2,4-Bis[4-(N,N-dibutylamino)phenyl]squaraine: X-ray crystal structure of a centrosymmetric dye and the second-order non-linear optical properties of its non-centrosymmetric Langmuir–Blodgett films

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Crystals of the title compound exist as a green monoclinic phase [space group $P2_1/c$ with a=9.046(1), b=19.615(2), c=9.055(1) Å, $\beta=116.107(5)^\circ$, Z=2] and a purple triclinic phase. The chromophore is both planar and centrosymmetric and its dimensions indicate a tendency towards a quinoidal structure with extensive delocalisation. The Langmuir-Blodgett (LB) films show two types of aggregation with absorption maxima at 655 nm and 540 nm. These monolayers also exhibit strong second harmonic generation (SHG) comparable to the intensity from films of hemicyanine dyes. The anomalous non-linear optical properties are attributed to a serendipitous non-centrosymmetric packing arrangement within the films and to an intermolecular charge transfer contribution to the bulk second-order susceptibility.

Current interest in organic materials for non-linear optics¹⁻⁵ stems from the high molecular hyperpolarizabilities of donor- $(\pi$ -bridge)-acceptor molecules and the potential applications of such materials in the electronics and communications industries. The non-linearities arise from the dependence of the polarization on the electric field of the incident radiation:

$$p = \alpha E + \beta E^2 + \gamma E^3 + \dots \tag{1}$$

$$P = \varepsilon_0 \left\{ \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots \right\}$$
(2)

 χ is the bulk susceptibility of the material and, hitherto, has been attributed to the tensor sum of the individual molecular components (α, β, γ) corrected for orientation and local field effects. As significant SHG can only occur in non-centrosymmetric media the studies to date have mainly concerned dipolar molecules and their alignment by an electric field⁵ or LB deposition.^{6,7} Thus, it has been widely accepted that the molecule, the smallest building block of any organic structure, should be acentric but this assumes that intermolecular interactions are weak. Contrary to this belief, we have recently discovered that centrosymmetric squaraine[†] dyes, previously studied as third-order materials,⁸⁻¹⁰ can give rise to strong second-order effects when deposited as LB films.11 The molecular hyperpolarizability (β) is zero but SHG can arise if there is an intermolecular charge transfer contribution to the susceptibility, $\chi^{(2)}$, and if the molecules aggregate in a manner that satisfies the symmetry requirements. This recent discovery¹¹ (reviewed by Brédas and Meyers¹²) has focused attention on the influence of intermolecular effects on the second-order properties. As part of our continuing work, we have observed SHG from anilinium¹¹ and indolinium¹³ derivatives of the squaraine dyes and, in this paper, we report the synthesis and X-ray crystal structure of 2,4-bis[4-(N,N-dibutylamino)phenyl]squaraine (Fig. 1) and the non-linear optical properties of its LB films.

Experimental

Synthesis

The method employed in the squaraine synthesis is that developed by Law and Bailey¹⁴ for their syntheses of unsym-

metrical squaraine derivatives. We have found this method to be superior to the original general procedure¹⁵ which employs a Dean-Stark apparatus to drive the condensation process. Thus, 2,4-bis[4-(N,N-dibutylamino)phenyl]squaraine wasobtained from the condensation of N, N-dibutylaniline (1.80 g, 2.00 cm^3 , 8.8 mmol) with squaric acid (0.5 g, 4.4 mmol) in a refluxing mixture of propan-2-ol (35 cm³) and tributyl orthoformate (3.00 cm³). After 4 h the intense blue solution was cooled depositing green crystals with a metallic sheen. This material was collected by filtration and the filtrate reduced in volume and cooled to afford a further crop of crystals. After drying in vacuo a total yield of 1.90 g (88% yield) was obtained, mp 188-190 °C, (Found: C, 78.9; H, 9.1; N, 5.6. C₃₂H₄₄N₂O₂ requires: C, 78.64; H, 9.07; N, 5.73%); $\delta_{\rm H}({\rm CDCl}_3; J/{\rm H_z})$ 1.00 (12 H, t, J 7), 1.40 (8 H, sextet, J 7), 1.64 (8 H, quintet, J 7), 3.42 (8 H, t, J 7), 6.70 (4 H, d, J 8), 8.46 (4 H, d, J 8); $\delta_{\rm C}({\rm CDCl}_3)$ 14.04 (3), 20.40 (2), 29.74 (2), 51.34 (2), 112.40 (1), 119.55 (0), 133.38 (1), 153.52 (0), 183.52 (0), 187.47 (0); m/z(FAB; NBA) 488.

The ¹H NMR (300 MHz) and ¹³C NMR (90 MHz) spectra were recorded on a Bruker AM300 spectrophotometer and the FAB mass spectrum on a VG Analytical 70-250-SE doublefocusing mass spectrometer.

