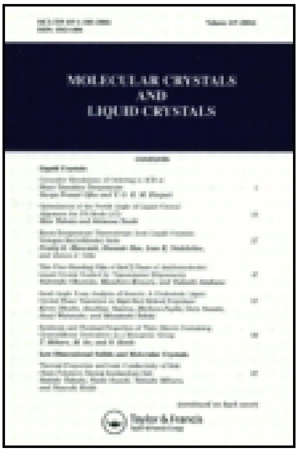

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Structure of 1,4-Bis(3-thianaphthyl)-Buta-1,3-Diyne

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1,4-bis(3-thianaphthyl)-buta-1,3-diyne, $C_{20}S_2H_{10}$, $M_r = 314.43$, m.p = 438 K, monoclinic, $P2_1/c$, $a = 13.276(1)$, $b = 3.958(1)$, $c = 14.120(3)$ Å. $\beta = 92.11(1)°$, $V = 741.45$ Å^3, $Z = 2$, $D_x = 1.408$ gm. cm^{-3}, $\mu = 3.36$ cm^{-1}, $F(000) = 324.0$, $\lambda(\mathrm{MoK}_\alpha) = 0.71073$ Å, $T = 300$ K, final R and wR are 0.0303 and 0.0433 respectively using 1022 observations used in structure factor calculation. The monomer structure (with $D = 3.664$ Å, $S_1 = 3.502$ Å and the angle $\tau_1 = 62.25°$) does not satisfy the requirements for topochemical polymerisation (Wegner, 1977).

Keywords: crystal structure, 1,4-Bis(3-Thianaphthyl-Buta-1,3-Diyne, Solid State reactivity, nematic

INTRODUCTION

In recent years, polydiacetylenes (PDAs) have gained paramount interest due to their large and fast non linear optical response[1] which is manifested in various applications such as ultrafast optical signal processing, optical waveguides, frequency multipliers etc. PDAs are obtained from diacetylenes having general formula $R—C \equiv C—C \equiv C—R'$, through a topochemical solid state polymerisation reaction[2,3] by thermal, mechanical and/or photochemical stimulations. Suitable molecular packing conditions are essential for polymerisation.[4,5] The substituents R and R′ affect molecular packing and hence reactivity in a subtle manner.

Further, some of the conjugated diacetylenes also show thermotropic liquid crystalline behaviour.[6] Consequently, there is additional interest in examining their structure-property relationship. On heating, the title compound goes into nematic phase at 165°C.

As a part of broad study aimed at understanding the structure-reactivity relationship in diacetylenes with formally conjugated substituents, structure determination of various diacetylenic compounds are carried out using single crystal X-ray diffraction technique. In this paper, we report the crystal structure of the title compound which, is found to be unreactive in the solid state.

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EXPERIMENTAL

The title compound 1, 4-bis (3′-thianaphthyl) buta-1, 3-diyne (TNDA), was synthesised by coupling of 3-ethynyl-thianaphthene[8] using the method of Fritzche and Hunig (1972).[9] Colourless needle shaped crystals of TNDA were obtained upon controlled crystallization from its solution in benzene.

A crystal of dimensions 0.125 × 0.075 × 0.40 mm was used for X-ray intensity data collection. Diffraction measurements were made on Enraf-Nonius CAD4 fully automated diffractometer with the use of graphite-monochromated MoK_α radiation. Preliminary investigations of the unit cell obtained by least squares fit to 25 randomly selected reflections revealed monoclinic symmetry. Two standard reflections, measured every one hour showed no significant intensity variation. A total of 1248 unique reflections were measured, in the range $2 \leq \theta \leq 25°$; $0 \leq h \leq 15, 0 \leq k \leq 4, -16 \leq l \leq 16$. The structure was solved with SHELXS 86,[10] taking 1022 reflections in least squares with $F_0 \geq 6\sigma(F_0)$. All the non-hydrogen atoms were located in the initial electron density map. All intramolecular bond distances and bond angles were within the expected range. The anisotropic full-matrix refinement of the non-hydrogen atoms and isotropic refinement of the hydrogen atoms fixed in calculated positions (C—H 0.95 Å) using the Enraf Nonius structure determination package[11] resulted in the convergence of the crystallographic reliability factors to R = 0.0303, $wR = 0.0433$ (where $w = k/[\sigma(F)^2 + P*F^2]$ with $k = 1.000$, $P = 0.04$ with 120 parameters. In the final difference map, the maximum and minimum electron densities were 0.201 and $-0.189\,\mathrm{e/Å^{-3}}$ respectively and $(\Delta/\sigma)_{\max} = 0.013$. A micro Vax 3100 was used for all the computations.

