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Polymorphism and DFT calculations of 1,4-bis(triisopropylsilyl)buta-1,3-diyne

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ABSTRACT

Two polymorph forms of 1,4-bis(triisopropylsilyl)buta-1,3-diyne were investigated by X-ray analysis. The polymorph grown from acetone solution crystallized in the monoclinic crystal system with one molecule in a general position of the asymmetric unit. A second polymorph grown from acetonitrile and ethanol solutions crystallized in the triclinic crystal system with a molecule located on an inversion center. The two polymorphs have slightly different molecular geometries and crystal packing motifs. The conformations found in these polymorphs were investigated and compared with five other rotamers as possible candidates for conformational polymorphs using DFT calculations.

1. Introduction

Polymorphism is a very important and well known phenomenon in different areas of chemistry and materials science, with particular relevance to the pharmaceutical industry [1]. According to McCrone [2] any compound can exhibit crystal polymorphism, although some crystal polymorphs may require much more time for their discovery compared to others due to differences in polymorph stability and availability *via* different crystal growth methods. Different types of hydrogen bonds, weak C—H···O, C—H···π and van der Waals interactions are very important forces for crystallization of organic compounds [3]. Crystal polymorphism is frequently observed for compounds that have movable fragments that can be oriented differently in space and is therein referred to as conformational polymorphism [4]. Although well-known the dependence of crystal polymorphism upon intramolecular conformations and intermolecular interactions is still not understood well enough to support structure/polymorph predictions. In this report we examine the comparative stability of molecular conformers of a rigid hydrocarbon wherein intermolecular interactions are at a minimum, allowing for a limited consideration of intramolecular interactions in relation to the discovery of crystal polymorphs.

2. Experimental section

2.1. Synthesis of 1,4-bis(triisopropylsilyl)buta-1,3-diyne

To a solution of TIPS-acetylene (0.870 mL, 3.22 mmol, 1.75 equiv) in dry THF was slowly added a solution of n-BuLi in hexanes (1.55 M, 2.3 mL, 3.6 mmol, 1.95 equiv) at −78 °C. The resulting mixture stirred at that temperature for 30 min, then slowly warmed up to room temperature and transferred to a vial containing $InCl_3$ (0.297 g, 1.32 mmol, 0.957 equiv). This mixture stirred at room temperature for 30 min and was added to a refluxing solution of 1,5-cyclooctadienepalladium (0) dichloride (0.0102 g, 35.7 μmol, 1.94 mol%), 1,1′-bis(diphenylphosphino)ferrocene (0.0224 g, 40.4 μmol, 2.20 mol%) and α,α′-dibromo-*p*-toluene (0.500 g, 1.84 mmol) in dry THF. This mixture stirred overnight under reflux. The product was concentrated *in vacuo*, extracted with diethyl ether, washed with water, purified by chromatography, and recrystallized from acetone to yield 0.268 g, 45.8%, m.p. 110–111 °C.

2.2. Single-crystal X-ray data collection and structure determinations

The crystal structure determination of polymorphs **1** and **2** was carried out using a Bruker SMART APEX2 CCD-based X-ray diffractometer equipped with a low-temperature device and Mo-target X-ray tube (wavelength = 0.71073 Å). The X-ray data were collected at 100(2) K. Data collection, indexing, and initial cell

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refinements were carried out using APEX2 [5], with frame integrations and final cell refinements carried out using SAINT [6]. An absorption correction was applied using the program SADABS [7]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in both compounds were placed in idealized positions and were refined using a riding model. The structures were solved by direct methods and refined using the SHELXTL program package software [8]. Both structures were examined using the Addsym subroutine of PLATON [9] to ensure that no additional symmetry could be applied to the models. Refinement details and structural parameters for polymorph **1** and **2** are summarized in Table 5.

3. Results and discussion

3.1. Synthesis and crystal structures of **1** and **2**

1,4-Bis(triisopropylsilyl)buta-1,3-diyne formed in the course of a reaction that intended to replace the halogen atoms in α,α'-dibromo-*p*-toluene with a functionalized terminal alkyne using a reported method from the literature [10]. The crystals of polymorph **1** were grown from acetone solution at 14 °C (Fig. 1, left). Parameters of the unit cell were collected for several crystals, but only the most suitable crystal was chosen for X-ray analysis. This compound crystallizes in the monoclinic crystal system with one molecule in a general position of the unit cell (Table 1). According to Cambridge Structural Database (CSD, Version 5.33, 2012 Release), the triclinic crystal structure of polymorph **2** was investigated earlier by Constable [11] et al. using single crystals grown from a CH_2Cl_2 solution. We attempted to obtain different polymorphs using various solvents (ethanol, diethyl ether, cyclohexane, ethanol and acetonitrile) and different crystal growth conditions (slow evaporations at room temperature and low temperature). From ethanol and acetonitrile solutions, 1,4-bis(triisopropylsilyl)buta-1,3-diyne crystallized as the triclinic polymorph **2** (Fig. 1, right), with one centrosymmetric molecule in the unit cell (thereby providing Z = 1 for the P-1 space group). As shown in Table 1, the two polymorphs have slightly different geometry along the central Si−C≡C−C≡C−Si backbone. In the structure of polymorph **2** this fragment is almost linear, whereas in the structure of polymorph **1** it is more curved (Fig. 1, Table 2).

