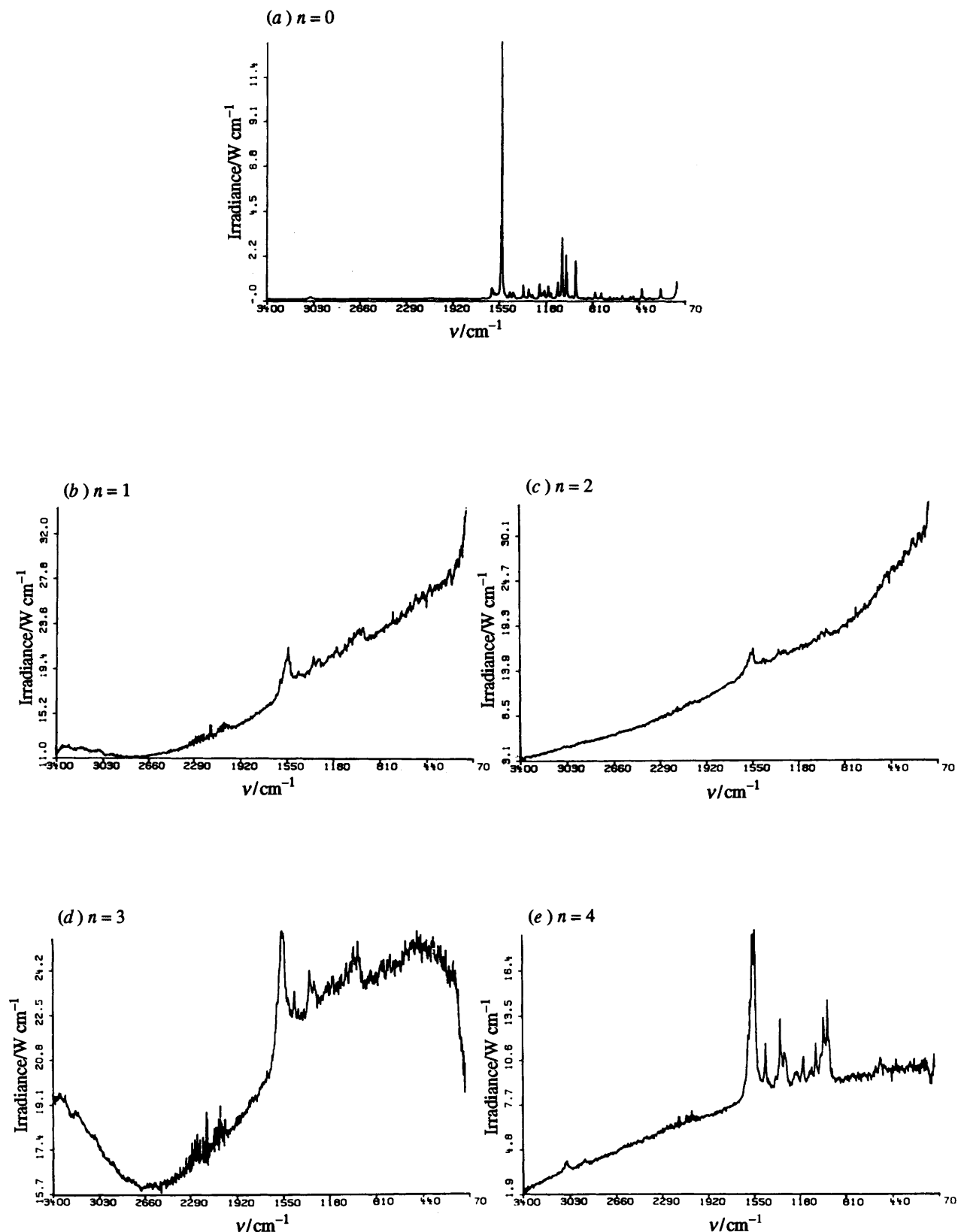


Fig. 2 Raman spectra of the oligomers **1**. The number of indanediylidene units is given by  $n$ .

and compression of the CC bonds, becomes strongly and selectively enhanced because of the existence of a sizeable electron-phonon coupling (the strong coupling between the motions of the nuclei and the  $p_z$  electronic cloud). This mode is generally labelled as the  $\nu_a$  ( $\mathcal{A}$ ) mode. If the delocalisation extends along the molecular chain, the mode may show frequency and intensity dispersion with conjugation length (CL). Generally, when CL increases, (i)  $\nu$  decreases, because the

force constants associated with the  $\mathcal{A}$  mode softens; and (ii) a strong intensity enhancement is observed which increases superlinearly with CL.

For the molecules studied in this investigation, each of the repeat units contains a large number of  $p_z$ -orbitals which may be involved in both intramolecular and intermolecular delocalisation. The selective intensity enhancement is immediately seen even with  $n = 0$  for the Raman line at  $1531 \text{ cm}^{-1}$

when compared with the line at  $3054\text{ cm}^{-1}$  associated with the stretching of aromatic C–H bonds. These bands are usually of medium strength in benzene or other simple aromatic systems.

