

1,4-Phenylenebis(methylene) bis(9H-carbazole-9-carbodithioate)

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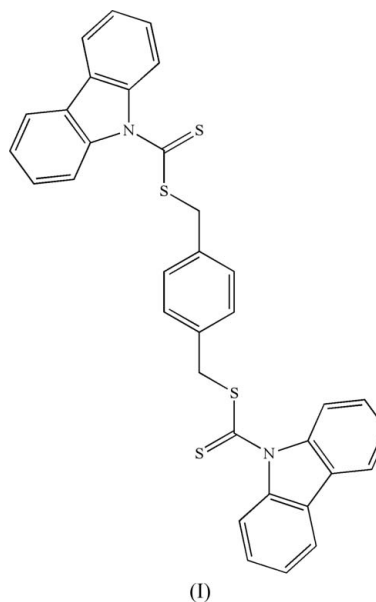
The molecules of the title compound, C₃₄H₂₄N₂S₄, lie across centres of inversion in the space group *P2₁/n*. The spacer unit linking the benzene rings and carbazole units is effectively planar, while the carbazole unit itself is slightly folded. Molecules are linked into sheets by a single C—H···π(arene) hydrogen bond and the hydrogen-bonded sheets are themselves linked into a three-dimensional framework structure by a single π–π stacking interaction.

Comment

Xanthate derivatives are versatile reagents for reversible addition–fragmentation chain transfer (RAFT) polymerization, capable of directing formation of a range of well controlled polymer architectures (Perrier *et al.*, 2004; Wan *et al.*, 2007), and we report here the structure of the title compound, (I) (Fig. 1), which was synthesized for use in such applications.

The molecules of (I) lie across inversion centres in the space group *P2₁/n*, with the reference molecule selected as that lying across $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 1). The carbazole unit deviates slightly from planarity, with dihedral angles between the central five-membered ring on the one hand, and, on the other hand, the outer rings containing atoms C1 and C8, respectively, of 4.9 (2) and 0.5 (2)°, while the dihedral angle between the two six-membered rings in this unit is 4.7 (2)°. This asymmetric folding may be contrasted with that observed in carbazole itself [Cambridge Structural Database (CSD; Allen, 2002) refcode CRBZOL04; Gerkin & Reppart, 1986], where the molecules lie across mirror planes in the space group *Pnma*, adopting a butterfly-type conformation with a dihedral angle of 2.5 (2)° between the two symmetry-related parts of the molecule. On the other hand, asymmetric folding has been reported in both *N*-methylcarbazole (CSD refcode NMCABZ; Popova & Chetkina, 1979) and in *N*-vinylcarbazole [VINCBZ (Tsutsui *et al.*, 1976) and VINCBZ01 (Tian *et al.*, 2006)], in both of which

$Z' = 2$. The spacer unit linking the carbazole and aryl ring systems, *i.e.* between atoms N9 and C21 (Fig. 1), adopts an effectively planar all-*trans* conformation; the maximum deviation from the mean plane through atoms N9/C10/S10/S11/C11/C21 is 0.037 (1) Å for atom S11 and 0.024 (3) Å for atom C11, to opposite sides of the mean plane. The overall molecular conformation can then be specified in terms of just two dihedral angles, those between the plane of the linker unit on the one hand, and the two ring systems on the other; for the aryl ring, this dihedral angle is 65.0 (2)°, while the corresponding value for the central ring of the carbazole unit is 29.0 (2)°.



The pattern of the bond distances in the carbazole unit (Table 1) is reminiscent of that in carbazole itself. Specifically, the bonds labelled here as C1–C2, C3–C4, C5–C6 and C7–C8 are the shortest bonds in the six-membered rings, while the C4A–C4B bond is the longest C–C bond in the carbazole unit; however, the two independent C–N bonds are longer than the corresponding bonds in carbazole. Overall, the distances indicate that there is effectively no peripheral electronic delocalization. The C10–S10 bond is short for its type (Allen *et al.*, 1987), while N9–C10 is long for its type, possibly indicative of rather little delocalization of the lone pair at N9 into the C=S double bond as a consequence of the relative orientation of the carbazole and spacer units.

The centrosymmetric molecules of (I) are linked by a combination of C—H···π(arene) hydrogen bonds and π–π stacking interactions to form a three-dimensional framework structure, whose formation is readily analysed in terms of the substructures (Ferguson *et al.*, 1998*a,b*; Gregson *et al.*, 2000) formed by the two types of interaction.