X-Ray crystallographic analysis

Single crystals were obtained by partial evaporation of a dilute solution of the dye in ethanol and, as previously reported¹⁶ for anilinium squaraines, two crystal polymorphs were observed. Crystals of a green monoclinic phase were separated and employed in the structural determination whereas those of the purple triclinic phase were deemed unsuitable for X-ray structural analysis.



Fig. 1 Molecular structure of 2,4-bis [4-(N,N-dibutylamino)phenyl]-squaraine

[†] Squaraine = cyclobutene-1,3-dione.

X-Ray intensity data were collected on an Enraf-Nonius four-circle diffractometer at 298 K using graphite crystal monochromated Mo-K α radiation (λ =0.71073 Å) to 2 θ =50°. Unit cell parameters were determined from the least-squares refinement for 25 reflections with 2θ <25°. 2536 independent reflections with $I > 2\sigma(I)$ were used for the structural analysis. Data were corrected for both Lorentz and polarization effects and empirical absorption correction was applied. The structure was solved by using SHELXS-86,¹⁷ and refined to residuals R_1 =0.0395 and wR_2 =0.1234 (SHELXL-93¹⁸) using full-matrix least-squares with anisotropic thermal parameters for all non-hydrogens. Hydrogens were located by difference methods and both positional and thermal parameters refined.

The crystallographic data and atomic coordinates are listed in Tables 1 and 2 while selected bond lengths are given in Fig. 2. Bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, and observed and calculated

Table 1 Crystallographic	data	for	2,4-bis(4-[N,N-dibutylamino)
phenyl]squaraine ^a			

empirical formula formula weight temperature wavelength crystal system space group unit cell dimensions	$C_{32}H_{44}N_2O_2$ 488.69 298(2) K 0.71073 Å monoclinic $P2_1/c$ $a = 9.0460(10) Å$ $b = 19.615(2) Å$ $c = 9.0550(10) Å$ $B = 116 107(5)^\circ$
volume	$1442.8(3) Å^3$
Ζ	2
density (calc)	1.125 Mg m ⁻³
absorption coefficient	0.069 mm^{-1}
F(000)	532
crystal size	$0.40 \times 0.32 \times 0.20 \text{ mm}^3$
θ range for data collection	2.08 to 24.96°
index ranges	$0 \le h \le 10, 0 \le k \le 23, -10 \le l \le 9$
reflections collected	2702
independent reflections	2536 [R(int) = 0.0376]
absorption correction	Psi scan
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	2536/0/252
goodness-of-fit on F^2	0.676
final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0395, wR_2 = 0.1234$
R indices (all data)	$R_1 = 0.1042, wR_2 = 0.2350$
largest diff. peak and hole	0.124 and $-0.139 \text{ e} \text{ Å}^{-3}$

Residuals R_1 and wR_2 are defined as $R_1 = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$ and $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$. Weighting scheme $w = [\sigma^2(F_0)^2 + (0.2084P)^2 + 1.85P]^{-1}$ where $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

Table 2 Atomic coordinates $(\times 10^4)$ and equivalent isotropic displacement parameters $(\times 10^3 \text{ Å}^2)$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	у	Z	U(eq)
O(1)	-1578(3)	9216(1)	477(4)	68(1)
N(1)	5975(3)	7704(1)	2156(4)	49(1)
C(1)	-723(4)	9640(2)	220(4)	47(1)
C(2)	934(4)	9645(2)	312(4)	43(1)
C(3)	2189(4)	9158(2)	728(4)	41(1)
C(4)	1994(4)	8496(2)	1236(4)	45(1)
C(5)	3221(4)	8024(2)	1681(4)	47(1)
C(6)	4750(4)	8177(2)	1674(4)	42(1)
C(7)	4941(4)	8841(2)	1161(4)	45(1)
C(8)	3705(4)	9306(2)	706(4)	45(1)
C(9)	7584(4)	7830(2)	2196(5)	53(1)
C(10)	8930(5)	7978(2)	3897(5)	66(1)
C(11)	8718(6)	8640(2)	4620(6)	74(1)
C(12)	10023(10)	8758(5)	6379(8)	112(1)
C(13)	5712(5)	7009(2)	2594(4)	51(1)
C(14)	4721(5)	6566(2)	1110(5)	55(1)
C(15)	4458(7)	5854(2)	1582(5)	70(1)
C(16)	3281(9)	5436(3)	125(7)	92(1)