The most relevant issue for the understanding of the electronic properties of the molecules studied in this investigation is the distinction between intra- and inter-molecular delocalisation of the  $p_z$ -orbitals. From a comprehensive study of the frequency dispersion with CL of several series of polyaromatic oligomers and polymers, including polyacetylene and polypyrrole,<sup>20</sup> it has been proposed that in aromatic systems there may be a preferential intra-unit pinning of  $p_z$ -electrons which competes with their inter-unit delocalisation. If this is the case, the Raman-active mode should show no softening, as is indeed observed in the oligomers 1.

An additional feature in the Raman spectra of the oligomers with  $n = 1$  to 4 in the  $1550\text{ cm}^{-1}$  range has to be accounted for. Even though the quality of the Raman spectra is not good, the  $\mathcal{A}$  mode is clearly observed: for  $n = 1$  this appears at  $1546\text{ cm}^{-1}$  with some asymmetry on the high frequency side; a line at  $1546\text{ cm}^{-1}$  with more pronounced scattering at higher frequencies is observed for  $n = 2$ ; for  $n = 3$ , the peak at  $1553\text{ cm}^{-1}$  is certainly the result of two overlapping lines of almost equal intensity, and clear separation into a doublet at  $1566$  and  $1548\text{ cm}^{-1}$  results for  $n = 4$ .

We tentatively assign the emerging peak at  $1566\text{ cm}^{-1}$  to the 'ring-stretching' (or localised intra-ring  $\mathcal{A}$  mode) of the units of the bulk, while the line at  $1548\text{ cm}^{-1}$  is ascribed to the similar vibration localised on the units at either end of the oligomeric chain. For  $n = 4$ , the qualitative intensity ratio of the  $1566$  and  $3057\text{ cm}^{-1}$  lines does not seem to indicate a large intensity enhancement.

In conclusion, the Raman spectra, interpreted on the basis of ECC theory, are consistent with a large intra-unit delocalisation of  $p_z$ -electrons and with very little inter-unit delocalisation. The reasons for such an effect may be the following: (i) The competition between the intra-unit pinning potential (*i.e.* aromaticity) and inter-unit delocalisation is dominated by the former. (ii) The indanediylidene units do not lie in the same plane and the oligomeric chain is conformationally distorted, thus reducing the value of the electron hopping integral at the N–N bond.

In either case the prospects for using polyazines related to the present oligomers as organic conductors do not seem favourable. This conclusion may extend to polyazines in general. On the other hand, the body of information that is being collected on materials for use in light emitting diodes suggest that, when  $\pi$ -bonds are localised within a molecular domain, electroluminescence seems to be favoured.<sup>21</sup> Since we have collected evidence that localisation within a limited domain does take place in the polyazines studied in this work, we suggest that this class of materials should be tested in electroluminescence experiments.

## Experimental

### Preparation of fluorenylidene terminated indane-1,3-dione azine oligomers

**Oligomeric azine 1 ( $n = 1$ ) and compound 2.** 1,3-Bis(hydrazone)indane (3.0 g, 17 mmol), mp  $189^\circ\text{C}$ , and fluoren-9-one (6.0 g, 33 mmol) in absolute ethanol (150 ml) containing a few drops of acetic acid were refluxed for 20 h. The precipitate was filtered off and washed with hot ethanol. The brown solid was refluxed for 48 h with ethanol using a Soxhlet extractor to give the product as greenish yellow crystals (4.6 g, 9.2 mmol, 54%); mp  $219\text{--}220^\circ\text{C}$ ;  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon_{\text{max}}/\text{l mol}^{-1}\text{ cm}^{-1}$ ) 356 (16 700), 342 (16 700), 268 (25 200);  $\nu_{\text{max}}/\text{cm}^{-1}$  1625, 1600;  $m/z$  (EI) 498 ( $\text{M}^+$ ), 342, 320, 305, 291, 249, 194, 179 (base), 164, 151, 128, 101, 76 ( $\text{C}_{35}\text{H}_{22}\text{N}_4$  requires: C, 84.32; H, 4.44; N, 11.24. Found: C, 84.18; H, 4.38; N, 11.44%).

The filtrate from the reaction mixture above was cooled slowly and refrigerated, leading to the precipitation of 3-(fluoren-9-ylidenehydrazono)indan-1-one hydrazone 2. It was recrystallised from ethanol and gave yellow crystals (1.2 g, 3.6 mmol, 21%); mp  $194\text{--}195^\circ\text{C}$ ;  $\nu_{\text{max}}/\text{cm}^{-1}$  3420, 3300, 1630, 1590;  $m/z$  (EI) 336 ( $\text{M}^+$ ), 320, 305, 228, 179, 128 (base), 103, 80 ( $\text{C}_{22}\text{H}_{16}\text{N}_4$  requires: C, 78.55; H, 4.79; N, 16.66. Found: C, 78.66; H, 4.78; N, 16.56%).

