Journal of Molecular Structure 1152 (2018) 261–265

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Conformational polymorphs of a novel TCNQ derivative carrying an acetylene group

Yuki Iida, Makoto Kataoka, Tsunehisa Okuno*

Department of Material Science and Chemistry, Wakayama University, Wakayama, 640-8510, Japan

A R T I C L E I N F O

Article history:
Received 25 July 2017
Received in revised form
20 September 2017
Accepted 20 September 2017
Available online 21 September 2017

Keywords:
X-ray crystal structure
Polymorph
TCNQ
DFT calculation
Solvation model

A B S T R A C T

TCNQ is one of the most important organic acceptors and lots of its derivatives have been prepared. However the reports on their crystal polymorphs are limited to their complexes, and simple polymorphs of TCNQ derivatives are uncommon. We succeeded in preparation of a novel TCNQ derivative, 2,2'-(2-(prop-2-yn-1-yloxy)cyclohexa-2,5-diene-1,4-diylidene)dimalononitrile, having a propynyloxy group on a substituent. This compound was found to have two crystal polymorphs depending on a solvent for recrystallization. In polymorph I, dimeric hydrogen bonds are formed between acetylenic hydrogens and cyano nitrogens with the molecule in an inversion symmetry. While, in polymorph II, the molecules make intermolecular hydrogen bonds between acetylenic hydrogens and cyano nitrogens with the molecule in 2_1 symmetry, forming a hydrogen bonded molecular helix along the *b* axis. Besides patterns of the intermolecular hydrogen bonds, difference was recognized in conformation of propynyloxy group. The molecule has an *anti* conformation in polymorph I and a *gauche* conformation in polymorph II. DFT calculation indicates that the *anti* conformer is less stable than the *gauche* one. But a solvation model suggests the *anti* conformer is estimated to be more stable in a toluene solution.

1. Introduction

Crystal polymorphism has been paid attention because crystal polymorphs can give us immense knowledge of intermolecular interaction or relationship between structure and properties such as conductivity or non-linear optical property [1]. For example, a charge transfer complex of TMTSF (4,4′,5,5′-tetramethyl-2,2′-bi(1,3-diselenolylidene)) molecules with TCNQ (2,2'-(cyclohexa-2,5-diene-1,4-diylidene)dimalononitrile) affords two kinds of polymorphs [2,3]. One makes a mixed stacking structure, showing semi-conducting property. The other forms a segregated stacking structure, giving metallic behavior.

TCNQ molecule, which was synthesized by Acker and Hertler in 1962 [4], is known to be a good electron acceptor. Since it forms stable mono and di anion salts with lithium, it and its derivatives have attracted interest from a viewpoint of cathodic materials [5]. Many researchers have prepared several TCNQ derivatives and their complexes. However, according to Cambridge Structural Database (CSD) [6], reported all crystal polymorphs of TCNQ or its derivatives are those of their complexes. The polymorphs of simple TCNQ derivatives have not been reported yet. We report herein preparation and crystal structures of a novel TCNQ derivative carrying a propynyloxy group, which gave conformational polymorphs depending on a solvent for recrystallization.

2. Experimental

2.1. General procedure

All chemicals were purchased from Kanto Chemical Co. Ltd. or Tokyo Kasei Kogyo Co. Ltd. and were used without further purification. Preparation of 2-(prop-2-yn-1-yloxy)terephthalic acid was carried out according to the literature [7]. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM–ECA–400 spectrometer in a deuterated solvent (chloroform–*d*1 *or* DMSO-*d*6) with tetramethylsilane as an internal standard. All ^{13}C NMR spectra were obtained with complete proton decoupling. IR spectra were recorded on a JASCO FT/IR–420 spectrometer by using a KBr pellet. Elemental analyses were carried out on a J-SCEINCE LAB MICRO CORDER JM10. Differential scanning calorimetric (DSC) measurements were performed on a SHIMADZU DSC-50 calorimeter.

---

* Corresponding author.
E-mail address: okuno@center.wakayama-u.ac.jp (T. Okuno).

https://doi.org/10.1016/j.molstruc.2017.09.075
0022-2860/© 2017 Elsevier B.V. All rights reserved.

Table 1
Crystal data for polymorphs I and II.

Polymorphs	I	II
Empirical formula	$C_{15}H_6N_4O$	
Formula weight	258.24	
Crystal system	*Monoclinic*	*Monoclinic*
Crystal size (mm)	0.07 × 0.06 × 0.04	0.09 × 0.09 × 0.07
Crystal color	Orange	Red
Space group	$P2_1/c$	$P2_1/n$
a (Å)	6.933(3)	10.546(4)
b (Å)	13.240(6)	7.266(2)
c (Å)	14.096(7)	16.413(6)
β (°)	99.772(8)	104.927(5)
V(Å^3)	1275.1(10)	1215.2(7)
Z	4	4
Dx (Mg/m^3)	1.345	1.411
μ (mm^{-1})	0.09	0.09
Theta range for data collection (°)	2.1–31.1	2.1–31.1
Limiting indices	$-8 \le h \le 8$, $-15 \le k \le 15$, $-15 \le l \le 16$	$-13 \le h \le 13$, $-9 \le k \le 8$, $-21l \le 16$
Reflections collected/unique	8580/2230	9662/2772
Reflections with $I > 2\sigma(I)$	1661	1918
Refined parameters/restrains	185/0	185/0
Goodness of Fit on F^2	1.08	1.07
R_1, wR_2	0.0510, 0.1593	0.0517, 0.1422
Data completeness	0.990	0.997
Data/restrains/parameters	1661/0/185	1918/0/185
Min. and Max. transmission	0.976 and 0.996	0.990 and 0.993
Largest diff. peak and hole (eÅ^{-3})	0.28, −0.23	0.35, −0.22