Fig. 2 Molecular conformation, atomic numbering scheme and selected bond distances (Å) and angles (°) of the chromophore. Squarate group: O(1)-C(1) 1.226(4), C(1)-C(2) 1.464(5), C(1')-C(2) 1.466(4); O(1)-C(1)-C(2) 135.2(3), C(2)-C(1)-C(2') 89.7(3), C(1)-C(2) -C(1') 90.3(3). Six-membered ring: C(3)-C(4) 1.414(4), C(4)-C(5) 1.364(5), C(5)-C(6) 1.418(5), C(6)-C(7) 1.417(4), C(7)-C(8) 1.360(4), C(8)-C(3) 1.411(4); C(3)-C(4)-C(5) 121.3(3), C(4)-C(5)-C(6) 121.5(3), C(5)-C(6)-C(7) 117.2(3), C(6)-C(7)-C(8) 120.9(3), C(7)-C(8)-C(3) 122.2(3), C(8)-C(3)-C(4) 117.0(3). Exocyclic bonds and angles: C(2)-C(3) 1.402(4), C(6)-N(1) 1.361(4); C(1)-C(2)-C(3) 134.3(3), C(1)-C(2)-C(3) 135.4(3), C(2)-C(3)-C(4) 120.7(3), C(2)-C(3)-C(8) 122.2(3), C(5)-C(6)-N(1) 120.8(3), C(7)-C(6)-N(1) 122.1(3). The symmetry transformation used to generate the equivalent atoms is <math>-x, -y+2, -z.

structure factors are provided as supplementary material. All data have been deposited at the Cambridge Crystallographic Data Centre (refer to Information for Authors, J. Mater. Chem., Issue No. 1).

Film deposition

The squaraine dye was spread from a 0.1 mg cm⁻³ chloroform solution onto the pure water subphase (MilliQ) of an LB trough (Nima Technology, Model 622), left for 10 min at *ca*. 25 °C and then compressed at 0.5 cm² s⁻¹. Films were deposited at 5 to 25 mN m⁻¹ by passing a hydrophilically treated glass slide vertically through the floating monolayer at 80 μ m s⁻¹ on the upstroke.

Second-harmonic generation

SHG measurements were performed in transmission using a Nd:YAG laser ($\lambda = 1.064 \mu m$) with the beam at 45° to the film. The apparatus is described in ref. 19.

Results and Discussion

X-Ray crystal structure

The molecule is centrosymmetric and with the exception of the four butyl groups is essentially planar. The asymmetric unit consists of half the molecule with the other half being symmetry generated across an inversion centre, centralized in the four-membered ring. The bond lengths are similar to those reported for other anilinium squaraines^{10,16} with a tendency towards a quinoidal structure with extensive delocalisation (Fig. 2). The exocyclic C-C and C-N bonds are 1.402(4) Å and 1.361(4) Å, respectively, whereas the contracted C-C bonds of the six-membered ring are C(4)-C(5)=1.364(4) Å and C(7)-C(8)=1.360(4) Å. These may be compared with averaged C-C lengths of 1.415(8) Å for the remainder of the donor group and 1.465(6) Å for the four-membered ring. The C-O bond length, 1.226(4) Å, is significantly shorter than the 1.244 Å to 1.253 Å reported for other anilinium squaraines,^{10,16} but the carbonyl length in these cases is probably influenced by neighbouring hydroxy groups in the ortho positions of the six-membered ring.

The packing arrangement consists of parallel stacks inclined



Fig. 3 Packing within the unit cell viewed down a

to the *ac* plane and a herringbone-type arrangement parallel to the *b* axis (Fig. 3). Common to other anilinium squaraines,^{12,16} the parallel stacking shows the molecules overlapping with the amino group (donor) aligned over the central ring (acceptor) with a mean perpendicular plane-to-plane spacing of *ca*. 3.9(1) Å. However, the closest intermolecular contacts are lateral interactions between O(1)...C(9) [3.382(4) Å; 1+x, y, z], O(1)...H(9a) [2.479(4) Å; 1+x, y, z] and O(1)...H(7) [2.618(4) Å; 1+x, y, z].

The crystal structure is centrosymmetric and thus, unlike the LB films below, the monoclinic crystals show no SHG. The same applies to the purple triclinic phase but we have been unsuccessful in growing crystals suitable for structural analysis.

LB films

The dye is an unconventional material for LB deposition as it has four short legs rather than a long hydrophobic chain. Nonetheless, the initial part of the π -A isotherm rises steeply before undergoing a structural rearrangement, or collapse, at 9 mN m⁻¹ with a corresponding area of *ca*. 82 Å² molecule⁻¹ (Fig. 4). This is consistent with the chromophore residing on its long edge as the dimensions, including the first CH₂ of each of the four butyl groups, obtained from the structural analysis are approximately $19 \times 7 \times 4$ Å³. A second transition is observed at 16 mN m⁻¹ with a corresponding area of *ca*. 50 Å² molecule⁻¹ and, once more, the isotherm rises steeply above 20 mN m⁻¹. The chromophores may adopt a vertical alignment at higher pressures although the reduction in area may also be attributed to partial collapse and bilayer formation.

