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Research Article

Molecular Structure and Crystal Packing of n-Type Semiconducting Material 3',3'-(1,4-Phenylene)bis{2'-(4''-trifluoromethyl)phenyl}acrylonitrile

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The exact molecular structure and the crystal packing of the n-type semiconducting material 3',3'-(1,4-phenylene)bis{2'-(4''-trifluoromethyl)phenyl}acrylonitrile was determined by a single crystal X-ray diffraction with twin treatment technique. The air-stable product was crystallized from dichloromethane-hexane mixed solution. The solid-state structure is the example of a typical π - π stacking with side intermolecular CN-H short contact networks.

1. Introduction

Organic semiconductors have attracted much attention to offer low-cost, flexible, and throwaway electronic applications, such as organic thin-film transistors (OTFT) and organic solar cells. Since thin-film transistor (TFT) is the most fundamental electronic device in electronic circuit, improvement of OTFT performance is desired [1–3]. Although there are many reports of new candidate organic semiconductor having high mobility, only few reports mentioned drifting characteristics of on-current in OTFTs at on-state [4, 5].

The n-type organic semiconductor with high performance transport characteristics is also strongly desired in organic electronics. Jones and coworkers have succeeded in achieving the air stability to peryleneimide derivatives by cyano (CN) and fluorine (F) substituent [6, 7]. Yasuda et al.

reported good p-type transport characteristics in *p*-phenylenevinylene-type oligomer, which represents the intrinsic stacking functionality by the *p*-phenylenevinylene structure as distyrylbenzene derivatives. Even in terms of n-type transport simple distyrylbenzene derivatives with electron-withdrawing trifluoromethyl substituents are not reported so far [8].

Recently, we reported excellent n-type transport characteristics of *p*-phenylenevinylene derivative of 3',3'-(1,4-phenylene)bis{2'-(4''-trifluoromethyl)phenyl}acrylonitrile having two cyano (CN) and two trifluoromethyl (CF₃) substituents [9]. We also reported the detailed synthetic methods of the compound and its analogues as Japan, Europe, and US patents [10].

Fabricated OTFTs were found to show relative high electron mobility of ca. $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with extremely stable n-type OTFT characteristics. Furthermore, the material has

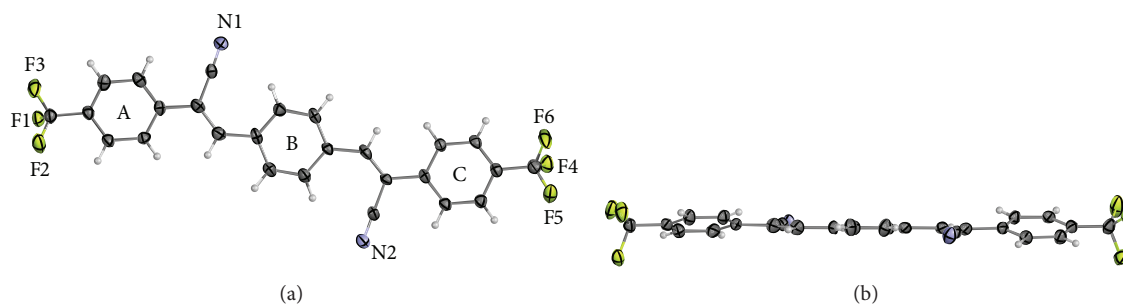


FIGURE 1: Top (a) and side (b) views of the molecules and thermal ellipsoids are drawn on 50% probability level. Blue and pale green ellipsoids show N and F atoms, respectively. A, B, and C show phenyl rings.

large advantages in terms of the simple procedure via one step synthesis. This should be one good candidate material for n-type organic semiconductor.

Herein, we reported X-ray structural determination of the title compound.

2. Materials and Methods

The title compound was prepared according to the previous reported literature [10].

