PERKIN 2

Synthesis and characterisation of some donor–acceptor substituted butadienes for second harmonic generation

Suresh Das,[*,a] **Mathew George,**[a] **Thomas Mathew**[a] **and C. V. Asokan**[b]

[a] *Photochemistry Research Unit, Regional Research Laboratory, Trivandrum 695 019, India*
[b] *School of Chemical Sciences, Mahatma Gandhi University, Kottayam 686 560, India*

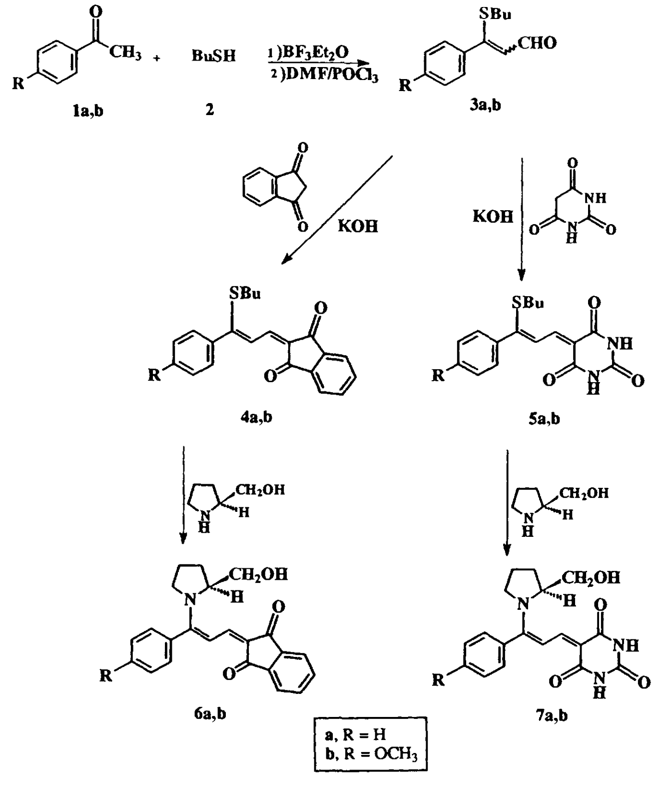
The synthesis and photophysical properties of some donor–acceptor linked butadiene derivatives 6a,b and 7a,b are described. Compounds 6a and 6b show anomalous red-shifted fluorescence bands in polar solvents which can be attributed to the formation of twisted intramolecular charge transfer (TICT) excited states. Powder second harmonic generation (SHG) measurements of these molecules indicated intensities of 0.45 times that of urea for 6a and 7a while negligible intensities are found for 6b and 7b.

The synthesis of new organic materials possessing non-linear optical properties (NLO) has been a subject of intense activity in recent years because of their potential applications in areas such as telecommunications, optical information processing and data storage.[1,2] The interest in organic materials has been primarily due to their ultrafast response times, the synthetic flexibility which permits the modification of molecular parameters required for optimising the NLO properties, as well as the ease with which these molecules can be incorporated into polymeric systems, either by physical mixing or through covalent bonding.[1–4] Most studies so far have focused on donor–acceptor π-conjugated molecules which tend to possess large second-order molecular polarisability (β).[5–11] However, molecules possessing large β values tend to crystallise into centrosymmetric space groups, which nullify the contribution of the individual molecules. The presence of chiral groups in the molecule can, however, ensure crystallisation into non-centrosymmetric space-groups.[1,12]

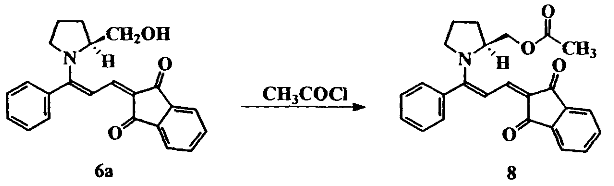
The second-order molecular polarisability β is a function of the spectroscopic and excited state properties of the molecule. It is proportional to (i) the dipole moment change between the ground and excited states and (ii) to the oscillator strength of the transition to the excited state. Molecules with large β values are therefore often characterised by intense charge transfer (ICT) transitions, which are highly solvatochromic.[5,6] The present work describes the synthesis and photophysical studies of four donor–acceptor linked butadiene molecules **6a,b** and **7a,b**. The electron donor in these cases is L-prolinol, which also ensures crystallisation into non-centrosymmetric space groups. The absorption and emission characteristics as well as the second-harmonic generation properties of these molecules are reported here.

Results and discussion

The donor-acceptor linked butadienes **6a,b** and **7a,b** were synthesised as shown in Scheme 1. The boron trifluoride-diethyl ether complex assisted addition of butanethiol to the starting acetophenones **1a,b** and subsequent Vilsmeier formylation leads to the formation of **3a,b**.[13] Aldol-type condensation of **3a** and **3b** with indane-1,3-dione or barbituric acid gives the corresponding butylsulfanyl-substituted dienones **4a,b** and **5a,b**. Substitution of the butylsulfanyl group of **4a,b** and **5a,b** with L-prolinol leads to **6a,b** and **7a,b**, respectively. Compounds **4a,b**, **5a,b**, **6a,b** and **7a,b** were characterised on the basis of analytical results and spectral data.



