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Crystal and Molecular Structure of the *bis*-Ethyl Urethane of 5,7-Dodecadiyn-1,12-diol (ETCD)

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Grown from ethyl acetate solution, the *bis*-ethylurethane of 5,7-dodecadiyn-1,12-diol is a monoclinic crystal, $a = 16.9740(16)$, $b = 4.9770(5)$, $c = 11.0874(11)$ Å; $\beta = 101.869(6)^\circ$; $Z = 2$; $V = 916.63(16)$ Å³. The crystal structure contains two N—H···O hydrogen bonds per molecule and has nearly ideal parameters ($d = 4.977$ Å, $\varphi = 45.8^\circ$, $R = 3.477$ Å) for solid-state polymerization.

Keywords: Diacetylene monomer, crystal structure, thermochromic polydiacetylenes

1. Introduction

The *bis*-ethylurethane of 5,7-dodecadiyn-1,12-diol (**1**) is a diacetylene monomer that is melt-stable and polymerizes, usually with ionizing radiation, to a polydiacetylene (PDA) that exhibits a largely reversible thermochromic phase transition near 125°C (1). This phase transition occurs not only in bulk crystalline specimens, but also in specimens of nanoscale dimension (2). The thermochromism is manifested in a shift in the peak of the specular reflectance from 635 nm at 25°C to 540 nm (a shift of 0.35 eV) above the transition. The structural changes that accompany this transition have been of interest since the initial reports of thermochromism (3, 4). In principle, this information is available from crystal structures, since complete structures are available for several PDAs (5). However, attempts to obtain the structures of PDA-1 and related PDA have led to observations of significant disorder in these crystals. It is our current hypothesis that there is a mismatch between the PDA chain growing in the monomer structure of **1** and related monomers. It is believed that this mismatch leads to mechanical strains in the PDA that are partially relieved as the material is heated to the phase transition (6). From the temperature dependent shielding of the acetylenic carbon resonances, variable temperature solid-state nuclear magnetic resonance studies of PDA-1 and related PDA (7) provide evidence for partial relief of mechanical strains. If

the degree of mechanical strain in PDA-1 is changing as a function of temperature, then the solid-state threshold ionization energy should also change. Ultraviolet photoelectron spectroscopy studies (8) revealed that the magnitude of the change in solid-state ionization energy was very close to that of the reported (4) spectral shift indicating that the structural changes are found in the valence band.

While this information indicates the involvement of mechanical strains in the thermochromic phenomena, it does not detail the changes in bond lengths and bond angles that occur. Again, this information is available, in principle, from crystal structure determinations. Nevertheless, attempts to obtain X-ray data have not proceeded beyond the determination of lattice constants for PDA-1 and several related PDA (4, 9–12). Further photographic studies of the PDA of the *bis*-*n*-propylurethane of 5,7-dodecadiyn-1,12-diol revealed significant disorder (13).

Another approach to a crystallographic study of a thermochromic PDA is to obtain the structure of monomer **1** and to study its conversion to PDA at intermediate stages by X-ray diffraction techniques. This paper reports the structure of **1** and the beginning of that study. An earlier structural study (14) reported the complete step-by-step conversion of a diacetylene monomer to a PDA.

2. Experimental

2.1. Synthesis

Monomer **1** was synthesized by Hay coupling of the ethylurethane of 5-hexyn-1-ol (15). Single crystals of **1** were grown from ethyl acetate solution.

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Table 1. Crystallographic data for **1**

Compound	<i>Bis-ethylurethane of 5,7-dodecadiyn-1,12-diol</i>
Chemical Formula	C ₁₈ H ₂₈ O ₄ N ₂
<i>a</i> , Å	16.9740(16)
<i>b</i> , Å	4.9770(5)
<i>c</i> , Å	11.0874(11)
β , °	101.869(6)
<i>V</i> , Å ³	916.63(16)
<i>Z</i> , <i>Z</i> =	2, 0.5
Formula Wt. g/mol	336.43
Space Group	<i>P</i> 2 ₁ / <i>c</i>
<i>T</i> , K	120(1)
Δ , Å	0.71073
ρ_{calc} , g cm ⁻³	1.219
<i>M</i> , mm ⁻¹	0.086
θ_{max} ; transmission factors	25.27°; 0.983–0.990
<i>R</i> ^a (<i>I</i> > 2 σ (<i>I</i>), 1140 data)	0.0458
<i>R</i> _w ^b (all 1616 data)	0.1243
<i>S</i> ^c	1.025
No. parameters	165

