N(2)—H(N2)	0.897 (44)	C(3)—C(4)	1.504 (4)
C(4)—C(5)	1.510 (3)	C(6)—C(7)	1.506 (3)
C(7)—C(8)	1.383 (4)	C(7)—C(12)	1.380 (4)
C(8)—C(9)	1.393 (3)	C(9)—C(10)	1.372 (4)
C(10)—C(11)	1.371 (4)	C(11)—C(12)	1.395 (3)
N(2)—N(1)—C(5)	103.2 (2)	N(2)—N(1)—C(6)	111.4 (2)
C(5)—N(1)—C(6)	116.0 (2)	N(2)—N(1)—H(N1)	105.7 (16)
C(5)—N(1)—H(N1)	109.6 (24)	C(6)—N(1)—H(N1)	110.3 (20)
N(1)—N(2)—C(3)	111.4 (2)	N(1)—N(2)—H(N2)	117.3 (18)
C(3)—N(2)—H(N2)	122.3 (21)	O—C(3)—N(2)	123.3 (3)
O—C(3)—C(4)	128.5 (3)	N(2)—C(3)—C(4)	108.2 (2)
C(3)—C(4)—C(5)	104.2 (2)	N(1)—C(5)—C(4)	103.8 (2)
N(1)—C(6)—C(7)	112.2 (2)	C(6)—C(7)—C(8)	120.9 (2)
C(6)—C(7)—C(12)	119.8 (2)	C(8)—C(7)—C(12)	119.3 (2)
C(7)—C(8)—C(9)	119.7 (3)	C(8)—C(9)—C(10)	120.8 (3)
C(9)—C(10)—C(11)	119.7 (2)	C(10)—C(11)—C(12)	119.9 (3)
C(7)—C(12)—C(11)	120.6 (2)		

The data were collected with a variable scan speed of 5.45–29.30° min⁻¹ in ω and a scan range of 0.60° + Kα separation. Background measurements were made with a stationary crystal and a stationary counter at the beginning and end of each scan, each for 25.0% of the total scan time. The structure was solved by direct methods and refined by full-matrix least squares using *SHELXTL-Plus* (Sheldrick, 1987). The H atoms bonded to C atoms were positioned theoretically with a geometrically fixed C—H distance of 0.96 Å, those bonded to N atoms were located from a difference Fourier map. The coordinates of the H atoms at N(1) and N(2) were refined. All H atoms were given a fixed isotropic displacement parameter of 0.08 Å² during refinement.

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1-(3-Quinolyl)-4-(2-thienyl)-1,3-butadiyne, $C_{17}H_9NS$

M. J. Barrow, G. H. W. Milburn and Z. Zeng

Department of Applied Chemical and Physical Sciences, Napier University, Edinburgh EH10 5DT, Scotland

A. Sarkar and S. S. Talwar

*Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400076, India*

Abstract

The S atom in the thiophene ring is disordered between positions 1 and 3. The molecular packing would not afford any facile mechanism for crystal-phase polymerization. The thiophene ring is rotated by 55° with respect to the plane of the quinoline system.

Comment

Diacetylenes (R—C≡C—C≡C—R') may undergo solid-state *trans*-1,4 polymerization upon thermal, photochemical or mechanical stimulation.
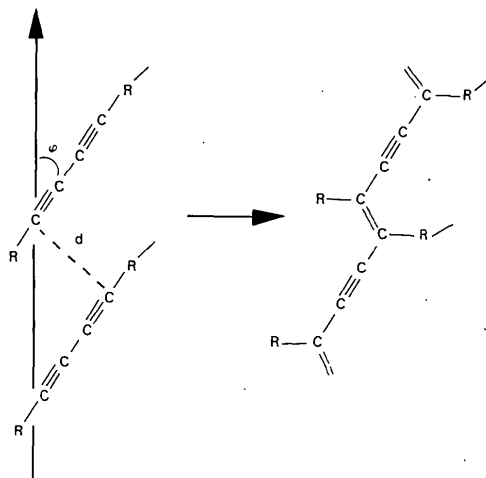
The reactivity of a diacetylene in the crystalline state is governed by the molecular packing of the monomer. Only those diacetylenes which have suitable packing conditions (stacking angle φ and contact distance d) will undergo facile polymerization (Baughman, 1974; Wegner, 1977; Bloor, 1982). The side groups, R and R', in diacetylenes influence the crystal packing through steric and electronic effects and hence determine the reactivity. Our present

studies are aimed at investigating the structure–reactivity relationships in diacetylenes with heteroaryl side groups, where these side groups are formally conjugated to the diyne system (Talwar, Kamath, Das & Sinha, 1990; Talwar, Kamath & Babu, 1989). Here we report the crystal structure of the title compound (2TQ), an unreactive unsymmetrical diacetylene with 2-thienyl and 3-quinolyl substituents.