DISCUSSION

The positional parameters and equivalent temperature factors for non-hydrogen atoms of the asymmetric unit (half of the molecule) are tabulated in Table 1, bond lengths in Table 2 and bond angles in Table 3. Figure 1 is the ORTEP[12] plot of the molecule and Figure 2 gives the molecular packing viewed down *b* axis. The molecules are stacked almost perpendicular to crystallographic *b* axis (Fig. 2). The two halves of the molecule are related by inversion symmetry with sulphur positioned in the five membered ring. The dihedral angle between the planes [C(3), C(4), S(1), C(6), —C(5)] and [C(5), C(6), C(7), C(8), C(9), C(10)] is 0.98(±2.35)° indicating that the two rings are coplanar. The bond lengths C(3)—C(2) = 1.421(2), C(2)—C(1) = 1.199(2), C(1)—C(1′) = 1.373(2), and C(3)—C(1′) = 3.993(2) Å indicate that C(3)—C(2)—C(1)—C(1′) are collinear. The molecules are stacked in layers down all the three axes.

Monomer packing requirements for solid state polymerisation have been specified [given in square brackets] for monomers with stacked structures (Fig. 3). In TNDA, these conditions are only partly satisfied. Thus

(i) *D*, distance between reacting centres C(1)—C(1′) in adjacent molecules is 3.664 Å [4.0 Å].

(ii) d_1, the separation between successive diacetylene molecules along the reaction axis i.e. *b* axis is 3.958 Å [$4.8 < d_1 < 5.6$ Å]

TABLE I

Positional parameters and their estimated standard deviations for the non-hydrogen atoms

Atom	x	y	z	$B(\text{Å}^2)$
S1	0.71593(4)	−0.0161(1)	0.17469(3)	4.05(1)
C1	0.5294(1)	−0.4342(5)	0.4655(1)	3.15(4)
C2	0.5800(1)	−0.3207(5)	0.4045(1)	3.16(4)
C3	0.6436(1)	−0.1874(5)	0.3349(1)	2.82(3)
C4	0.6232(1)	−0.1952(5)	0.2398(1)	3.60(4)
C5	0.7392(1)	−0.0269(4)	0.3585(1)	2.77(3)
C6	0.7875(1)	0.0776(5)	0.2765(1)	3.02(3)
C7	0.8814(1)	0.2340(5)	0.2833(2)	4.10(4)
C8	0.9260(1)	0.2790(6)	0.3703(2)	4.69(5)
C9	0.8787(2)	0.1788(6)	0.4522(2)	4.60(5)
C10	0.7857(2)	0.0278(5)	0.4465(1)	3.62(4)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3^* [a^{2*}B(1,1)+b^{2*}B(2,2)+c^{2*}B(3,3)+ ab(\cos\Psi)^*B(1,2)+ac(\cos\beta)^*B(1,3)+bc(\cos\alpha)^*B(2,3)]$

TABLE II

Bond distance (Å) with e. s. d's in parentheses

S(1)—C(4)	1.717(2)	C(5)—C(6)	1.406(3)
S(1)—C(6)	1.735(2)	C(5)—C(10)	1.385(3)
C(1)—C(2)	1.198(2)	C(6)—C(7)	1.391(3)
C(2)—C(3)	1.421(2)	C(7)—C(8)	1.356(3)
C(3)—C(4)	1.361(2)	C(8)—C(9)	1.394(3)
C(3)—C(5)	1.446(2)	C(9)—C(10)	1.371(3)

