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Structure of 1,4-Bis(2-pyridyl)-1,3-butadiyne

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Abstract. $C_{14}H_8N_2$, $M_r = 204$, m.p. 393 K, monoclinic, $P2_1/n$, $a = 6.2411(7)$, $b = 3.973(1)$, $c = 21.467(3)$ Å, $\beta = 92.77(1)^\circ$, $V = 531.64$ Å³, $Z = 2$, $D_x = 1.274$, D_m (by flotation in aqueous KI) = 1.282 g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.835$ cm⁻¹, $F(000) = 212$, $T = 295$ K, $R = 0.0411$ for 687 observed reflections. The crystals undergo thermal polymerization to form a coloured amorphous polymer, most likely a poly-diacetylene, although the reacting atoms are separated by 4.237(3) Å. The bond lengths C(6)–C(7) = 1.192(3) and C(5)–C(6) = 1.442(3) Å. The pyridyl rings are planar and parallel to each other.

Introduction. Diacetylenes ($R-C\equiv C-C\equiv C-R$, where R is a substituent group) undergo polymerization in the solid state upon thermal stimulation or exposure to high-energy radiation. Not all diacetylenes are reactive, only those diacetylenes polymerize which have suitable packing features in the crystals (Baughman, 1974; Wegner, 1977; Bloor, 1982). The substituent group R influences the packing and reactivity in a subtle manner through steric and electronic effects. Our study is directed towards examining the reactivity of diacetylenes in which the substituent R is an aromatic heterocycle in formal conjugation with the diacetylene unit. In this paper we report the crystal structure of the title compound (DP), which is found to be reactive

despite the reacting atoms being separated by more than 4.0 Å.

Experimental. The title compound was prepared by coupling 2-ethynylpyridine using the method of Fritzsche & Hunig (1972). Crystallization from acetone gave colourless needle-shaped crystals. Preliminary X-ray studies indicated that the crystal undergoes some changes on exposure to X-rays. However, crystals which have been annealed for some time remain unchanged on exposure to X-rays. The crystals, on annealing, acquire a light-brown colour due to the formation of a small amount of polymer. Crystals used for X-ray study were annealed for 10 h at 388 K and are estimated to have less than 5% polymer. The presence of a small amount of the polymer did not interfere in the structure determination of the monomer (see below). A crystal of dimensions $0.20 \times 0.25 \times 0.32$ mm was selected for data collection with an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation, ω – 2θ scan. Unit-cell parameters, obtained by oscillation and Weissenberg photographs, were refined by least-squares analysis using 21 reflections, $5 < \theta < 12^\circ$, on the diffractometer. Intensities of two standard reflections recorded every 30 min showed no significant changes. Data were collected in the range $2 < \theta < 25^\circ$ (resolution $d = 0.84$ Å, $h_{\max} = 7$, $k_{\max} = 4$, $l_{\min} = -25$, $l_{\max} = 25$). 1162 reflections gave 1083 unique reflections after averaging

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for non-H atoms with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
N(1)	2875 (3)	-616 (5)	6571 (1)	56 (2)
C(1)	4351 (4)	837 (7)	6955 (1)	61 (3)
C(2)	6452 (4)	1326 (7)	6814 (1)	59 (3)
C(3)	7109 (4)	304 (7)	6248 (1)	59 (3)
C(4)	5640 (4)	-1202 (6)	5838 (1)	50 (2)
C(5)	3554 (3)	-1585 (6)	6015 (1)	43 (2)
C(6)	1985 (3)	-3101 (6)	5587 (1)	49 (2)
C(7)	730 (3)	-4301 (6)	5214 (1)	49 (2)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) with e.s.d.'s in parentheses