Table 1
X-ray crystallographic data and processing parameters for both polymorphs.

Empirical formula	$C_{22}\cdot H_{42}\cdot Si_2$	$C_{22}\cdot H_{42}\cdot Si_2$
CCDC number	1059369	296407
Formula weight	362.74	362.74
Temperature/K	100(2)	100(2)
Radiation, wavelength [Å]	MoKα, 0.71073	MoKα, 0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	P-1
a [Å]	14.066(2)	7.1239(7)
b [Å]	7.6321(12)	7.9193(7)
c [Å]	22.105(3)	10.6987(10)
α [°]	90	89.094(1)
β [°]	96.898(2)	81.808(1)
γ [°]	90	79.467(1)
cell volume [$Å^3$]	2355.9(6)	587.32(10)
ρ calcd [g cm^{-3}]	1.023	1.026
Z	4	1
Dimension [mm^3]	0.44 × 0.37 × 0.06	0.43 × 0.39 × 0.24
μ (MoKα) [mm^{-1}]	0.153	0.153
F(000)	808	202
Crystal color, shape	colorless, plate	colorless, block
Absorption correction	[c]	[c]
Reflections collected	21221	7305
Independent reflections	5210	2632
R_{int}	0.0313	0.0195
Data/restraints/parameters	5210/0/229	2632/0/115
[a]R1 [I ≥ 2σ(I)]	0.0324	0.0288
[b]*w*R2 (all data)	0.0906	0.0800
GOF on F^2	1.003	1.036
Δρ(max), Δρ (min) (e/$Å^3$)	0.373, −0.148	0.47, −0.278

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $R2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{½}$.
[c] semi-empirical from equivalents.

Table 2
Selected bond distances and angles in both polymorphs.

	Monoclinic **1**	Triclinic **2**
Bond distances/Å		
Si1−C1	1.850(1)	1.854(1)
C1−C2	1.207(2)	1.211(1)
C2−C3/C2A	1.381(2)	1.381(2)
C3−C4	1.212(2)	
C4−Si2	1.845(1)	
Bond angles/°		
Si1−C1−C2	176.1(1)	175.7(1)
C1−C2−C3/C2A	179.5(1)	179.7(1)
C2−C3−C4	179.6(1)	
C3−C4−Si2	174.9(1)	

Table 3
Position and interactions of methyl groups.

	I	II	D	C	B	E	A
Me_{sc}	4	4	3	4	5	3	6
Me_{sc}/Me_{sc}	1	1	0	2	2	1	3
Me_{ap}/Me_{ap}	2	2	3	2	1	3	0
(Total)	(6)	(6)	(6)	(7)	(7)	(7)	(9)

Table 4
Structural comparison of the seven rotamers: average $C_{(sp)}$−Si−$C_{(3°)}$ angle (°), average *synclinal* methyl-to-methyl distance (Å), average *periplanar* methyl-to-methyl distance (Å).

	I	II	D	C	B	E	A
$C_{(sp)}$−Si−$C_{(3°)}$ θ	107.28	106.70	104.98	107.51	107.75	105.70	108.41
d Me_{sc}	3.82	3.66	–	3.74	3.56	3.81	3.53
d Me_{ap}	3.80	3.76	3.75	3.87	–	3.71	–

Table 5
Interconversion equilibria of rotamers.

K_{II-I}	1
K_{D-I}	30
K_{C-I}	40
K_{B-I}	50
K_{E-I}	200
K_{B-II}	30
K_{E-II}	100
K_{E-C}	5
K_{B-C}	1
K_{A-B}	30

In the crystals of both polymorphs, we found a number of weak methyl C−H···π (alkyne) interactions dictating a solid-state structure. In the polymorph **1**, there are two intermolecular C−H contacts (C12−H12A···C2 2.85 Å and C21−H21A···C3 2.85 Å) that link molecules in chains along the *a*-axis (Fig. 2, left). Polymorph **2** also has two weak intermolecular contacts (C11−H11A···C2/C2A 2.86 Å) that link molecules in tapes along the *a*-axis (Fig. 2, right). In both polymorphs molecular packings form rows along the *b*-axis (Fig. 3), although they have different mutual arrangement in their crystals. For instance, in case of polymorph **1** such rows form zigzags along the *a*-axis, and in polymorph **2** they do not. According to differential