Single crystals of 3',3'-(1,4-phenylene)bis{2'-(4''-trifluoromethyl)phenyl}acrylonitrile were obtained at room temperature from a solution of chloroform/n-hexane (v/v = 1/1). Cutting of the crystals were almost impossible, because the crystal shapes were thin and twin. Therefore, the X-ray diffraction data of the crystal was treated using PLAT program by TwinABS technique [11].

The data collection was performed on a Bruker APEX II KY CCD diffractometer equipped with graphite-monochromatized (Doubly Curved Silicon Crystal) Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) from a sealed microfocus tube and a nominal crystal to area detector distance of 80 mm. A crystal of the compound mounted on a Mitegen Micromount was automatically centered on a Bruker APEX II crystallographic system. Generator settings were 50 kV, 30 mA. Data collection temperature was -183°C (90 K). Data were acquired using three sets of ω scans at different ϕ settings. The frame width was 0.5° .

APEX2 software was used for preliminary determination of the unit cell. Determination of integral intensities [11] and unit cell refinement were performed using SAINT program [12]. The integration of the data yielded a total of 3627 reflections to a maximum θ angle of 25.03° (0.84 \AA resolution). Suitable single crystals for X-ray structure analysis were not obtained because of the crystals were twin shapes; therefore, we used twin crystal treatment programs [13].

The constants for the triclinic unit cell are $a = 6.835(2) \text{ \AA}$, $b = 8.708(3) \text{ \AA}$, $c = 17.860(5) \text{ \AA}$, $\alpha = 100.124(3)^\circ$, $\beta = 98.771(3)^\circ$, $\gamma = 94.010(3)^\circ$, and $V = 1029.1(5) \text{ \AA}^3$.

Data were corrected for absorption effects with SADABS using the multiscan technique [14]. The average residual for symmetry equivalent reflections is $R_{\text{int}} = 4.24\%$ and $R_\sigma =$

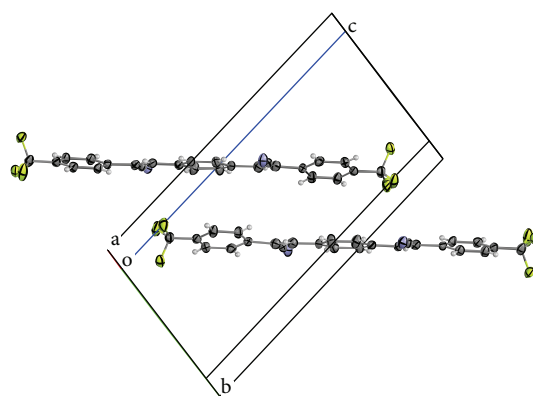


FIGURE 2: Molecular packing of the compound and thermal ellipsoids are drawn on 50% probability level. Blue and pale green ellipsoids show N and F atoms, respectively.

5.97%. XPREP [15] determined the space group to be $P-1$, with $Z = 2$ for the formula unit, $\text{C}_{26}\text{H}_{14}\text{F}_6\text{N}_2$.

The standard deviation for an observation of unit weight was 0.964. Unit weights were used.

The structure was solved with SHELXS [16] and subsequent structure refinements were performed with SHELXL [17]. The final anisotropic full-matrix least-squares refinement on F_o^2 with 308 variables converged at $R_1 = 6.02\%$ for the observed data and $wR_2 = 15.53\%$ for all data. The standard deviation for an observation of unit weight was 0.964. Unit weights were used (least squares function minimized: (SHELXL-2013): $\sum w(F_o^2 - F_c^2)^2$ where w is the least squares weights. Standard deviation of an observation of unit weight: $[\sum w(F_o^2 - F_c^2)^2 / (N_o - N_v)]^{1/2}$ where N_o is the number of observations, N_v is the number of variables). The largest peak on the final difference electron density synthesis was 0.510 e/\AA^3 and the deepest hole was -0.306 e/\AA^3 with an RMS deviation of 0.06 e/\AA^3 . On the basis of the final model, the calculated density is 1.508 g cm^{-3} and $F(000) = 476$.