A single C—H···π(arene) hydrogen bond (Table 2) links the reference molecule directly to four other molecules; thus, the reference molecule centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ acts as a hydrogen-bond donor to the two molecules centred at (0, 0, 0) and (1, 1, 1) and it acts as an acceptor of hydrogen bonds from the two molecules centred at (0, 1, 0) and (1, 0, 1). In this manner,

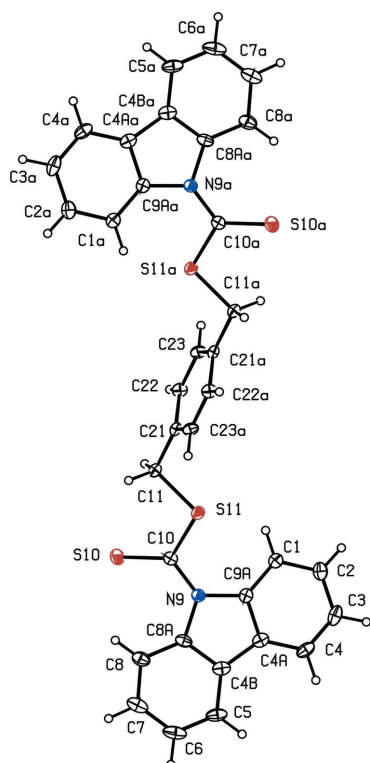


Figure 1
The molecule of (I), showing the atom-labelling scheme. Atoms marked with the suffix 'a' are at the symmetry position $(-x + 1, -y + 1, -z + 1)$. Displacement ellipsoids are drawn at the 30% probability level.

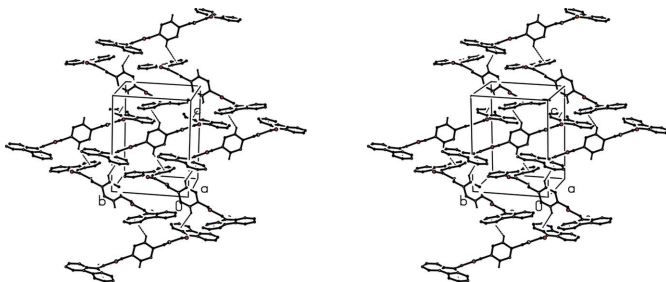


Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a sheet parallel to $(10\bar{1})$ and built using a single $C-H \cdots \pi(\text{arene})$ hydrogen bond. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

the $C-H \cdots \pi(\text{arene})$ hydrogen bond links the molecules into a sheet lying parallel to $(10\bar{1})$ (Fig. 2). The molecules of (I) are also weakly linked into chains by a $\pi-\pi$ stacking interaction between the carbazole units of adjacent molecules. The aryl ring containing atom C4A in the reference molecule centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ makes a dihedral angle of $4.7(2)^\circ$ with the aryl ring containing atom C4B at $(-x, 2 - y, 1 - z)$ and forming part of the molecule centred at $(-\frac{1}{2}, \frac{3}{2}, \frac{1}{2})$: the ring-centroid separation is $3.872(2) \text{ \AA}$, with a ring-centroid offset of *ca* 1.32 \AA . Propagation by inversion of this interaction generates a chain of π -stacked molecules running parallel to the $[1\bar{1}0]$ direction (Fig. 3) and this chain links the hydrogen-bonded sheets into a three-dimensional framework. It is interesting to note that, while the central aryl ring acts as a twofold donor of hydrogen

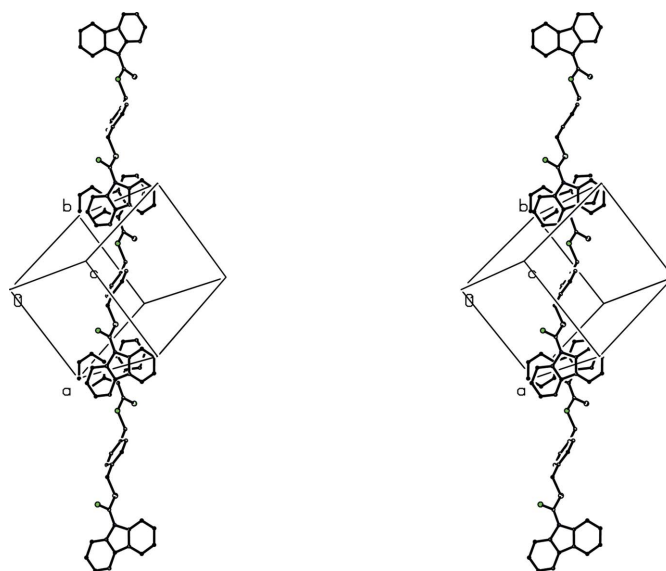


Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a π -stacked chain parallel to $[1\bar{1}0]$. For the sake of clarity, all H atoms have been omitted.

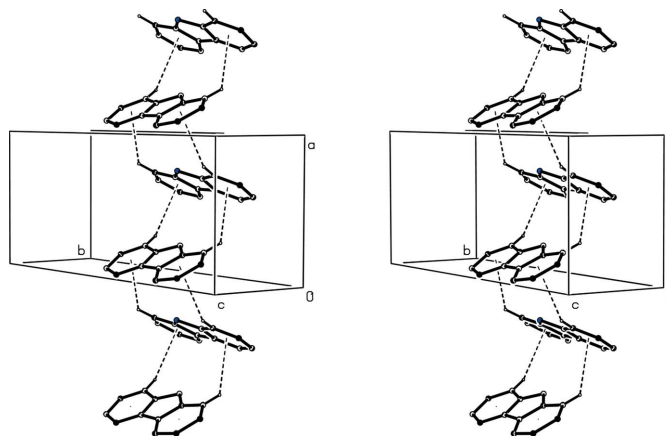


Figure 4
A stereoview of part of the crystal structure of carbazole, showing the formation of a hydrogen-bonded chain of rings along $[100]$. The deposited atomic coordinates (CSD refcode CRBZOL04; Gerkin & Reppart, 1986) have been used and, for the sake of clarity, H atoms not involved in the motif shown have been omitted.