2.2. *Crystallographical analysis*

Single crystals of the compounds with sufficient quality for X-ray crystallographic analyses were obtained by slow evaporation from a toluene-hexane solution for polymorph I or a dichloromethane-hexane solution for polymorph II. X-ray crystallographic data of the compound were obtained by a RIGAKU Saturn 724 + CCD device using multi-layered mirror monochromatic Mo *Kα* radiation at 93 K. The structures were solved by a direct method (SHELXD2013) and were refined by full-matrix least-squares method (SHELXL2013) [8]. The positions of non−H atoms were obtained from difference Fourier maps and were refined anisotropically. The C_{sp}− H atoms were obtained from difference Fourier maps and were refined isotropically. The remaining C−bound H atoms were obtained by calculation (Csp^2−H = 0.95 Å; methylene Csp^3−H = 0.99 Å) and were refined as riding on their parent C atoms. U_{iso}(H) values of the H atoms were set at $1.2U_{eq}$ (parent C atoms).

2.3. *DFT calculations*

DFT calculations were performed on Gaussian09 software [9] with B3LYP 6-311G(*d,p*) level. The initial structures for calculations were set at both crystal structures. Correction of BSSE for dimers were executed by the counterpoise method [10,11].

2.4. *Materials*

2,2'-(2-(prop-2-yn-1-yloxy)cyclohexa-2,5-diene-1,4-diylidene) dimalononitrile (**1**) [7,11]

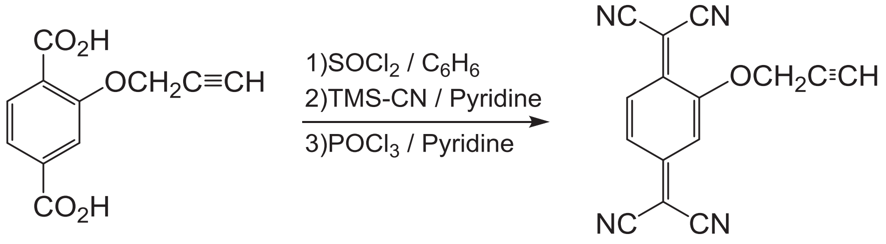
Thionyl chloride (3.6 mL, 51.0 mmol) was added to a solution of 2-(prop-2-yn-1-yloxy)terephthalic acid (1.13 g, 5.1 mmol) in dry benzene (41 mL), and the solution was refluxed for 18 h under argon atmosphere. Excess thionyl chloride and benzene were removed by distillation. Dry pyridine (4.5 mL) and trimethylsilyl cyanide (3.20 mL, 25.5 mmol) was added to the residue, and the solution was stirred for 4 h at 100 °C under argon atmosphere. After removal of pyridine and trimethylsilyl cyanide by distillation, dry pyridine (6.8 mL) and phosphoryl chloride (2.30 mL, 25.5 mmol) was added to the residue and stirred for 30 min at room temperature. The solution was poured into cold water and was extracted by dichloromethane. The organic layer was washed twice with brine and dried over sodium sulfate. After filtration, it was concentrated under reduced pressure. The residual black solid was purified by column chromathography (SiO_2, CH_2Cl_2) to give 0.57 g (43%) of 2,2'-(2-(prop-2-yn-1-yloxy)cyclohexa-2,5-diene-1,4-diylidene)dimalononitrile as red powder.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.77 (t, J = 2.4 Hz, 1H), 4.97 (d, J = 2.4 Hz, 2H), 6.83 (d, J = 1.5 Hz, 1H), 7.38 (dd, J = 1.5, 9.6 Hz, 1H), 7.48 (d, J = 9.6 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 57.30, 73.97, 79.57, 85.97, 87.57, 105.37, 111.78, 111.94, 112.11, 112.17, 128.94, 131.30, 145.55, 152.44, 154.80. IR (KBr/*cm*$^{-1}$): 3280.8 ($\nu_{\text{C-H}}$), 3061.9 ($\nu_{\text{C-H}}$), 2221.6 ($\nu_{C\equiv N}$), 2125.6 ($\nu_{C\equiv C}$). Anal. Calc. for $C_{15}H_6N_1O_1$: C, 69.77; H, 2.34; N, 21.70%. Found: C, 69.97; H, 2.44; N, 21.46%.

3. Results and discussion

The TCNQ derivative (**1**) was prepared from 2-(prop-2-yn-1-yloxy)terephthalic [7] acid (Scheme 1). A terephthalic acid derivative was treated by $SOCl_2$ followed by TMSCN, and the crude product was reacted with $POCl_3$ to give **3** in 43% yield. This TCNQ derivative was found to have polymorphs, I and II. Polymorph I and II was obtained by recrystallization from a toluene-hexane and a dichloromethane-hexane solution, respectively. The crystallographic data are listed in Table 1, and the selected bond lengths and angles are summarized at Table S1.

Fig. 1(a) and (b) show the asymmetric units of polymorph I and II. TCNQ moieties of both polymorphs have a similar structure. By comparison with TCNQ, steric repulsion can be detected between C9−N1 cyano group and the O1 oxygen, where the C1−C7−C9 angles are 126.63(19) ° for polymorph I and 126.84(15) ° for polymorph II. Difference in a molecular structure between the polymorphs is recognized at the torsion angle of C2−O1−C13−C14. The



1

Scheme 1. Preparation of compound **1**.