(*E*)-4,4'-Bis(1,3-benzoxazol-2-yl)-stilbene at 150 and 375 K

M. Amine Fourati, Thierry Maris, C. Géraldine Bazuin and Robert E. Prud'homme*

Département de Chimie, Université de Montréal, CP 6128, Succ. Centre-Ville, Montréal, Québec, Canada H3C 3J7
Correspondence e-mail: re.prudhomme@umontreal.ca

The title compound, a chromophore of formula $C_{28}H_{18}N_2O_2$, crystallizes with the molecule lying on an inversion centre to give one-half of a crystallographically independent molecule in the asymmetric unit. The molecule is almost planar, with slight deviation of the benzene rings from the mean molecular plane. The structure is characterized by a herringbone packing arrangement arising from C—H···π and π–π intermolecular interactions. The benzoxazole group is disordered between two orientations, with occupancy factors of 0.669 (10) and 0.331 (10) at 150 K [0.712 (7) and 0.288 (7) at 375 K].

Comment

The title compound, hereinafter denoted BBS, belongs to the well known class of stilbenes where conjugation between the two phenyl groups allows UV excitation to induce conversion between the *E* and *Z* isomers, making these compounds useful as photoactive switches (Irie, 2000; Momotake & Arai, 2004). This compound is generally employed as a fluorescent brightener in textiles (Bischoff *et al.*, 2001), detergents and other materials (Bur & Roth, 2004). It is also used as an additive for food and consumer packaging materials, due to its compliance with the US Food and Drug Administration regulations (Jervis, 2003). In addition, BBS has applications in host–guest systems as a molecular probe of deformation and temperature in polymer films (Pucci *et al.*, 2005, 2007; Sing *et al.*, 2009). The anisotropic flat shape of the molecule can be exploited to produce polarized light by adding the chromophore to oriented macromolecular matrices (Pucci *et al.*, 2006).
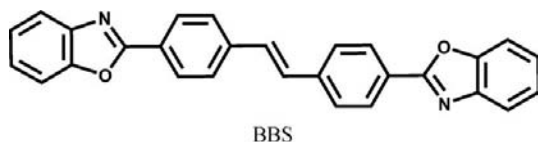
BBS

Fig. 1 shows the fluorescence spectrum of BBS diluted in poly(1,4-butylene succinate) (PBS) at various concentrations,

similar to data reported by Pucci *et al.* (2007). At low concentrations, the fluorescence spectra resemble the spectrum of BBS in tetrachloroethane solution (Pucci *et al.*, 2005, 2007), with emission bands centred at 410, 434 and 464 nm. These spectra are associated with isolated BBS monomers molecularly dispersed in the amorphous phase of PBS. Increasing the BBS concentration from 0.02 to 0.2wt% induces the emergence of a broad emission band centred at about 500 nm, and is accompanied by a colour change from blue to green. The broad band is attributed to the formation of BBS aggregates, favoured by π–π interactions of BBS molecules in planar conformation, thus allowing excimer emission (Pucci *et al.*, 2005, 2007).

For more precise information on BBS stacking characteristics, we report here the single-crystal structure of BBS crystallized from a solution of 1,2-dichlorobenzene. The inset in Fig. 1 shows that the fluorescence spectrum of the yellow bulk powder displays only the broad band centred at about 500 nm and none of the three bands characteristic of isolated BBS molecules. This indicates that the powder is composed only of excimer-forming aggregates. The latter can be assumed to have the same structure as in the PBS films, as supported by the observation that the X-ray powder diffraction pattern of the bulk sample is consistent with the calculated pattern obtained from the experimental single-crystal data. This allows a correlation to be made between the single-crystal structure of BBS and excimer emission in BBS-containing films.