bonds, it neither accepts any hydrogen bonds nor participates in any $\pi-\pi$ stacking interactions. By contrast, the carbazole unit both accepts a hydrogen bond and participates in the $\pi-\pi$ stacking but, despite the large number of $C-H$ bonds present, the carbazole unit does not act as a hydrogen-bond donor.

It is thus of interest briefly to compare the molecular aggregation in compound (I) with that in carbazole, which was not discussed in the original report (Gerkin & Reppart, 1986). While there are neither $N-H \cdots \pi(\text{arene})$ hydrogen bonds nor aromatic $\pi-\pi$ stacking interactions present in the crystal structure of carbazole, symmetry-related pairs of $C-H \cdots \pi(\text{arene})$ hydrogen bonds link molecules related by a 2_1 screw axis along $[100]$ into a chain of rings (Bernstein *et al.*, 1995) running parallel to the $[100]$ direction (Fig. 4), so that the

mode of supramolecular aggregation in carbazole is very different from that found in compound (I).

Experimental

For the synthesis of compound (I), a mixture of KOH (0.02 mol) and 9*H*-carbazole (0.02 mol) in dimethyl sulfoxide (50 ml) was stirred vigorously at room temperature for 2 h; carbon disulfide (0.02 mol) was then added dropwise over a period of 15 min, and the mixture was stirred for a further 3 h. 1,4-Bis(chloromethyl)benzene (0.01 mol) was added to the resulting mixture, forming a yellow solution. This solution was poured into a large excess of water, and the yellow precipitate that formed was collected by filtration. Recrystallization from a dichloromethane–methanol mixture (1:1 *v/v*) gave yellow crystals suitable for single-crystal X-ray diffraction (yield 32%, m.p 472–473 K).

Crystal data

| | |
|--------------------------------|---|
| $C_{34}H_{24}N_2S_4$ | $V = 1354.2 (4) \text{ \AA}^3$ |
| $M_r = 588.83$ | $Z = 2$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation |
| $a = 10.296 (2) \text{ \AA}$ | $\mu = 0.38 \text{ mm}^{-1}$ |
| $b = 10.0793 (19) \text{ \AA}$ | $T = 120 \text{ K}$ |
| $c = 13.137 (2) \text{ \AA}$ | $0.52 \times 0.17 \times 0.10 \text{ mm}$ |
| $\beta = 96.646 (14)^\circ$ | |

Data collection

| | |
|---|--|
| Bruker–Nonius KappaCCD diffractometer | 15566 measured reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 2003) | 2520 independent reflections |
| $T_{\min} = 0.869$, $T_{\max} = 0.963$ | 1880 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.062$ |

Refinement

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.052$ | 181 parameters |
| $wR(F^2) = 0.099$ | H-atom parameters constrained |
| $S = 1.13$ | $\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$ |
| 2520 reflections | $\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$ |

Table 1

Selected geometric parameters (\AA , $^\circ$).

| | | | |
|----------------|-------------|-----------------|--------------|
| C1–C2 | 1.371 (4) | C8A–N9 | 1.419 (3) |
| C2–C3 | 1.386 (4) | N9–C9A | 1.422 (3) |
| C3–C4 | 1.364 (5) | C9A–C1 | 1.384 (4) |
| C4–C4A | 1.377 (4) | C4A–C9A | 1.393 (4) |
| C4A–C4B | 1.437 (4) | C4B–C8A | 1.389 (4) |
| C4B–C5 | 1.392 (4) | N9–C10 | 1.381 (3) |
| C5–C6 | 1.353 (5) | C10–S10 | 1.630 (3) |
| C6–C7 | 1.376 (5) | C10–S11 | 1.741 (3) |
| C7–C8 | 1.378 (4) | S11–C11 | 1.793 (3) |
| C8–C8A | 1.382 (4) | C11–C21 | 1.497 (4) |
| C9A–N9–C10–S11 | –28.2 (3) | C10–S11–C11–C21 | –179.58 (18) |
| N9–C10–S11–C11 | 177.53 (19) | S11–C11–C21–C22 | 117.4 (3) |

All H atoms were located in difference maps, and then treated as riding atoms in geometrically idealized positions, with C–H distances of 0.95 (aromatic) or 0.99 \AA (CH_2) and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

Cg represents the centroid of the C1–C4/C4A/C9A ring.

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|----------------------------------|-------|--------------|--------------|----------------|
| C22–H22 \cdots Cg ⁱ | 0.95 | 2.89 | 3.666 (3) | 140 |

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

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3251). Services for accessing these data are described at the back of the journal.

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