Scheme 1



Scheme 2

The ^{13}C NMR spectra of compounds **6a,b** and **7a,b** show twin peaks for some of the carbon atoms. This may be attributed to the presence of two isomeric forms due to restricted rotation around the N–C bond (involving prolinol), resulting from the delocalisation of the nitrogen lone pair. The ^{13}C NMR spectrum of **6a** in $CDCl_3$ containing trifluoroacetic acid indicated that only a single isomer was present. Protonation of nitrogen would prevent delocalisation of the nitrogen lone pair resulting in the formation of a single isomer, due to free rotation around the C–N bond. The ^{13}C NMR spectrum of the acylated form of **6a** (**8**, Scheme 2) also showed twin peaks for some of the carbon atoms, thus ruling out the

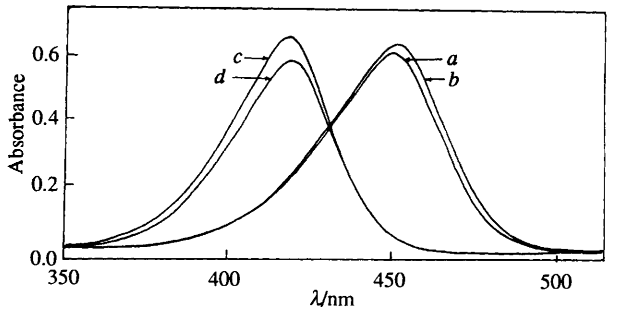


Fig. 1 Absorption spectra of (*a*) **6a**, (*b*) **6b**, (*c*) **7a** and (*d*) **7b** in methanol

Table 1 Absorption and emission maxima of **6a** and **6b** in various solvents

	Absorption/nm		Emission/nm	
Solvent	**6a**	**6b**	**6a**	**6b**
Benzene	457	459	554	560
Dichloromethane	456	458	556	581
Chloroform	458	460	581	591
Ethyl acetate	454	455	552	581
Acetone	454	455	587	575
Acetonitrile	452	453	591	601
DMF	456	457	593	583
DMSO	458	459	602	589
Methanol	452	452	609	588

Table 2 Absorption and emission maxima of **7a** and **7b** in various solvents

	Absorption/nm		Emission/nm	
Solvent	**7a**	**7b**	**7a**	**7b**
Chloroform	425	425	456	466
Ethyl acetate	422	425	466	456
Acetonitrile	419	419	452	456
DMF	424	423	463	455
DMSO	424	425	452	455
Methanol	419	420	452	454

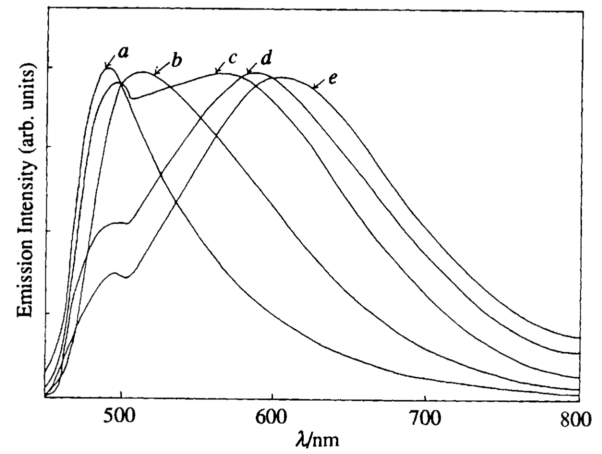


Fig. 2 Emission spectra of **6a** normalised at the maxima in (*a*) ethyl acetate, (*b*) chloroform, (*c*) acetone, (*d*) dimethylformamide and (*e*) dimethyl sulfoxide

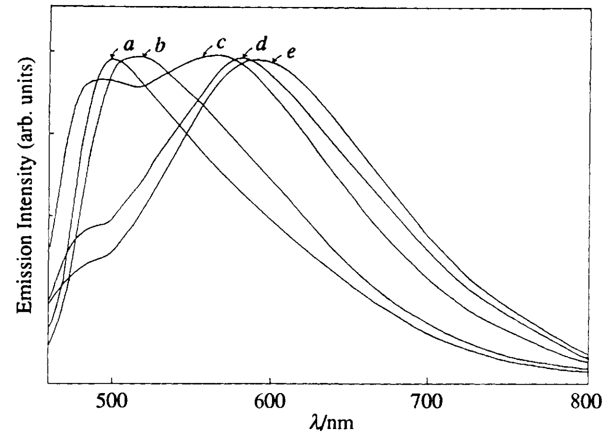


Fig. 3 Emission spectra of **6b** normalised at the maxima in (*a*) dichloromethane, (*b*) chloroform, (*c*) acetone, (*d*) dimethylformamide and (*e*) dimethyl sulfoxide

role of intramolecular hydrogen bonding in the formation of the isomers. Compounds **6a,b** and **7a,b** can also exist in the *E* and *Z* isomeric forms.