Hydrogen atoms at carbon atoms were added geometrically and refined using a riding model, whereas the hydrogen atoms at nitrogen and oxygen atoms were exact localized and refined isotropically with bond restraints of 93 pm for

TABLE 1: Crystallographic data.

Empirical formula	$C_{26}H_{14}F_6N_2$	
Formula weight	468.39	
Temperature	90 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P - 1$ (number 2)	
Unit cell dimensions	$a = 6.841(7)$ Å	$\alpha = 100.113(11)^\circ$
	$b = 8.712(8)$ Å	$\beta = 98.727(9)^\circ$
	$c = 17.874(17)$ Å	$\gamma = 93.979(10)^\circ$
Volume	$1031.5(17)$ Å ³	
Z	2	
Density (calculated)	1.508 g cm ⁻¹	
Absorption coefficient	0.127 mm	
$F(000)$	476	
Crystal size	$0.30 \times 0.15 \times 0.10$ mm	
Theta range for data collection	2.852 to 25.03°	
Index ranges	$-8 \leq h \leq 8, -10 \leq k \leq 10, 0 \leq l \leq 21$	
Reflections collected	3627	
Independent reflections	3627 [$R(\text{int}) = 0.0424$]	
Reflections	[$I > 2.0 \text{ sigma}(I)$] 2043	
Completeness to theta = 25.03°	99.5%	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3627/0/308	
Goodness-of-fit on F^2	0.964	
Final R indices [$I > 2 \text{ sigma}(I)$]	$R_1 = 0.0602, wR_2 = 0.1433$	
R indices (all data)	$R_1 = 0.1015, wR_2 = 0.1553$	
Largest diff. peak and hole	0.510 and -0.306 eÅ ⁻³	

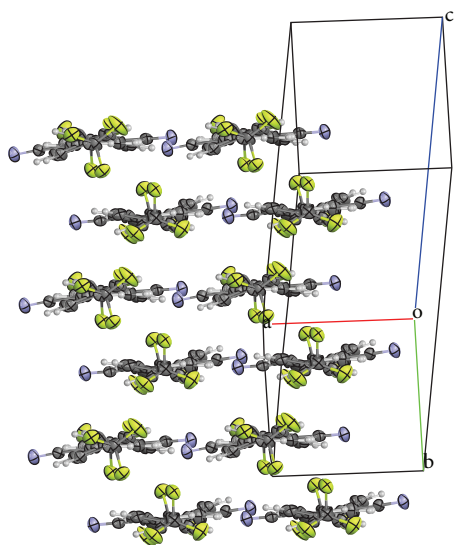


FIGURE 3: One-dimensional columnar packing of the molecules in the crystal. Thermal ellipsoids are drawn on 50% probability level. Blue and pale green ellipsoids show N and F atoms, respectively.

aromatic and cyanoethenyl C–H. All nonhydrogen atoms were refined with anisotropic displacement parameters. The

detector distance was 40 mm and the swing angle (fixed 2θ) were -20° .

This slightly high R_1 and the low measured fraction_theta_full/_max value 0.977 in CIF data were due to the twin crystal treatment.

The details of the crystallographic data were shown in Table 1.

3. Results and Discussion

Suitable single crystals of 3',3'-(1,4-phenylene)bis{2'-(4''-trifluoromethyl)phenyl}acrylonitrile for X-ray structure analysis were not obtained because of the crystals were twin shapes; therefore, we used twin crystal treatment programs [11]. To the best of our knowledge no bis-cyanoethene compound has been characterized in the crystal state.

The compound crystallizes in the noncentrosymmetric space group $P - 1$ (number 2) with two almost planar molecules in the cell (Figure 1).

Selected bond lengths and angles are also listed in Table 2.