Fig. 1 shows a view of the molecule with the atomic labelling scheme and Fig. 2 shows the unique molecule in projection down the b axis.
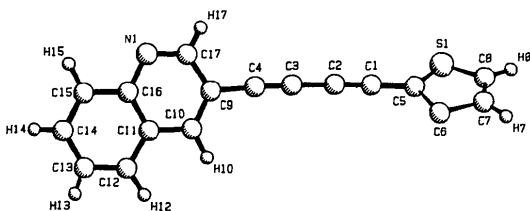

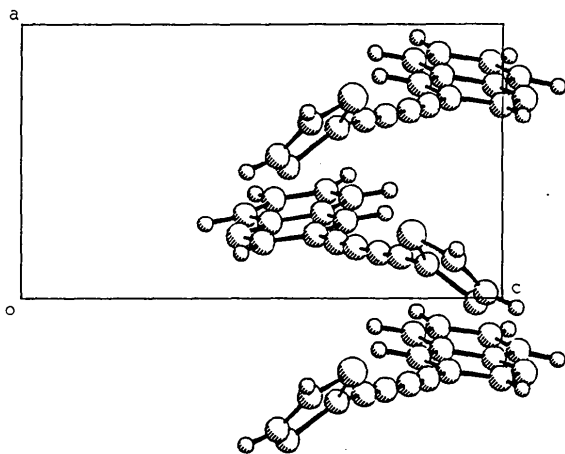Fig. 1. View of the title molecule showing the atomic labelling scheme.

Fig. 2. View of the asymmetric unit in projection down the b axis showing the neighbouring molecules above (at $\frac{1}{2}+x$, y, $\frac{3}{2}-z$) and below (at $-\frac{1}{2}+x$, y, $\frac{3}{2}-z$).

Trial refinements suggested an almost equal distribution of S atoms between the positions of S1 and C6. The shortest distance between the S1 and C6 atoms in neighbouring molecules is 3.86 Å; this occurs between C6 (at x, y, z) and S1 (at $-\frac{1}{2}+x$, y, $\frac{3}{2}-z$). These equivalent positions are shown in Fig. 2. The partial H atoms attached to C6 and S1 were not located experimentally but, as Fig. 2 suggests, these H atoms would not interfere in molecular packing and so would not impose a regular alternation of S and C.

The diacetylenic bond lengths and angles are within the range of values observed in diacetylenes with formally conjugating side groups (Naveenchandra & Shrivastava, 1987). In 2TQ the C5—C1

bond distance [1.424 (8) Å] is marginally shorter than the C4—C9 bond distance [1.448 (8) Å] and this suggests that the thiophene ring is more effectively conjugated to the diacetylene chain than the quinoline ring. This would be consistent with the nonplanarity of the heteroaryl substituents since within each molecule the thiophene ring is rotated by 55° with respect to the plane of quinoline system. The pyridine ring and the benzene ring within the quinoline system are themselves mutually inclined but only by 1°.

Despite C_{sp}—C_{sp} contacts as short as 3.49 Å ($C2\cdots C2$ at $-\frac{1}{2}+x$, y, $\frac{3}{2}-z$), 2TQ is unreactive to crystal-phase polymerization. Fig. 2 shows that the molecular packing in 2TQ does not involve the aligned and inclined stacking of diacetylene units that is typical of crystals that do undergo polymerization.

It is pertinent to contrast 2TQ with the crystal structures of the symmetrical diacetylenes 2DP ($R = R' = $ 2-pyridyl) (Swaminathan, Sinha, Kamath, Talwar & Bohra, 1989), 3DQ ($R = R' = $ 3-quinolyl) (Das, Sinha, Talwar, Kamath & Bohra, 1990) and 2DT ($R = R' = $ 2-thienyl) (Sarkar, Talwar, Das & Sinha, 1993). 2DP and 3DQ crystallize in monoclinic space groups with individual molecules packed in parallel inclined stacks, where the heteroaryl groups within a molecule are in the same (parallel) plane. 2DT also crystallizes in a monoclinic space group with the molecules packed in parallel inclined stacks along the a axis; however, within a molecule, planes containing the thiophene rings are inclined at an angle of 65.6°. The thiophene rings in 2DT are disordered in the same way as in 2TQ.