Two solid crystalline forms of the compound **6a** having different melting points could be separated by crystallising them from different solvents. The crystallisation from a mixture (1 : 1) of dimethyl sulfoxide (DMSO) and water gave yellow needles (mp 219–220 °C), while crystallisation from benzene provided a red solid (mp 181–182 °C). However, mixtures of both solids were obtained when other solvents such as ethanol and acetonitrile were used. In solutions, the two isomeric forms exist in equilibrium and have identical IR, NMR and UV spectra. It has been found that the red solid that was obtained from benzene could be converted into the yellow form by recrystallisation from a mixture of DMSO–water. Similarly, the yellow form could be converted to the red form by recrystallising it from benzene. However, the other compounds in the series **6b**, **7a** and **7b** were crystallised in a single form, in each case.

Absorption and emission spectra

The absorption spectra of **6a,b** and **7a,b** in methanol are shown in Fig. 1. These spectra show fairly sharp absorption bands with maxima at 452 nm for **6a,b** and 419 nm for **7a,b**. The absorption maxima of **6a,b** and **7a,b** in a variety of solvents are shown in Tables 1 and 2, respectively. It is evident from these Tables that the absorption spectra of **6a,b** and **7a,b** are not very sensitive to the polarity of the solvent.

Although the effect of solvent polarity on the absorption spectra of **6a,b** is small, its effect on the emission spectra is striking. Figs. 2 and 3 show the emission spectra of **6a** and **6b** in solvents of varying polarity. In less polar solvents such as dichloromethane, the emission spectra show a maximum around 498 nm and a broad tail in the longer wavelength region [curve (*a*) Figs. 2 and 3] in each case. With increasing solvent polarity there is a relative increase in the emission intensity at the longer wavelengths and in highly polar solvents such as acetonitrile, dimethyl sulfoxide and methanol, two distinct emission bands are clearly visible in each case. Whereas the positions of the shorter wavelength emission bands remain fairly constant with increasing solvent polarity, the long wavelength bands shift to the red in each case, indicating their charge transfer character. These results are summarised in Table 1.

The increase in the Stokes shift with increasing solvent polarity reveals an increase in the dipole moment on excitation. The difference of the dipole moment $\Delta\mu_{eg}$ between the excited and ground states can be calculated from the Lippert–Mataga equation [eqn. (1)],[14] where a is the radius in Å of the spherical

$$\Delta\nu_{st} = \Delta\nu_{abs} - \Delta\nu_{em} = \frac{2\Delta\mu_{eg}^{2}}{hca^{3}}\Delta f + \text{constant} \qquad (1)$$

cavity in Onsager's theory of reaction field and Δf is a solvent polarity parameter dependent upon the solvent refractive index (n) and the relative permittivity (ε) [eqn. (2)].

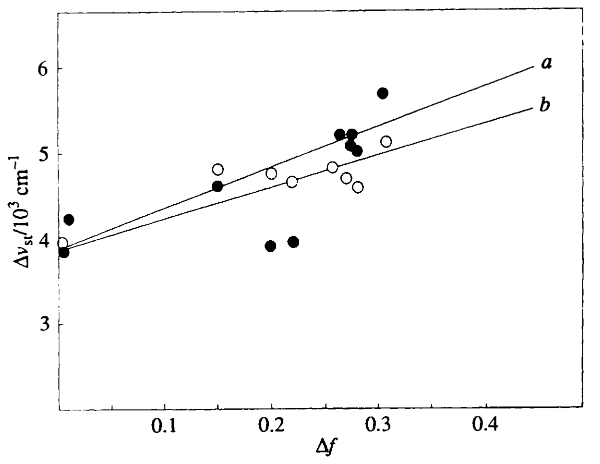


Fig. 4 Solvatochromic plots of Stokes shift ($\Delta\nu_{st}$) for (*a*, ●) **6a** and (*b*, ○) **6b** as a function of solvent polarity parameter (Δf)

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (2)$$

Fig. 4 shows the plots of $\Delta\nu_{st}$ *versus* Δf for **6a** and **6b**. The observed scatter in the points may arise due to the difficulty in ascertaining the λ_{max} of the long wavelength bands in solvents where the two bands merge together.† $\Delta\mu_{eg}$ was estimated from the slope of the plots of eqns. (3) and (4)[15] using $a = 4.8$ and

$$\frac{\Delta\nu_{st}}{\Delta f} = \frac{2}{hc_o}\left(\frac{\Delta\mu_{eg}{}^2}{a^3}\right) \quad (3)$$

$$\Delta\mu_{eg} = 0.01\left(\frac{\Delta\nu_{st}}{\Delta f}\right)a^3 \quad (4)$$

4.9 Å for **6a** and **6b**, respectively, which were determined by the addition of atomic volumes.[16] $\Delta\mu_{eg}$ was obtained as 6.98 and 6.39 for **6a** and **6b**, respectively. These values are relatively high, indicating the CT nature of the long wavelength emission. In contrast to **6a,b**, the emission bands of **7a,b** are relatively insensitive to solvent polarity (Figs. 5 and 6) and these results are summarised in Table 2.