$$^a R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b R_w = \frac{[\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(F_o^2)^2]^{1/2}}$$

$$^c S = [\sum w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$$

2.2. X-ray structure determination

A single crystal of **1** was selected and mounted on a MiTe-Gen loop using Paratone oil. The crystal was placed on a Bruker-Nonius Kappa Apex2 diffractometer, equipped with graphite-monochromated MoK α radiation, and optically centered. All diffractometer manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software (16). Preliminary cell constants were obtained from three sets of 12 frames. Data collection was carried out at 120 K, using a frame time of 30 sec and a detector distance of 60 mm. The optimized strategy used for data collection consisted of three phi and one omega scan sets, with 0.5° steps in phi or omega; completeness was 97.8%. A total of 2237 frames were collected. Final cell constants were obtained from the xyz centroids of 2141 reflections after integration. From the systematic absences, the observed metric constants and intensity statistics, space group *P*2₁/*c* was cho-

Table 2. Relevant Bond Lengths (Å) and Angles (E) for **1**

O(1)–C(3)	1.355(3)	C(4)–C(5)	1.507(3)
O(1)–C(4)	1.448(2)	C(5)–C(6)	1.519(3)
O(2)–C(3)	1.212(3)	C(6)–C(7)	1.529(3)
N(1)–C(2)	1.453(3)	C(7)–C(8)	1.459(3)
N(1)–C(3)	1.335(3)	C(8)–C(9)	1.202(3)
C(1)–C(2)	1.510(3)	C(9)–C(9) ^a	1.376(4)
C(3)–O(1)–C(4)	114.42(16)	O(1)–C(4)–C(5)	108.32(18)
C(2)–N(1)–C(3)	119.85(19)	C(4)–C(5)–C(6)	110.15(19)
N(1)–C(2)–C(1)	111.57(19)	C(5)–C(6)–C(7)	112.46(19)
O(1)–C(3)–O(2)	123.71(19)	C(6)–C(7)–C(8)	111.8(2)
O(1)–C(3)–N(1)	111.45(19)	C(7)–C(8)–C(9)	176.7(2)
O(2)–C(3)–N(1)	124.8(2)	C(8)–C(9)–C(9) ^a	179.8(3)

$$a = (2-x, -y, -z)$$

sen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using SIR-92 (17), and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* program (18); drawings were prepared using CAMERON (19). All nonhydrogen atoms were refined using anisotropic displacement parameters; hydrogen atoms were refined using isotropic displacement parameters. The final least-squares refinement converged to $R_1 = 0.0458$ ($I > 2\sigma(I)$, 1140 data) and $wR_2 = 0.1243$ (F^2 , 1616 data, 165 parameters). Table 1 shows crystallographic data, while Table 2 shows relevant bond lengths and angles.

3. Results and discussion

The molecular structure of **1** is shown in Figure 1; bond lengths and angles (Table 2) lie within normal ranges (5). The asymmetric unit in space group *P*2₁/*c* contains one-half of the molecule shown; the full molecule occupies a crystallographic center of symmetry. Figure 2 shows a partial packing diagram of **1** projected down the crystallographic *c* axis. There are two strong N(1)–H(1)···O(2, 1 + *x*, *y*, *z*) hydrogen bonds nearly parallel to the crystallographic *b* direction. The N···O distance is 2.896 Å, with an N–H···O angle of 173.9°.

The solid-state reactivity of diacetylene monomers is usually discussed in terms of a monomer stacking distance *d*, the angle between the diacetylene rod and the stacking

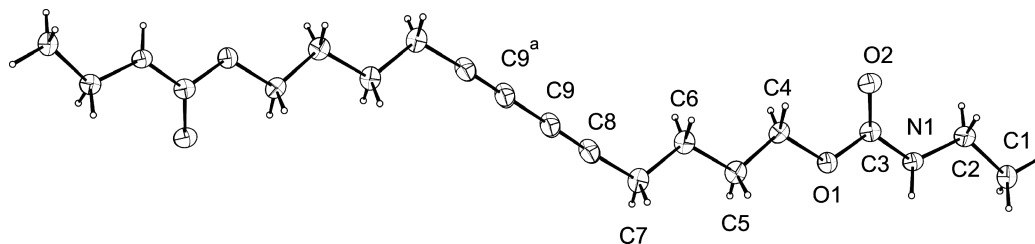


Fig. 1. Molecular structure of **1**, showing labeling of the asymmetric unit and 50% probability ellipsoids for atoms refined using anisotropic displacement parameters.