TABLE III

Bond Angles (°) with e. s. d's in parentheses

C(4)—S(1)—C(6)	91.52(9)	C(6)—C(5)—C(10)	119.4(2)
C(1)—C(2)—C(3)	177.60(2)	S(1)—C(6)—C(5)	111.5(1)
C(2)—C(3)—C(4)	124.90(2)	S(1)—C(6)—C(7)	127.9(2)
C(2)—C(3)—C(5)	122.8(1)	C(5)—C(6)—C(7)	120.6(2)
C(4)—C(3)—C(5)	112.3(2)	C(6)—C(7)—C(8)	118.7(2)
S(1)—C(4)—C(3)	113.4(1)	C(7)—C(8)—C(9)	121.3(2)
C(3)—C(5)—C(6)	111.2(1)	C(8)—C(9)—C(10)	120.5(2)
C(3)—C(5)—C(10)	129.4(2)	C(5)—C(10)—C(9)	119.5(2)

(iii) $\tau_1 = 62.25° \, [\tau_1 \approx 45°]$ and
(iv) $S_1 = 3.502 \, [3.4 < S_1 < 4.0]$

TNDA is unreactive in solid state due to a close packed structure and large τ, restricting the movement of reacting centres required for polymerisation reaction.

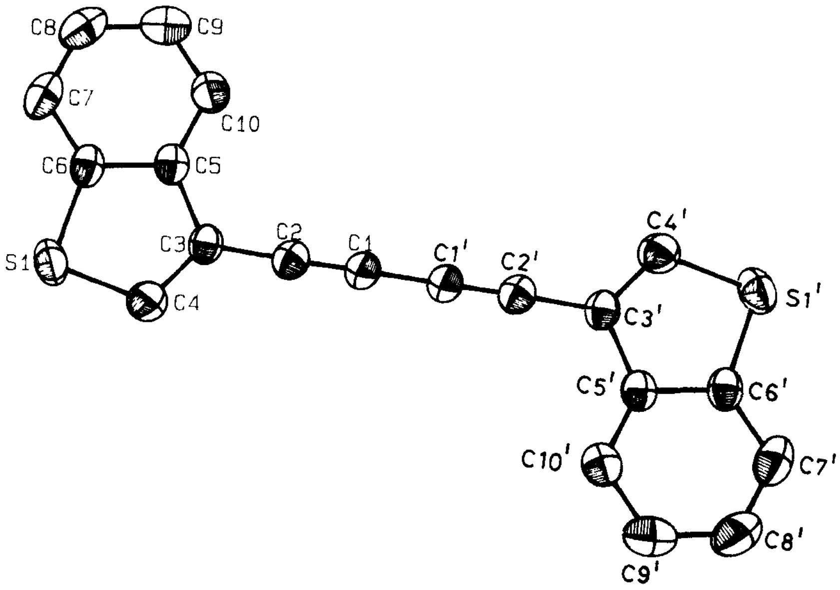

FIGURE 1 ORTEP plot of the molecule with thermal ellipsoids at 50% probability.

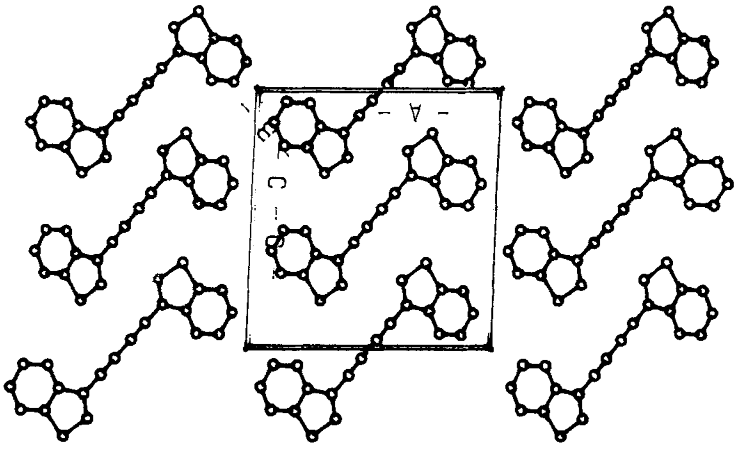

FIGURE 2 Packing of the molecules. Projection of the unit cell down *b* axis.