Dual luminescence in donor–acceptor linked conjugated systems has been extensively studied since Lippert first discovered it for 4-(dimethylamino)benzonitrile (DMABN) in polar solvents.[17] The twisted intramolecular charge transfer (TICT) model developed to describe this phenomenon explains the dual fluorescence as occurring from two configurations of the excited state of the same molecule. The Franck–Condon excited state and a low lying TICT-state with a perpendicularly twisted geometry in which the amine lone pair axis is twisted perpendicular to the phenyl group and involving charge transfer. The increasing dipole moment for increasingly twisted geometries provides the driving force for the twist towards the TICT conformation with maximum charge separation *via* the polar solvent induced energetic stabilisation.[17-20] Other models have also been proposed to explain the phenomenon of dual luminescence;[21-23] however, TICT is currently the most favoured one. Since its discovery in DMABN, dual luminescence has been observed in numerous related singly bonded donor–acceptor molecules.[18] The results obtained for these donor–acceptor substituted butadienes can, however, be explained on the basis of the recently developed biradicaloid charge transfer model (BCT), in which the theory of TICT has been merged with the theory of biradicaloid states in order to understand the twisted single and double bonds within the same framework.[18-24] This theory has been successfully applied to explain the photophysical properties of several stilbene dyes.[25] In such systems, the excited state can undergo a twist across one of the single bonds adjacent to the double bonds, leading to the TICT state. Alternatively, twisting of the double bond can occur. Upon introduction of substituents which produce large enough electronic asymmetry, TICT formation is favoured. In weaker donor–acceptor systems, intramolecular fluorescence quenching can occur due to twisting of the double bond which will lead to ultrafast non-radiative deactivation.

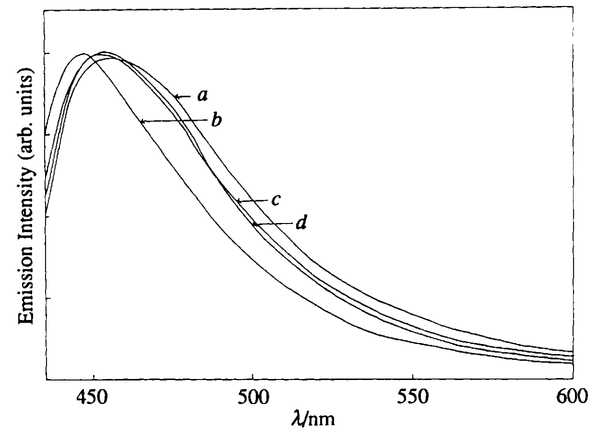


Fig. 5 Emission spectra of **7a** normalised at the maxima in (*a*) chloroform, (*b*) dimethylformamide, (*c*) methanol and (*d*) acetonitrile

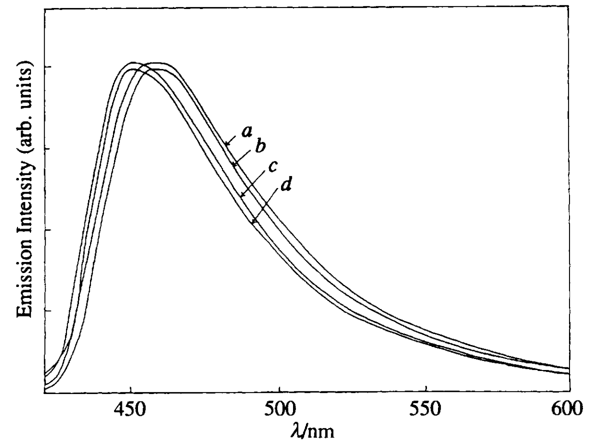


Fig. 6 Emission spectra of **7b** normalised at the maxima in (*a*) ethyl acetate, (*b*) acetonitrile, (*c*) dimethylformamide and (*d*) dimethyl sulfoxide

For **6a** and **6b** in polar solvents, charge-transfer would be highly favoured which would lead to a large electronic asymmetry rendering the TICT pathway involving a twist of the N–C bond, much more competitive than the twisting of the double bonds, leading to relative enhancement of the long wavelength bands in polar solvents. The absence of dual emission in **7a** and **7b** shows that the double bond twisting is much more efficient for these molecules. This may be attributed to the barbituric acid moieties in **7a** and **7b**, being weaker acceptors relative to the indanedione moieties in **6a** and **6b**.

The quantum yields of fluorescence (Φ_f) of these molecules are very low. Φ_f decreases with increasing solvent polarity for **6a** and **6b**. In a non-polar solvent such as benzene, Φ_f values for **6a,b** are 5.6×10^{-4} and 1.4×10^{-3}, respectively, whereas they are 1.5×10^{-4} and 2.0×10^{-4} respectively, in methanol. The quantum yields of fluorescence of **7a** and **7b**, however, were relatively insensitive to the nature of the solvent. In methanol, for example, the Φ_f for both **7a** and **7b** is 1.0×10^{-3}.