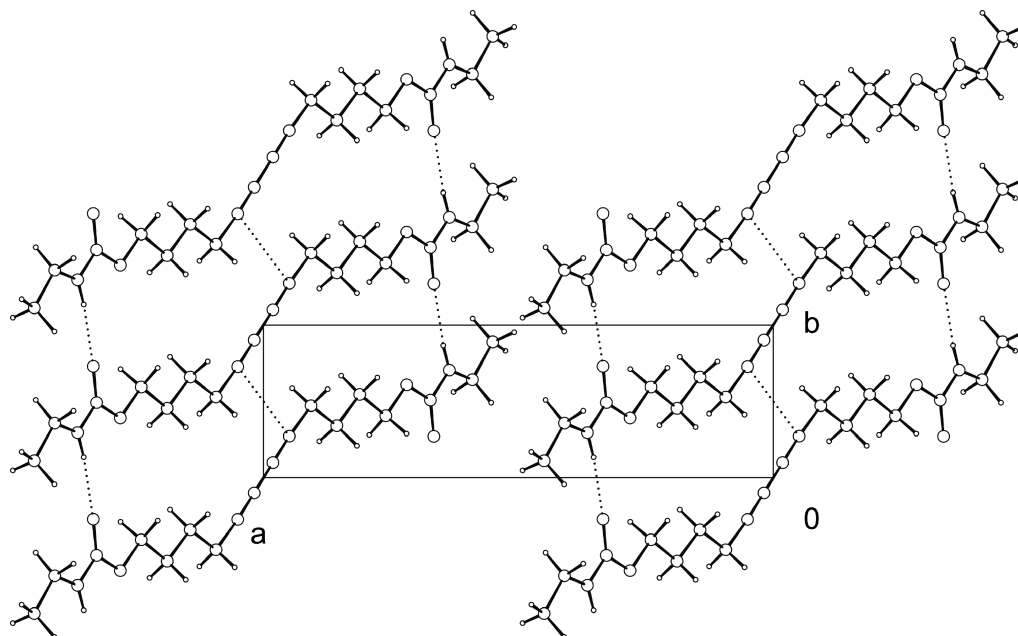


Fig. 2. Partial packing diagram of **1** projected down the crystallographic c axis. Dotted lines along the crystallographic b direction show the two $\text{N-H}\cdots\text{O}$ hydrogen bonds per molecule, while dotted lines at $\approx 45^\circ$ to the b axis show the putative 1,4-addition pathway.

axis, φ , and R , the distance between reacting atoms C_1 and C_4^1 (the corresponding atoms in **1** are $\text{C}(8)$ and $\text{c}(8, 2-x, 1-y, z)$). (5) Optimal values are $d \sim 5 \text{ \AA}$, $\varphi \sim 45^\circ$, and $R < 4 \text{ \AA}$. From the crystal structure of **1**, $d = 4.977 \text{ \AA}$, $\varphi = 45.8^\circ$ and $R = 3.477 \text{ \AA}$. On the basis of these observed values **1** should be an ideal case for solid-state reactivity. Figure 2 also shows the R contact of 3.477 \AA .

Further experiments will focus on irradiation of **1** with ^{60}Co γ -rays to intermediate stages of conversion, with X-ray structure determinations at each stage, leading to a final determination at full conversion, if possible.

4. Conclusions

The bis-ethylurethane of 5,7-dodecadiyn-1,12-diol crystallizes in the monoclinic space group $P2_1/c$, with $a = 16.9740(16)$, $b = 4.9770(5)$, $c = 11.0874(11) \text{ \AA}$; $\beta = 101.869(6)^\circ$; $Z = 2$; $V = 916.63(16) \text{ \AA}^3$. The crystal structure is free of disorder, and contains two $\text{N-H}\cdots\text{O}$ hydrogen bonds per molecule. Inspection of the intermolecular contacts and orientations reveals that the structure has nearly ideal parameters ($d = 4.977 \text{ \AA}$, $\varphi = 45.8^\circ$, $R = 3.477 \text{ \AA}$) for solid-state polymerization.

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