C(1)-N(1)	1.338 (3)	C(4)-C(3)	1.377 (3)
C(5)-N(1)	1.342 (3)	C(5)-C(4)	1.382 (3)
C(2)-C(1)	1.374 (4)	C(6)-C(5)	1.442 (3)
C(3)-C(2)	1.363 (4)	C(7)-C(6)	1.192 (3)
C(5)-N(1)-C(1)	115.8 (2)	C(4)-C(5)-N(1)	123.7 (2)
C(2)-C(1)-N(1)	124.1 (2)	C(6)-C(5)-N(1)	116.9 (2)
C(3)-C(2)-C(1)	119.1 (2)	C(6)-C(5)-C(4)	119.4 (2)
C(4)-C(3)-C(2)	118.6 (2)	C(7)-C(6)-C(5)	177.4 (2)
C(5)-C(4)-C(3)	118.7 (2)		

symmetry-equivalent reflections. Lp corrections but no absorption correction. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1986). H atoms were located by difference Fourier maps. Structure refinement by *SHELX76* (Sheldrick, 1976) using least squares based on F values, with anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms. Number of parameters refined: 89, including H atoms. In the final calculation, 392 reflections with $|F_o| < 5\sigma(|F_o|)$ and 4 reflections for which $F_o < F_c$ with $(F_o - F_c)/\sigma(|F_o|) > 4.0$ were omitted. $(\Delta/\sigma)_{max} = 0.003$ and $\Delta\rho$ in the final difference Fourier map -0.1255 to $0.1065 \text{ e \AA}^{-3}$. For 687 reflections $R = 0.0411$, unit weights. C-H distances in the range $0.97(2)$ – $1.02(2) \text{ \AA}$. A CYBER-180 computer was used for all calculations. Atomic scattering factors those of *SHELX76*.

Discussion. Table 1 gives the atomic coordinates and equivalent isotropic temperature factors of the non-H atoms of the asymmetric unit (half of the molecule).* Bond lengths and bond angles are given in Table 2. Fig. 1 gives a *PLUTO* drawing (Motherwell & Clegg, 1978) of the molecule and Fig. 2 is the unit-cell packing diagram, viewed down the b axis. The structure of the

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares-plane details have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51463 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

carbon analogue of DP, *i.e.* diphenyldiacetylene, has been reported (Weibenga, 1940) and some of the corresponding values are given here in square brackets. The two halves of the molecule are related by inversion symmetry. The pyridyl rings are planar, with a maximum deviation of $-0.0049(5) \text{ \AA}$, and parallel to each other. The bond lengths $C(6)-C(7) = 1.192(3)$ [$1.18(3)$], $C(7)-C(7') = 1.379(4)$ [$1.39(3)$] and $C(6)-C(7') = 2.571(4) \text{ \AA}$ indicate that $C(6)-C(7)-C(7')$ is linear. The bond length $C(5)-C(6) = 1.442(3)$ [$1.44(3)$] \AA . The angle $C(5)-C(6)-C(7) = 177.4(2)^\circ$ and the torsion angle $C(7)-C(6)-C(5)-N(1) = 148(5)^\circ$. It is noteworthy that the presence of a small amount of polymer in the crystal chosen for this study does not interfere in the structure determination. Indeed, it was found that even in a 50 h annealed sample the reflections were identical in all respects with those of the monomer. Extraction studies established that 50 h annealed crystals contain about 80% polymer, which is found to be amorphous. In our opinion the lack of change in the X-ray diffraction pattern occurs because of the amorphous nature of the polymer formed in these reactions.

Monomer packing and reactivity have received much attention in diacetylene polymerization (Bloor, 1982). According to Bloor, when separation D (Fig. 3) is less

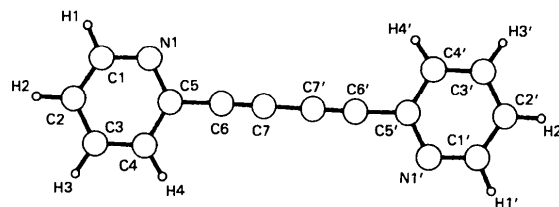


Fig. 1. A general view of the molecule.