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† The λ_{max} of the CT bands were estimated by subtracting the LE band from the observed emission spectrum assuming a symmetric shape of the LE bands.

Second harmonic generation

The second harmonic generation (SHG) efficiency of these compounds were examined by the powder reflection technique using a Nd:YAG pulsed laser (1064 nm, 11 ns pulses). Urea was used as the reference compound. The results are shown in Table 3. The yellow crystals of **6a** showed an activity of 0.46 times that of urea, whereas the red solid did not show any activity. This may be due to reabsorption of the light at 532 nm by the red crystals. Compound **6b** recrystallised only in one form from all the solvents and these crystals were not found to be SHG active. Compound **7a** showed SHG activity of 0.45 times that of urea, whereas **7b** showed an activity of 0.05 times urea. Substitution by the methoxy group as in **6b** and **7b** does not affect the solvatochromic properties. However, second harmonic generation is not observed with both **6b** and **7b**. This may be due to the possibility that the methoxy groups in **6b** and **7b** affect in some way the bulk properties. However, we could not obtain the good quality crystals required for determining the X-ray structures of these compounds.

Experimental

Melting points are uncorrected and were recorded on a Buchi-530 melting point apparatus. The IR spectra were determined on a Perkin-Elmer Model 882 infrared spectrophotometer. Absorption spectra were recorded on a Shimadzu UV 2100 spectrophotometer. Emission and excitation studies were carried out on a SPEX-Fluorolog F-112X spectrofluorometer. Quantum yields were measured by the relative method using optically matched dilute solutions. Rhodamine 6G having a quantum yield of fluorescence of 0.90 in ethanol[26] was used as reference for **6a** and **6b**, whereas anthracene having a fluorescence quantum yield of 0.27 in ethanol[27] was used as the reference for **7a** and **7b**. Unless otherwise stated, NMR spectra were recorded on a JEOL 90 MHz NMR spectrometer with tetramethylsilane as internal standard (*J* values quoted in Hz). Optical rotations were measured using a Jasco DIP-370 Digital Polarimeter and are given in units of 10^{-1} deg cm^2 g^{-1}.

Measurement of second harmonic generation efficiency

The SHG activities of **6a,b** and **7a,b** were compared with that of urea using the Kurtz and Perry method.[28] The samples were ground and graded by use of standard sieves (100–150 μm) and loaded on a microscopic slide with a sample thickness of 1 mm.

An applied Photophysics Model LKS-50 laser kinetic spectrometer using a Spectra Physics GCR-12 series Nd:YAG laser (1064 nm, 11 ns, 400 mJ pulse^{-1}) was used for these studies. The laser beam was directed unfocused on to the sample kept at 45° angle to the laser beam. The emission was collected from the front face of the sample at 90° angle to the laser beam. After removal of the fundamental beam using filters and a monochromator, the 532 nm signal was detected by a photomultiplier and stored on a Philips model PM 3323 digital oscilloscope. The signals were averaged over several shots.

Materials

Reagent grade reactants and solvents were used as received from Chemical Suppliers. Extremely dry solvents were prepared by adopting reported procedures. Spectroscopic grade solvents were used for all measurements.

Synthesis of [3-(butylsulfanyl)propenylidene]-indanediones 4a,b and -pyrimidinetriones 5a,b

Equimolar amounts of the aldehydes **3a,b** and the corresponding active methylene compounds were dissolved in the minimum amount of dry methanol. A few drops of 10% alcoholic KOH were then added and the mixture was set aside for 1 h in each case. The products formed were filtered and purified by repeated recrystallisation from suitable solvents.

Table 3 Results of SHG measurements of **6a**, **6b**, **7a** and **7b**

Compound	SHG activity (× urea)
Urea	1.0
6a (red)	0.0
6a (yellow)	0.46
6b	0.0
7a	0.45
7b	0.04

2-(3-Butylsulfanyl-3-phenylprop-2-enylidene)indane-1,3-dione 4a. This compound was prepared from 3-butylsulfanyl-3-phenylprop-2-enal **3a** (200 mg, 0.9 mmol) and indane-1,3-dione (132 mg, 0.9 mmol). The product was chromatographed using silica gel (230–400 mesh) in a flash column. Elution of the column with a mixture (1:9) of ethyl acetate and hexane yielded a pure sample of the title compound **4a** as an orange solid (250 mg, 80%), mp 116–117 °C [from a mixture (1:9) of ethyl acetate and hexane]; ν_{max}/cm^{-1} 3050, 2920 (CH), 1670 (CO) and 1570 (C=C); λ_{max}(CH$_3$OH)/nm 248.5 (ε/dm^3 mol^{-1} cm^{-1} 25 600), 271.8sh (19 500), 391.3 (38 200) and 438.0 (23 000); δ_H(CDCl$_3$) 0.90–1.10 (3 H, t, *J* 7, CH$_3$), 1.25–1.91 (4 H, m, CH$_2$CH$_2$), 3.05–3.20 (2 H, t, *J* 7, SCH$_2$) and 7.10–8.15 (11 H, m, aromatic-H and vinylic-H); δ_C(CDCl$_3$) 13.42, 21.93, 29.59, 32.73, 117.07, 122.17, 122.37, 123.63, 128.44, 129.30, 130.02, 134.19, 134.34, 135.81, 140.01, 140.46, 141.65, 167.16, 190.31 and 190.67 (Found EI-MS: *m/z* 348.1178. C$_{22}$H$_{20}$O$_2$S requires *M*, 348.1184).