Several diacetylenes with large τ, are known to be unreactive or poorly reactive in solid state.[4,5,7]

Single crystal X-ray structure determination of 1,4-bis(2-thianyl)buta-1,3-diyne (2DT) has also been carried out by us[13] (Das, Sinha, Sarkar and Talwar, to be published). Comparison of the structure of TNDA with that of diacetylene with thiophene substituents (2DT) (Fig. 4) points to significant influence of the fused benzene ring on packing of TNDA. Studies of structure of 2DT, [space group $P2_1/n$,

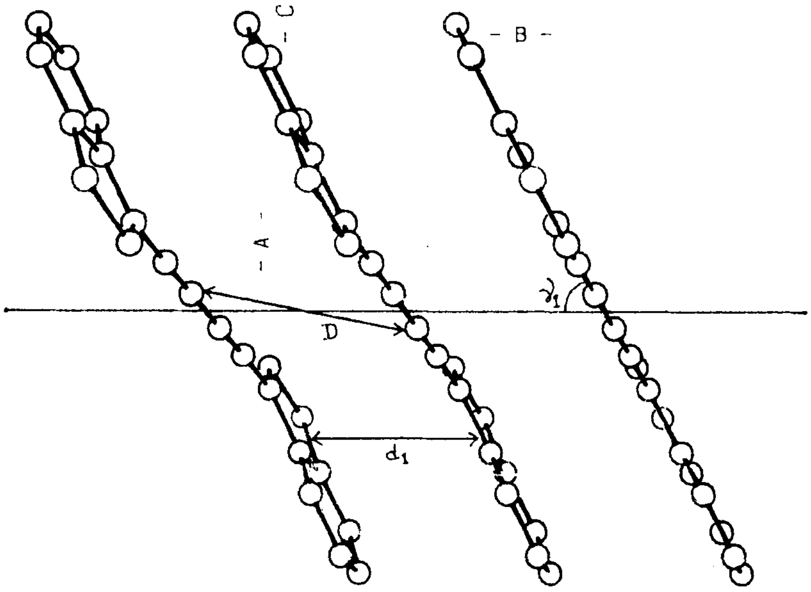

FIGURE 3 Stacking of molecules along *b* axis.

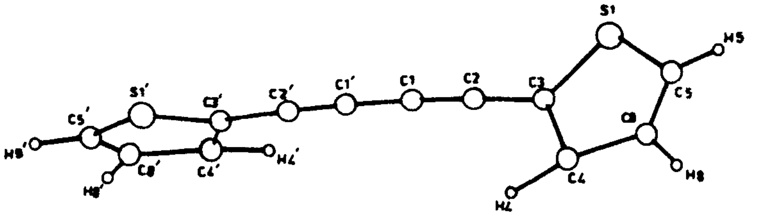

FIGURE 4 General view of 2DT molecule.

$Z = 2$] show that the thiophene units on both sides of the diacetylene unit have different orientations with unequal occupation probabilities for sulphur in the thiophene rings on either side of the diacetylene backbone in addition to different occupation probabilities of sulphur within the rings. As such, disorder is observed in the structure of 2DT. The thiophene rings of a 2DT molecule make a dihedral angle of $\approx 65^\circ$. The fused benzene ring in thionaphthene enhances order as well as coplanarity of TNDA. This is due to enhanced π-interaction of the adjacent molecules within a stack and a close packed structure.

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