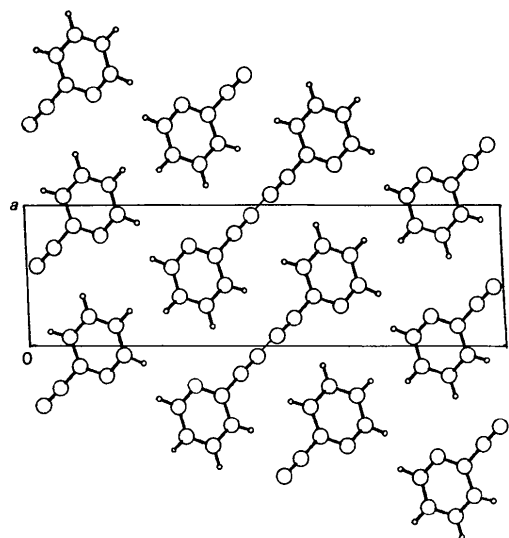


Fig. 2. The unit-cell packing diagram.

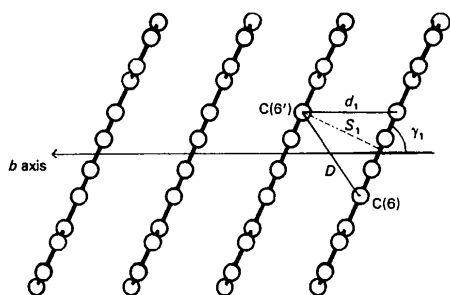


Fig. 3. Monomer packing requirements with limits $3.4 < S_1 < 4.0 \text{ \AA}$ and $\gamma_1 \approx 45^\circ$.

than 4.0 \AA between the reacting atoms [C(6) and C(6')] and there is a unique reacting axis the topochemical polymerization reaction can occur. In DP, $D = 4.237(3) \text{ \AA}$, well outside the limit. However, in terms of Wegner's monomer packing requirements for d_1 , γ_1 and S_1 ($= d_1 \sin \gamma_1$) the values for DP are $3.973(1) \text{ \AA}$ (along the b axis), $66.2(2)^\circ$ and $3.635(3) \text{ \AA}$, respectively. Though D and γ_1 (in Fig. 3) are well outside the limits ($D < 4.0 \text{ \AA}$, $3.4 < S_1 < 4.0 \text{ \AA}$ and $\gamma_1 \approx 45^\circ$), S_1 is within the prescribed limit suggesting low polymerization reactivity for DP. However, we note that DP undergoes thermal and photochemical polymerization to form a coloured amorphous polymer. Although formation of poly-

diacetylenes of poor crystallinity in topochemical reaction is known (Bloor, 1982), especially in the absence of a unique reaction direction (axis), the possibility that the reaction is non-topochemical cannot be eliminated. Details of the polymerization of DP are being studied.

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The Structures of (R,S)-2,2'-(1,2-Ethanediyldiimino)bis-1-butanol Dihydrochloride at 295 and 333 K. A Reversible Phase Transition

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Abstract. (R,S)-N,N'-Bis(1-hydroxymethylpropyl)-ethylenediammonium chloride, $C_{10}H_{26}N_2O_2^+ \cdot 2Cl^-$, (RSET), $M_r = 277.23$, monoclinic, $P2_1/n$, $a = 6.509(1)$, $b = 23.292(4)$, $c = 5.1453(8) \text{ \AA}$, $\beta = 92.41(1)^\circ$, $V = 779.4(4) \text{ \AA}^3$, $Z = 2$, $D_x = 1.181$, $D_m = 1.160 \text{ Mg m}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$, $\mu = 0.399 \text{ mm}^{-1}$, $F(000) = 300$, $R = 0.046$ for 1397 unique observed reflections at $T = 295 \text{ K}$ (RSET-295). $a = 6.671(3)$, $b = 22.75(1)$, $c = 5.179(3) \text{ \AA}$, $\beta = 92.76(3)^\circ$, $V = 785(1) \text{ \AA}^3$, $D_x = 1.173 \text{ Mg m}^{-3}$, R

$= 0.087$ for 715 unique observed reflections at $T = 333 \text{ K}$ (RSET-333). The main effect of the phase transition is a fifteen degree rotation of the ions around the centres of symmetry. The differences in bond lengths and bond angles between (RSET-295) and (RSET-333) are less than 0.06 \AA and 4.6° respectively.

Introduction. (S,S)-2,2'-(1,2-Ethanediyldiimino)bis-1-butanol dihydrochloride, ethambutol dihydrochloride,