2-[3-Butylsulfanyl-3-(4-methoxyphenyl)prop-2-enylidene]-indane-1,3-dione 4b. Treatment of aldehyde **3b** (2 g, 8 mmol) with indane-1,3-dione (1.17 g, 8 mmol) gave the crude product **4b**, which was further purified by flash chromatography over silica gel using a mixture (1:1) of benzene and hexane, to give the title compound **4b** as an orange solid (2.25 g, 74%), mp 112–113 °C [from a mixture (1:1) of chloroform and hexane]; ν_{max}/cm^{-1} 2933, 2864 (CH), 1678 (CO) and 1599 (C=C); λ_{max}(CH$_3$OH)/nm 442 (ε/dm^3 mol^{-1} cm^{-1} 71 910) and 267 (11 529); δ_H(CDCl$_3$) 0.90–1.10 (3 H, t, *J* 7, CH$_3$), 1.45–2.00 (4 H, m, CH$_2$CH$_2$), 3.00–3.20 (2 H, t, *J* 7, SCH$_2$), 3.9 (3 H, s, OCH$_3$) 6.95–7.35 (2 H, dd, *J* 10, vinylic-H) and 7.45–8.10 (10 H, m, aromatic-H); δ_C(CDCl$_3$) 13.42, 21.93, 29.68, 32.87, 55.16, 113.97, 116.86, 122.11, 122.32, 123.21, 128.20, 130.94, 134.10, 134.25, 140.49, 140.58, 141.65, 161.31, 167.61, 190.55 and 190.79.

5-(3-Butylsulfanyl-3-phenylprop-2-enylidene)pyrimidine-2,4,-6(1*H*,3*H*,5*H*)-trione 5a. Treatment of aldehyde **3a** (200 mg, 0.09 mol) with barbituric acid [pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione] (116 mg, 0.09 mol) and work-up in the usual manner gave the title compound **5a** (221 mg, 74%) mp 227–228 °C [from a mixture (1:1) of ethyl acetate and methanol]; ν_{max}/cm^{-1} 3200 (NH), 3000, 2920, 2860 (CH), 1670 (CO) and 1560 (C=C); λ_{max}(CH$_3$OH)/nm, 248 (ε/dm^3 mol^{-1} cm^{-1} 8740) and 372 (25 900); δ_H([^{2}H$_6$]DMSO) 0.70–1.00 (3 H, t, *J* 7, CH$_3$), 1.15–1.85 (4 H, m, CH$_2$CH$_2$), 2.95–3.05 (2 H, t, *J* 7, SCH$_2$), 7.30–8.20 (7 H, m, aromatic-H and vinylic-H) and 11.10 (2 H, s, NH); δ_C([^{2}H$_6$]DMSO) 16.84, 25.01, 32.98, 35.69, 114.57, 121.38, 132.23, 132.74, 133.97, 139.13, 151.84, 153.78, 166.70, 167.05 and 171.47 (Found FAB-MS: *m/z* 331.1166. C$_{17}$H$_{18}$N$_2$O$_3$S + H requires *M*, 331.1116).

5-[3-Butylsulfanyl-3-(4-methoxyphenyl)prop-2-enylidene]-pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione 5b. Compound **5b** was prepared from **3b** (2 g, 8 mmol) and barbituric acid (1.02 g, 8 mmol). The reddish brown product obtained was purified by flash chromatography over silica gel using a mixture (1:4) of ethyl acetate and chloroform to give a pure sample of the title compound **5b** (1.9 g, 65%), mp 191–192 °C (from acetone); ν_{max}/cm^{-1} 3745 (NH), 3048, 2842 (CH), 1653 (CO), 1604, 1575 (C=C); λ_{max}(CH_3OH)/nm 418 (ε/dm^3 mol^{-1} cm^{-1} 37 000), 262sh (9730) and 229 (20 000); δ_H([$^2H_6$]DMSO) 0.75–1.10 (3 H, t, *J* 7, CH_3), 1.25–1.85 (4 H, m, CH_2CH_2), 2.90–3.15 (2 H, t, *J* 7, SCH_2), 3.85 (3 H, s, OCH_3), 7.00–8.15 (6 H, m, aromatic-H and vinylic-H) and 11.05 (2 H, s, NH); δ_C([$^2H_6$]DMSO) 13.39, 21.57, 29.60, 32.37, 55.43, 110.48, 114.30, 114.59, 117.61, 127.84, 130.23, 131.06, 149.02, 150.37, 161.29, 163.29, 163.73 and 168.60 (Found FAB-MS: *m*/*z* 361.1222. $C_{18}H_{20}N_2O_4S$ + H requires *M*, 361.1215).