The LB film spectra are significantly shifted from the absorption in chloroform (λ_{max} =633 nm, half width at half maximum=13 nm) and the film colour is dependent upon the deposition pressure. Deposition below 9 mN m⁻¹, the first transition pressure, gives rise to an absorption maximum at 665 to 670 nm whereas, at higher pressures, deposition results in the emergence of a second peak at *ca.* 540 nm (Fig. 5; Table 3). This is characteristic of the formation of different types of aggregate and this type of behaviour has been extensively documented for various squaraine dyes.²⁰⁻²⁴ Aggregation in LB films has been studied by Law and co-workers^{23,24} and



Fig. 4 Surface pressure versus area isotherm of the dye spread from chloroform solution at ambient temperature (ca. 18 °C) and compressed at 0.5 cm² s⁻¹



Fig. 5 Absorption spectra of LB monolayers deposited at 5 mN m^{-1} (lower spectrum) and 25 mN m^{-1} (upper spectrum)

 Table 3 Dependence of the spectra and non-linear optical properties

 of freshly prepared LB films on the deposition pressure

$\pi/mN m^{-1}$	λ_{\max}/nm	absorbance/layer ⁻¹	SHG ^a /au
5-8	665-670 ^b	0.026	0.5
20-25	540	0.060	0.5
	665	0.037	

^{*a*} The SHG is relative to the intensity obtained from monolayer films of the hemicyanine dye, (E)-4-[2-(4-dimethylaminophenyl)ethenyl]-*N*-docosylpyridinium bromide. ^{*b*} Weak shoulder at *ca.* 540 nm.

the spectral differences attributed to changes in the molecular orientation and intermolecular overlap. By comparison with the published work of Law and Chen²³ the band at 540 nm probably corresponds to a face-to-face arrangement with dipole-dipole interactions between the central groups of adjacent chromophores whereas the absorption at *ca*. 665 nm involves charge transfer between the donor and acceptor parts of neighbouring molecules. For films deposited above 16 mN m⁻¹, the second transition pressure, both bands result and the absorbance of each is stronger than those reported for similar dyes.^{23,24} There may be a mixture of phases and the possibility of multilayer formation in this high pressure regime.

LB films of this centrosymmetric molecule have unusual non-linear optical properties in so far as they exhibit strong SHG, similar in magnitude to that obtained from films of

hemicyanine dyes.²⁵ The second harmonic intensity from freshly prepared films, deposited at 5-8 mN m⁻¹, is reproducible but decays to 50% of the original value within ca. 4 h and to only 5% within 24 h. This is accompanied by a decrease in absorbance at 667 nm with the gradual emergence of the second absorption band at 540 nm. Thus, it is assumed that the optical properties are influenced by the formation of an alternative aggregate with loss of the non-centrosymmetric packing arrangement. Surprisingly, the SHG is independent of the deposition pressure although the spectra of films deposited at 20-25 mN m⁻¹ are very different (Fig. 5; Table 3). In all cases the second harmonic intensity diminishes with time whereas films of the previously reported N-hexyl-N-methylamino analogue have remained stable over a period of several months.11

The phenomenon of SHG has been traditionally associated with donor-(π -bridge)-acceptor materials^{1,2} but, as explained previously,11 the structural criteria for SHG may be satisfied if adjacent chromophores adopt a non-parallel arrangement and if the repeating dimer motif does not pack centrosymmetrically. For conventional donor– $(\pi$ -bridge)–acceptor materials the intramolecular charge transfer contribution to the molecular hyperpolarizability (β) is larger than the sum of all other effects.²⁶ Since our observed SHG is as strong as that obtained for conventional second-order materials it is clear that there must be a significant intermolecular charge transfer contribution to the bulk susceptibility and that dimers, or higher aggregates, are responsible for the unusual non-linear optical behaviour.

Conclusions

In this work we have reported the crystal structure of a centrosymmetric molecule and SHG from its LB films. These results are significant as they conclusively show that intermolecular charge transfer has a profound effect on the second-order non-linear optical properties of organic dyes. Additionally, the magnitude of the SHG arising from such intermolecular charge transfer is comparable with that observed from films of donor- $(\pi$ -bridge)-acceptor molecules. In calculations which utilise SHG data (the determination of the chromophore tilt angle from the polarization dependence and β from $\chi^{(2)}$ it has been widely assumed that the intermolecular contribution is insignificant compared with that of the intramolecular component.²⁷ However, it is apparent that polar materials may be susceptible to strong intermolecular interactions and this should be taken into account. In addition, the existing design rules should be broadened to include intermolecular complexes as well as donor– $(\pi$ -bridge)–acceptor molecules as promising candidates for SHG. This is particularly relevant to LB film structures where alternate layers of amphiphilic donors and amphiphilic acceptors may be deposited to give significant SHG at the layer boundaries.

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