From the single-crystal structure analysis at 150 K, it is found that the molecule of BBS is almost planar and lies on an inversion centre located at the mid-point of the C=C bond (Fig. 2). The mean planes of the central benzene rings and the central alkene group are twisted relative to one another by 6.66 (13)°, but the angle between the benzene rings and the benzoxazolyl groups is only 2.30 (16)°. Moreover, the structure of BBS features a network composed of layers in the *bc*
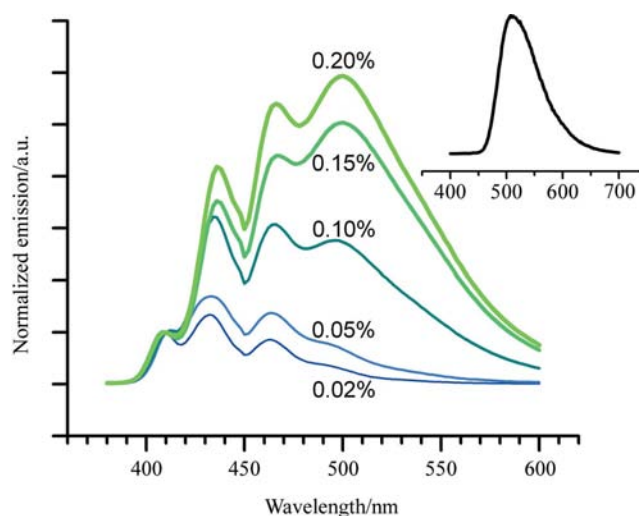
Figure 1
Fluorescence spectra of BBS molecules dispersed at various concentrations (wt%) in poly(1,4-butylene succinate) films normalized relative to the peak at 410 nm. Inset: fluorescence spectrum of BBS pellets (compacted powder) containing only BBS aggregates.
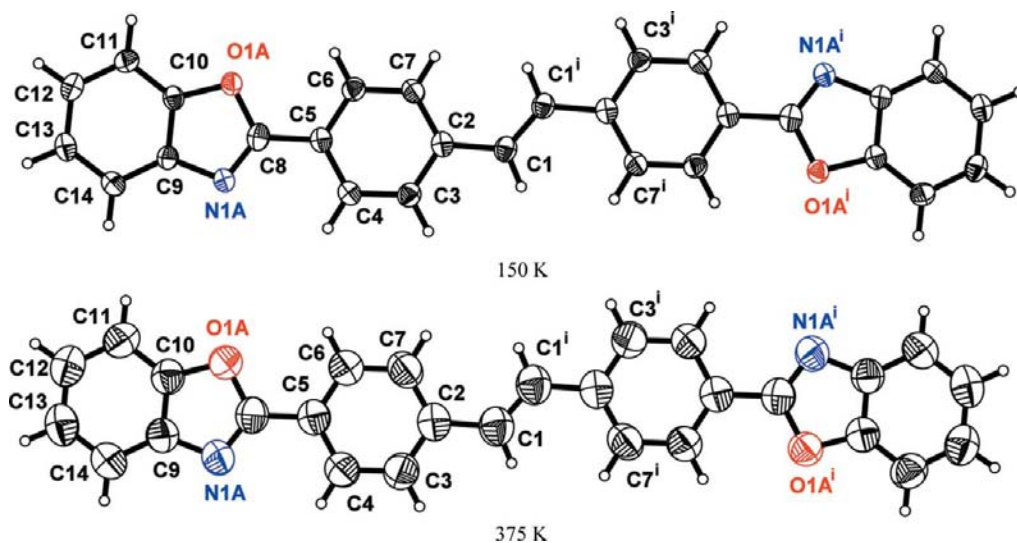
Figure 2
The molecular structure of BBS at 150 and 375 K, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Only one component of the disordered benzoxazolyl ring is shown. [Symmetry code: (i) $\frac{3}{2} - x$, $-y - \frac{1}{2}$, $-z$.]

plane, with molecules packed in a well-defined herringbone pattern (Fig. 3), similar to that of stilbene (Harada & Ogawa, 2001, 2004) but unlike other stilbene derivatives (Foitzik *et al.*, 1991; Ohba *et al.*, 2002; Soto Bustamante *et al.*, 1995).

Within the layers, the flat molecules are packed *via* π–π stacking interactions and C—H⋯π contacts. The π–π stacking interactions feature a short centroid–centroid distance of 3.6565 (7) Å between the central benzene ring ($Cg3$) and the terminal benzene ring ($Cg4^{ii}$), with a dihedral angle of 2.28 (6)° between ring planes [symmetry code: (ii) *x*, *y* − 1, *z*]. The π-stacked molecules are staggered relative to one another and the benzene rings overlap at a perpendicular distance of 3.3914 (5) Å. Moreover, a C—H⋯π contact (Fig. 3) involves atom H12, with a distance to the terminal benzene ring centroid $Cg4^{iii}$ of 2.77 (1) Å [symmetry code: (iii) $\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$].