Synthesis of [3-(2-hydroxymethylpyrrolidinyl)propenylidene]-indanediones 6a,b and -pyrimidinetriones 7a,b

Equimolar amounts of butysulfanyl-substituted pentadienones **4a,b** and **5a,b** and L-prolinol were dissolved in dry methanol and refluxed for 2 h. The product formed was purified in each case by column chromatography.

2-[3-(2-Hydroxymethylpyrrolidinyl)-3-phenylprop-2-enylidene]indane-1,3-dione 6a. Treatment of indane-1,3-dione **4a** (152 mg, 0.47 mmol) with L-prolinol (47 mg, 0.47 mmol) gave a reddish brown solid, which was chromatographed over silica gel (230–400 mesh) using a flash column. Elution with a mixture (3:17) of ethyl acetate and chloroform gave reddish brown crystals of the title compound **6a** (95 mg, 60%), mp 181–182 °C (from benzene); ν_{max}/cm^{-1} 3300 (OH), 3060, 2950, 2880 (CH), 1630 (CO) and 1590 (C=C); λ_{max}(CH_3OH)/nm 239 (ε/dm^3 mol^{-1} cm^{-1} 4250) and 451.7 (14 800); δ_H($CDCl_3$) 1.60–2.40 (5 H, m, CH_2CH_2 and OH), 3.10–3.40 (2 H, m, NCH_2), 3.45–4.05 (2 H, m, OCH_2), 4.20–4.60 (1 H, m, NCH) and 7.10–7.90 (11 H, m, aromatic-H and vinylic-H); δ_C($CDCl_3$) 22.44, 22.97, 27.59, 50.24, 52.95, 60.86, 61.61, 62.65, 63.04, 103.58, 104.27, 114.32, 114.80, 120.62, 120.80, 120.98, 127.51, 128.08, 128.64, 129.78, 132.58, 132.76, 133.42, 139.59, 141.00, 146.52, 167.88, 168.36, 191.51, 191.72, 191.89 and 192.31 (Found FAB-MS: *m*/*z* 359.1504. $C_{23}H_{21}NO_3$ requires *M*, 359.152 14) $[\alpha]_D^{25}$ −328.82 (*c* 0.01 in methanol).

2-[3-(2-Hydroxymethylpyrrolidinyl)-3-(4-methoxyphenyl)-prop-2-enylidene]indane-1,3-dione 6b. Treatment of indane-1,3-dione **4b** (2 g, 5.65 mmol) with L-prolinol (570 mg, 5.65 mmol) gave a crude product, which was further purified by flash chromatography over silica gel using a mixture (1:1) of ethyl acetate and chloroform. Recrystallisation gave reddish-brown crystals of the title compound **6b** (1.9 g, 87%) mp 198–199 °C (from benzene); ν_{max}/cm^{-1} 3444 (OH), 2915, 2875 (CH), 1643 (CO) and 1615, 1569 (C=C); λ_{max}(CH_3OH)/nm 452 (ε/dm^3 mol^{-1} cm^{-1} 132 500), 268 (111 100) and 240sh (75 750); δ_H($CDCl_3$) 1.80–2.40 (5 H, m, CH_2CH_2 and OH), 3.10–3.40 (2 H, m, NCH_2), 3.45–4.05 (2 H, m, OCH_2), 3.90 (3 H, s, OCH_3), 4.25–4.55 (1 H, m, NCH) and 6.9–7.85 (10 H, m, aromatic-H and vinylic-H); δ_C($CDCl_3$) 22.37, 22.94, 27.44, 50.21, 53.04, 55.04, 60.68, 61.49, 62.62, 103.94, 104.66, 113.76, 114.29, 120.77, 124.41, 125.27, 128.73, 129.66, 131.15, 132.34, 132.64, 139.45, 140.85, 146.52, 160.30, 160.51, 168.15, 168.62, 191.48, 191.78 and 192.16; $[\alpha]_D^{26}$ 353.91 (*c* 0.0112 in methanol).