Experimental

Crystal data

$C_{17}H_9NS$	Mo $K\alpha$ radiation
$M_r = 259$	$\lambda = 0.7107$ Å
Orthorhombic	Cell parameters from 14
$Pbca$	reflections
$a = 6.98\,(2)$ Å	$\theta = 4$–$10.5°$
$b = 29.76\,(2)$ Å	$\mu = 0.23$ mm^{-1}
$c = 12.491\,(7)$ Å	$T = 298$ K
$V = 2594.7$ Å^3	Needles
$Z = 8$	$0.72 \times 0.56 \times 0.24$ mm
$D_x = 1.32$ Mg m^{-3}	Pale yellow
$D_m = 1.32$ Mg m^{-3}	
D_m measured by flotation in aqueous KI	

Data collection

Stoe Stadi-2 circle diffractometer	982 observed reflections $[F_o > 4\sigma(F_o)]$
ω-step scans	$\theta_{max} = 25°$

Absorption correction: analytical (*SHELX*76; Sheldrick, 1976)

$h = 0 \rightarrow 7$
$k = 0 \rightarrow 35$
$l = 0 \rightarrow 14$

2207 measured reflections
2207 independent reflections

2 standard reflections
frequency: 90 min
intensity variation: ±3%

Refinement

Refinement on F
$R = 0.064$
$wR = 0.065$
982 reflections
134 parameters
All H-atom parameters refined

$(\Delta/\sigma)_{max} = 0.06$
$\Delta\rho_{max} = 0.3$ e Å⁻³
$\Delta\rho_{min} = -0.3$ e Å⁻³
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for S1, C5, C6, C7 and C8.

	x	y	z	U_{iso}/U_{eq}
S1	0.2333 (5)	0.28996 (8)	0.81118 (26)	0.0804 (20)
C5	0.1250 (9)	0.24497 (18)	0.8429 (4)	0.043 (3)
C6	−0.0172 (4)	0.24865 (9)	0.94599 (20)	0.0729 (17)
C7	0.0209 (13)	0.30025 (25)	0.9668 (7)	0.070 (6)
C8	0.1432 (13)	0.32046 (24)	0.8991 (7)	0.066 (5)
N1	0.2294 (8)	0.00089 (15)	0.4535 (3)	0.0485 (13)
C1	0.1521 (9)	0.20376 (19)	0.7870 (5)	0.0509 (17)
C2	0.1684 (9)	0.16861 (17)	0.7432 (5)	0.0475 (16)
C3	0.1882 (9)	0.12748 (18)	0.6951 (5)	0.0479 (15)
C4	0.2077 (10)	0.09129 (19)	0.6556 (5)	0.0509 (17)
C9	0.2344 (9)	0.04662 (17)	0.6122 (4)	0.0420 (15)
C10	0.2850 (10)	0.01151 (18)	0.6744 (5)	0.0481 (15)
C11	0.3126 (8)	−0.03099 (17)	0.6268 (4)	0.0432 (15)
C12	0.3703 (10)	−0.06920 (22)	0.6861 (6)	0.0621 (18)
C13	0.3931 (12)	−0.10959 (25)	0.6344 (7)	0.0700 (22)
C14	0.3632 (11)	−0.11338 (24)	0.5252 (6)	0.0666 (21)
C15	0.3064 (10)	−0.07711 (20)	0.4658 (5)	0.0554 (18)
C16	0.2796 (9)	−0.03451 (17)	0.5165 (4)	0.0416 (15)
C17	0.2077 (10)	0.03989 (19)	0.5018 (5)	0.0483 (17)
H7	−0.036 (11)	0.3112 (21)	1.031 (6)	0.088 (25)
H8	0.181 (11)	0.3527 (26)	0.905 (6)	0.13 (3)
H10	0.313 (9)	0.0133 (16)	0.757 (5)	0.067 (17)
H12	0.397 (8)	−0.0641 (16)	0.766 (5)	0.066 (18)
H13	0.452 (14)	−0.1288 (27)	0.680 (7)	0.15 (3)
H14	0.384 (14)	−0.1402 (29)	0.488 (8)	0.17 (4)
H15	0.274 (9)	−0.0790 (18)	0.384 (5)	0.080 (19)
H17	0.168 (8)	0.0651 (17)	0.458 (4)	0.062 (17)