**Oligomeric azine 1 ( $n = 2$ ).** Compound 2 (0.3 g, 0.89 mmol) with a few drops of acetic acid in absolute ethanol (25 ml) was refluxed for 24 h. The precipitate was filtered and washed with hot ethanol. The dark yellow solid was extracted with ethanol for 48 h using a Soxhlet extractor to give the product as deep yellow crystals (0.33 g, 0.52 mmol, 58%); mp  $238\text{--}240^\circ\text{C}$ ;  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon_{\text{max}}/\text{l mol}^{-1}\text{ cm}^{-1}$ ) 356 (13 900), 268 (26 200);  $\nu_{\text{max}}/\text{cm}^{-1}$  1625, 1595;  $m/z$  (EI) 641 ( $\text{M}^+$ ), 498, 463, 447, 430, 355, 321, 305, 284, 270, 179 (base), 165, 151, 128, 89, 76 ( $\text{C}_{44}\text{H}_{28}\text{N}_6$  requires: C, 82.48; H 4.40; N, 13.12. Found: C, 82.29; H, 4.42; N, 13.29%).

**Oligomeric azine 1 ( $n = 3$ ).** Compound 2 (0.3 g, 0.89 mmol) and indane-1,3-dione (0.065 g, 0.45 mmol) in absolute ethanol (25 ml) containing a few drops of acetic acid were refluxed for 24 h, the reaction being monitored by TLC. At this time the reaction was incomplete, so 2 drops of concentrated sulfuric acid were added and the mixture left to reflux for a further 20 h. The precipitate was filtered off and washed with hot ethanol. Soxhlet extraction with ethanol as before gave the product as deep yellow crystals (0.21 g, 0.27 mmol, 60%); mp  $241\text{--}243^\circ\text{C}$ ;  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon_{\text{max}}/\text{l mol}^{-1}\text{ cm}^{-1}$ ) 352 (16 700), 260 (25 200);  $\nu_{\text{max}}/\text{cm}^{-1}$  1630, 1600;  $m/z$  (EI) 783 ( $\text{M}^+$ ), 641, 607, 523, 499, 464, 322, 285, 270, 195, 180 (base), 160, 145 ( $\text{C}_{53}\text{H}_{34}\text{N}_8$  requires: C, 81.31; H, 4.38; N, 14.31. Found: C, 81.27; H, 4.25; N, 14.48%).

**Oligomeric azine 1 ( $n = 4$ ).** (i) **Indane-1,3-dione azine 3.** Indane-1,3-dione (3.0 g, 20.5 mmol) and hydrazine hydrate (0.5 ml, 10.3 mmol) in absolute ethanol (100 ml) containing a few drops of acetic acid were refluxed for 24 h. The precipitate was filtered off and washed with hot ethanol to give the indane-1,3-dione azine as greenish yellow crystals (2.9 g, 10 mmol, 97%); mp  $240\text{--}241^\circ\text{C}$ ;  $\nu_{\text{max}}/\text{cm}^{-1}$  1710, 1630, 1600, 1260, 770;  $m/z$  (EI) 288 ( $\text{M}^+$ ), 273, 259, 246, 213, 185, 158, 129, 97, 81, 69, 57 (base) ( $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_2$  requires: C, 74.99; H, 4.20; N, 9.72. Found: C, 74.83; H, 4.09; N, 9.85%).

(ii) **Oligomeric azine 1 ( $n = 4$ ).** Compound 2 (0.3 g, 0.89 mmol) and indane-1,3-dione azine (0.1 g, 0.45 mmol) in absolute ethanol (25 ml) containing a few drops of acetic acid were refluxed for 24 h and for a further 30 h after the addition of two drops of concentrated sulfuric acid. The precipitate was filtered off and washed with hot ethanol. Soxhlet extraction as before gave the product as deep yellow crystals (0.36 g, 0.39 mmol, 87%); mp  $262\text{--}263^\circ\text{C}$ ;  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon_{\text{max}}/\text{l mol}^{-1}\text{ cm}^{-1}$ ) 354 (13 900), 266 (26 100);  $\nu_{\text{max}}/\text{cm}^{-1}$  1630–1600, 1280, 750, 725  $\text{cm}^{-1}$  ( $\text{C}_{62}\text{H}_{40}\text{N}_{10}$  requires: C, 80.50; H, 4.36; N, 15.14. Found: C, 80.48; H, 4.26; N, 15.26%).

### Electrochemical measurements

These were carried out at room temperature using a PAR 173/276 potentiostat controlled using an Apple II Europlus computer equipped with PAR software. The working and counter electrodes were platinum with a silver wire pseudo-reference calibrated from time to time against chloranil ( $E_{\text{R1}} = 0.11\text{ V vs. SCE}$ ).<sup>22</sup> observed potentials have been corrected to the SCE scale and are accurate to 10 mV.

### Spectral measurements

Infrared spectra of the materials suspended in KBr pellets were recorded using Nicolet 7000 and 850 FT–IR interferometers. Raman spectra of the solid samples in NMR tubes were recorded with a Nicolet 910 FT–Raman interferometer, using an exciting line ( $\lambda = 1.064\text{ micron}$ ) from a Nd-YAG laser.

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