5-[3-(2-Hydroxymethylpyrrolidinyl)-3-phenylprop-2-enylidene]pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione 7a. Treatment of pyrimidinetrione **5a** (100 mg, 0.303 mmol) with L-prolinol (30 mg, 0.303 mmol) gave a yellow product, which was purified by flash chromatography over silica gel (230–400 mesh). Elution of the column with a mixture (1:4) of methanol and ethyl acetate gave the title compound **7a** (53.9 mg, 52%), mp 270–271 °C (from methanol); ν_{max}/cm^{-1} 3480 (NH), 3120 (OH), 3000, 2920, 2840 (CH), 1660 (CO) and 1600 (C=C); λ_{max}(CH_3OH)/nm 237.2 (ε/dm^3 mol^{-1} cm^{-1} 11 300) and 419.3 (60 600); δ_H(500 MHz, [$^2H_6$] DMSO)‡ 1.85–2.02 (2 H, m, CH_2), 2.03–2.20 (2 H, m, CH_2), 3.00–3.15 (2 H, m, NCH_2), 3.30–3.48 (2 H, m, OCH_2), 4.25–4.30 (1 H, m, NCH), 4.85 and 5.15 (1 H, t, *J* 6, OH), 7.10–7.64 (7 H, m, aromatic-H and vinylic-H), 10.22–10.25 (1 H, d, *J* 8, NH) and 10.25–10.30 (1 H, s, NH); δ_C([$^2H_6$]DMSO) 25.40, 26.11, 30.11, 30.74, 56.83, 62.90, 62.63. 65.44, 66.75, 101.42, 101.95, 108.28, 108.79, 131.40, 131.73, 132.33, 133.25, 133.43, 136.32, 137.34, 154.40, 156.61, 167.65, 167.92, 172.57 and 172.90 (Found FAB-MS: *m*/*z* 342.1464. $C_{18}H_{19}N_3O_4$ + H requires *M*, 342.1454); $[\alpha]_D^{25}$ −152.13 (*c* 0.095 in methanol).

5-[3-(2-Hydroxymethylpyrrolidinyl)-3-(4-methoxyphenyl)-prop-2-enylidene]pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione 7b. Compound **7b** was prepared from pyrimidinetrione **5b** (1.5 g, 4.16 mmol) and L-prolinol (420 mg, 4.16 mmol). Purification by flash chromatography on silica gel using a mixture (1:19) of methanol and ethyl acetate gave the title compound **7b** (1.18 g, 76%), mp 280–281 °C (from methanol); ν_{max}/cm^{-1} 3434 (NH), 3109 (OH), 2999, 2824 (CH), 1664 (CO) and 1615 (C=C); λ_{max}(CH_3OH)/nm 420 (ε/dm^3 mol^{-1} cm^{-1} 67 900), 267 (41 500) and 232sh (24 350); δ_H([$^2H_6$]DMSO)‡ 1.75–2.40 (4 H, m, CH_2CH_2), 3.05–3.25 (2 H, m, NCH_2), 3.65–3.80 (2 H, m, OCH_2), 3.85 (3 H, s, OCH_3), 4.20–4.55 (1 H, m, NCH), 7.05–7.75 (6 H, m, aromatic-H and vinylic-H) and 10.25 (2 H, s, NH); δ_C([$^2H_6$]DMSO) 25.61, 26.32, 30.23, 30.86, 58.99, 63.14, 66.93, 101.00, 101.57, 109.03, 109.53, 117.92, 128.42, 129.40, 133.73, 154.61, 156.79, 163.89, 164.01, 167.83, 168.19, 173.20 and 173.53 (Found FAB-MS: *m*/*z* 372.1559. $C_{19}H_{21}N_3O_5$ + H requires *M* 372.1556); $[\alpha]_D^{25}$ 213.94 (*c* 0.012 in methanol).

2-[3-(2-Acetoxymethylpyrrolidinyl)-3-phenylprop-2-enylidene]indane-1,3-dione 8. Treatment of indane-1,3-dione **6a** (100 mg, 0.28 mmol) with acetyl chloride (22 mg, 0.28 mmol) in refluxing benzene (dry, 20 cm^3) for 2 h gave compound **8**, which was further purified by flash chromatography over silica gel using a mixture (1:1) of ethyl acetate and chloroform, to give the title compound **8** as a brown solid (109 mg, 95%), mp 113–114 °C [from a mixture (1:1) of chloroform and hexane]; ν_{max}/cm^{-1} 2984, 2372 (CH), 1650 (CO) and 1563 (C=C); λ_{max}(CH_3OH)/nm 452 (ε/dm^3 mol^{-1} cm^{-1} 40 850), 268 (43 300) and 240sh (27 000); δ_H($CDCl_3$) 1.60–2.4 (7 H, m, CH_2CH_2 and $COCH_3$), 3.60–3.90 (2 H, m, NCH_2), 4.20–4.50 (2 H, m, OCH_2), 4.60–4.80 (1 H, m, NCH) and 6.90–8.00 (11 H, m, aromatic-H and vinylic-H); δ_C($CDCl_3$) 20.52, 22.22, 22.82, 27.62, 49.52, 52.03, 53.28, 58.00, 59.01, 62.74, 63.84, 102.96, 103.46, 115.58, 116.14, 120.80, 121.19, 127.60, 127.90, 128.26, 128.56, 128.82, 129.75, 132.43, 132.64, 132.82, 133.54, 139.83, 141.18, 146.37, 166.98, 167.58, 169.94, 170.59, 191.18 and 191.98; $[\alpha]_D^{26}$ −71.84 (*c* 0.01 in methanol).

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