Table 2. *Selected geometric parameters (Å, °)*

S1—C5	1.588 (6)	S1—C8	1.558 (9)
N1—C16	1.360 (7)	N1—C17	1.317 (7)
C1—C2	1.186 (8)	C1—C5	1.424 (8)
C2—C3	1.371 (8)	C3—C4	1.192 (8)
C4—C9	1.448 (8)	C5—C6	1.630 (6)
C6—C7	1.580 (8)	C7—C8	1.344 (12)
C7—H7	0.95 (7)	C8—H8	1.00 (8)
C9—C10	1.349 (8)	C9—C17	1.405 (8)
C10—C11	1.411 (8)	C10—H10	1.05 (6)
C11—C12	1.416 (9)	C11—C16	1.401 (8)
C12—C13	1.374 (10)	C12—H12	1.02 (6)
C13—C14	1.384 (11)	C13—H13	0.90 (9)
C14—C15	1.369 (10)	C14—H14	0.94 (9)
C15—C16	1.429 (8)	C15—H15	1.05 (6)
C17—H17	0.95 (5)		
C5—S1—C8	97.1 (4)	S1—C5—C1	122.7 (5)
S1—C5—C6	115.5 (4)	S1—C8—C7	116.1 (6)
S1—C8—H8	120 (5)	C16—N1—C17	116.6 (5)
N1—C16—C11	123.6 (5)	N1—C16—C15	117.7 (5)
N1—C17—C9	124.0 (5)	N1—C17—H17	117 (3)
C2—C1—C5	177.0 (6)	C1—C2—C3	178.6 (7)
C1—C5—C6	121.8 (4)	C2—C3—C4	178.3 (7)
C3—C4—C9	177.5 (6)	C4—C9—C10	121.9 (5)

C4—C9—C17	118.8 (5)	C5—C6—C7	95.3 (4)
C6—C7—C8	116.0 (7)	C6—C7—H7	114 (4)
C8—C7—H7	130 (4)	C7—C8—H8	124 (5)
C10—C9—C17	119.3 (5)	C9—C10—C11	119.1 (5)
C9—C10—H10	125 (3)	C9—C17—H17	119 (3)
C11—C10—H10	116 (3)	C10—C11—C12	122.6 (5)
C10—C11—C16	117.3 (5)	C12—C11—C16	120.1 (5)
C11—C12—C13	119.3 (7)	C11—C12—H12	116 (3)
C11—C16—C15	118.7 (5)	C13—C12—H12	125 (3)
C12—C13—C14	121.1 (7)	C12—C13—H13	108 (5)
C14—C13—H13	129 (5)	C13—C14—C15	120.9 (7)
C13—C14—H14	123 (6)	C15—C14—H14	116 (6)
C14—C15—C16	119.9 (6)	C14—C15—H15	123 (3)
C16—C15—H15	117 (3)		

The space group and approximate cell parameters were obtained from oscillation and Weissenberg photographs (Cu $K\alpha$ radiation). Intensity data (Mo $K\alpha$) were corrected for Lorentz, polarization and absorption effects using *SHELX*76 (Sheldrick, 1976). All non-H atoms were located by direct methods using *SHELXS*86 (Sheldrick, 1985). The S atom was disordered between positions 1 and 3 in the thiophene ring. All H atoms, apart from that attached to C6 (or S1) were located from difference Fourier syntheses. The structural parameters were refined by full-matrix least squares using *SHELX*76, with anisotropic displacement parameters for S1, C5, C6, C7 and C8, and isotropic displacement parameters for all other atoms. The disordering of the thiophene ring was investigated by various trial refinements. A total of 22 electrons, 16 from S and six from C, have to be distributed between the positions as S1 and C6. A satisfactory model was obtained using the S atomic scattering factor for both S1 and C6. The site occupation factors were eventually fixed such that there were 10.5 electrons at the position S1 and 11.5 electrons at the position C6. The final least-squares weighting scheme was $w = 1/[1 + 0.0144(25 - F_o)^2]$ for $F_o < 25$, and $w = 1/[1 + 0.00213(F_o - 25)^2]$ for $F_o > 25$

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