trans-Stilbenes and diazobenzenes are known to be subject to orientational disorder, described as a pedal-like motion wherein the pair of benzene rings rotates around the central double bond like a bicycle pedal (Harada & Ogawa, 2001; Bouwstra *et al.*, 1984). This disorder is dynamic with inter-conversion between the major and minor conformers, the relative populations of which vary with temperature. At lower temperatures, the low occupancy factor of the minor conformer can make the disorder almost invisible (Harada & Ogawa, 2004). Usually, this disorder is detected by a short-ening of the central double bond (Masciocchi *et al.*, 2005) and by the appearance in the final Fourier difference map of two residual peaks in the vicinity of the central double bond that arise from the minor conformer (Harada & Ogawa, 2001, 2004). This was examined for BBS by measuring two different single crystals grown from the same solution, one at 150 K and the other at 375 K. The distance of the central C1=C1^i double bond is 1.331 (2) Å at 150 K and 1.306 (2) Å at 375 K [symmetry code: (i) $\frac{3}{2} - x$, $-y - \frac{1}{2}$, $-z$]. At 150 K, the value compares well with the normal expected value for a double

bond, and the difference Fourier map calculated after the final refinement of BBS (Spek, 2009) did not reveal any significant residual peaks in the region of the C=C bond. At 375 K, the central double bond is significantly shorter than expected but no residual peaks were detected in the final difference Fourier map. This may indicate that at 375 K the crystal is near the onset of dynamic disorder.

On the other hand, disorder related to the benzoxazolyl moiety was detected by the *checkCIF* (Spek, 2009) procedure performed at the end of the refinement. Two bonds, N1—C8 and O1—C10, failed the Hirshfeld difference test (Hirshfeld, 1976), with a very large s.u. of 15 for N1—C8. Examination of the final atomic displacement ellipsoid plot showed that the ellipsoids for atoms N1 and O1 are smaller and larger, respectively, than those for the other atoms of the molecule. These features were attributed to a substitutional disorder between O and N atoms sharing the same position. Such a statistical disorder in benzoxazolyl derivatives has been described previously (Norman *et al.*, 2002; Zhuang *et al.*, 2002). The occupancy factors of the N and O atoms were refined, giving a ratio of 0.66:0.34 between the two possible confor-mations for the crystal measured at 150 K.

The single-crystal structure of BBS confirms that the BBS molecules have an essentially planar conformation with
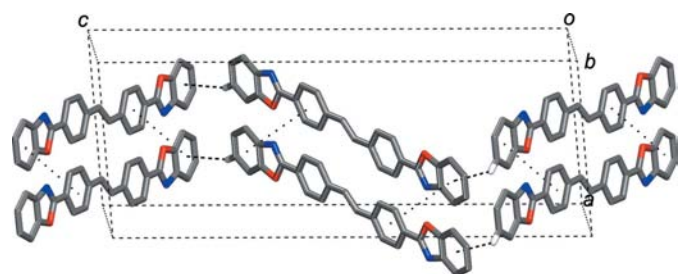
Figure 3
A view of the C—H⋯π and π–π stacking interactions (dotted lines) in one layer of π-stacked molecules of BBS at 150 K.

extensive π–π stacking interactions that allow for excimer formation, giving rise to the emission band centred at 500 nm. More specifically, the molecules are packed into a two-dimensional herringbone network, held together by inter-molecular π–π and C—H⋯π interactions. The perpendicular distance of 3.46 Å and the centroid–centroid distances of 3.6–3.7 Å between π-stacked molecules are very close to the pyrene interplanar stacking distance of 3.53 Å (Gilbert & Baggott, 1991). This distance is within the range of 3–4 Å that is considered necessary for excimer formation to take place (Gilbert & Baggott, 1991).

Experimental

4,4′-Bis(1,3-benzoxazol-2-yl)stilbene (BBS) was obtained from Aldrich (97%, m.p. > 573 K) and used without further purification. Yellow needle-like crystals of BBS suitable for X-ray diffraction analysis were obtained by slow evaporation from a solution in 1,2-dichlorobenzene. Poly(1,4-butylene succinate) (PBS) (Bionolle 1001) was obtained from Showa Highpolymer (Japan). PBS–BBS blends were prepared by melt-processing in a Plasti-Corder Brabender mixer, type DDRV501/DIGI-SYS, using 20 g of the polymer and 0.02–0.2wt% of the chromophore. Films with a thickness of about 80–120 μm were obtained by compression moulding between two aluminium foils in a Carver Laboratory Press at 473 K, followed by slow cooling to room temperature. Fluorescence emission spectra were recorded at ambient temperature using an Edinburgh Instruments FLS-920 fluorimeter, operating at an excitation wavelength of 377 nm.

Compound (I) at 150 K

Crystal data

$C_{28}H_{18}N_2O_2$ $V = 1950.72$ (12) Å³
$M_r = 414.44$ $Z = 4$
Monoclinic, $C2/c$ Cu $K\alpha$ radiation
$a = 11.2449$ (4) Å $\mu = 0.71$ mm⁻¹
$b = 6.0053$ (2) Å $T = 150$ K
$c = 29.0699$ (11) Å $0.28 \times 0.04 \times 0.03$ mm
$\beta = 96.4280$ (17)°

Data collection

Bruker Microstar diffractometer   17375 measured reflections
Absorption correction: multi-scan   1778 independent reflections
(SADABS; Bruker, 2009)   1606 reflections with $I > 2\sigma(I)$
$T_{min} = 0.874$, $T_{max} = 0.979$ $R_{int} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$ 4 restraints
$wR(F^2) = 0.091$ H-atom parameters constrained
$S = 1.05$ $\Delta\rho_{max} = 0.21$ e Å⁻³
1778 reflections $\Delta\rho_{min} = -0.15$ e Å⁻³
152 parameters

Compound (I) at 375 K

Crystal data

$C_{28}H_{18}N_2O_2$ $V = 2028.08$ (17) Å³
$M_r = 414.44$ $Z = 4$
Monoclinic, $C2/c$ Cu $K\alpha$ radiation
$a = 11.3459$ (5) Å $\mu = 0.69$ mm⁻¹
$b = 6.0578$ (3) Å $T = 375$ K
$c = 29.6234$ (15) Å $0.60 \times 0.18 \times 0.05$ mm
$\beta = 95.073$ (3)°

Table 1
Comparison of bond lengths (Å) in BBS at 150 and 375 K.

Bond	150 K	375 K
C1—C1^i	1.331 (2)	1.306 (2)
C1—C2	1.4656 (17)	1.4659 (14)
C2—C3	1.3981 (17)	1.3854 (15)
C2—C7	1.3990 (17)	1.3940 (16)
C3—C4	1.3853 (17)	1.3837 (14)
C4—C5	1.3917 (17)	1.3906 (15)
C5—C6	1.3957 (17)	1.3796 (14)
C5—C8	1.4520 (17)	1.4474 (14)
C6—C7	1.3760 (17)	1.3796 (14)
C8—N1A	1.270 (5)	1.270 (3)
C8—O1A	1.382 (4)	1.382 (3)
C9—N1A	1.405 (4)	1.398 (3)
C10—O1A	1.377 (3)	1.383 (2)
C9—C10	1.3878 (17)	1.3737 (14)
C9—C14	1.3845 (17)	1.3773 (14)
C10—C11	1.3802 (17)	1.3791 (15)
C11—C12	1.3855 (17)	1.3854 (16)
C12—C13	1.3935 (18)	1.3732 (17)
C13—C14	1.3862 (18)	1.3795 (15)

Symmetry code: (i) $\frac{3}{2} - x$, $-y - \frac{1}{2}$, $-z$.

Data collection

Bruker SMART 6000 diffractometer   13180 measured reflections
Absorption correction: multi-scan   12519 independent reflections
(SADABS; Bruker, 2009)   9599 reflections with $I > 2\sigma(I)$
$T_{min} = 0.825$, $T_{max} = 0.966$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$ 4 restraints
$wR(F^2) = 0.176$ H-atom parameters constrained
$S = 1.09$ $\Delta\rho_{max} = 0.19$ e Å⁻³
12519 reflections $\Delta\rho_{min} = -0.16$ e Å⁻³
153 parameters

The initial unit-cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 10.0° scan in 33 frames over three different parts of the reciprocal space. The final unit cell was obtained from the xyz centroids of 7849 selected reflections at 150 K (4605 reflections at 375 K) after integration using the SAINT-Plus software package (Bruker, 2009).

H atoms were positioned geometrically and refined with a riding model, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C). The benzoxazolyl group shows orientational disorder. It was assumed that atoms N1A and O1B, and atoms O1A and N1B share close positions and the same atomic displacement parameters. During refinement, similarity restraints were applied to the C=N and to the C—O distances. Atoms O1A and O1B were constrained to have the same atomic displacement parameters, as were N1A and N1B. With these restraints, the occupancy factors converged to 0.669 (10) and 0.331 (10) for N1A/O1A and N1B/O1B, respectively, for the crystal measured at 150 K [0.712 (7) and 0.288 (7) at 375 K].

For the crystal measured at 375 K, analysis of the refined solution using PLATON/TwinRotMat (Spek, 2009) indicated nonmerohedral twinning about a twofold rotation axis [001]. The TwinRotMat routine was used to prepare a modified hkl file for use with the HKLF5 option in SHELXL97 (Sheldrick, 2008). The resulting twin fractions were 0.1102 (16) and 0.8898 (16).

For both data sets, data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008);

organic compounds

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3316). Services for accessing these data are described at the back of the journal.

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