Triple bond lengths of the cyano groups were 1.145 Å for C9N1 and 1.148 Å for C19N2, respectively. On the other hand, the bond angle consisting of cyanoethenyl C–CN triple bonds

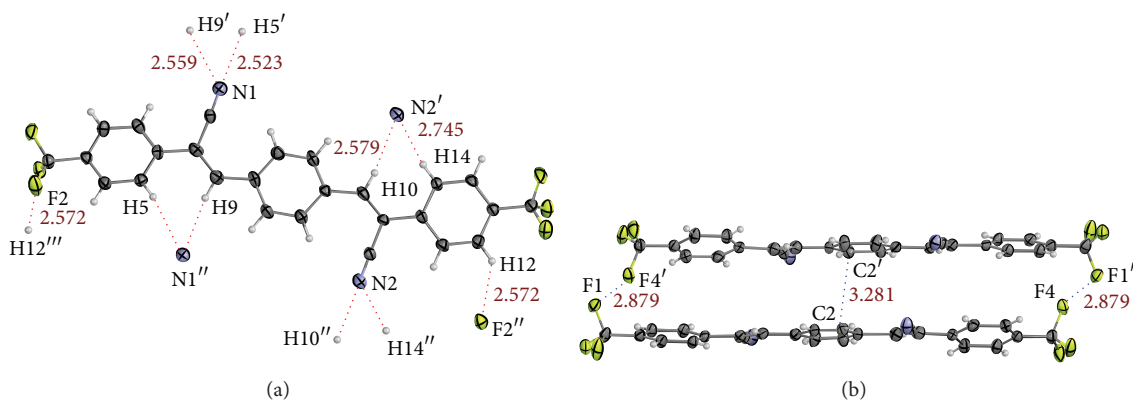


FIGURE 4: Meaningful short contacts (Å) of the compound. Top view (a) and side (b) views were shown. Thermal ellipsoids are drawn on 50% probability level. Blue and pale green ellipsoids show N and F atoms, respectively.

TABLE 2: Selected bond lengths [Å] and angles [°].

Selected bond lengths		Selected bond angles	
C9–N1	1.145(6)	C8–C9–N1	177.8(4)
C19–N2	1.148(6)	C18–C19–N2	178.5(4)
C7–C8	1.358(4)	C7–C8–C9	122.4(3)
C8–C9	1.448(6)	C17–C18–C19	121.4(3)
C17–C18	1.335(4)		
C18–C19	1.434(6)		

TABLE 3: Intermolecular short contacts [Å].

Short contacts (between the columns)		Short contacts (between molecules in the column)	
N1–H5'	2.523		
N1–H9'	2.559		
H10–N2'	2.579	C2–C2'	3.281
H14–N2'	2.745	F1–F4'	2.879
F2–H12'''	2.572		
H12–F2''	2.572		

are slightly twisted, the angles are 117.80° for C8–C9–N1 and 178.45° for C18–C19–N2, respectively.

3',3'-(1,4-phenylene)bis{2'-(4''-trifluoromethyl)phenyl}acrylonitrile might seem almost planar. Three phenyl ring planes A (defined by C1, C2, C3, C4, C5, and C6), B (defined by C10, C11, C12, C13, C14, and C15), and C (defined by C20, C21, C22, C23, C24, and C25) were slightly leaned (Figure 1), and the plane angles between three phenyl moieties are 12.57° for A–B, 19.76° for A–C, and 32.30° for B–C, respectively. This may be due to the staggered one-dimensional array columnar crystal packing. In this reason electron carrier mobility between the molecules seems to be not good compared with the nearly perfect planar compound. Nevertheless, the n-type semiconducting property was very good that we previously reported [9, 10].

Crystal packing of the compound was shown in Figure 2. Surprisingly, long axes of all the molecules are oriented along the Miller axis [010] in the crystal. And good intermolecular π - π interaction can be observed; the shortest length between the stacking molecules is ca. 3.28 Å. This value is slightly smaller than sum of Van der Waals radii of carbon atom.

Furthermore, the molecules build up slightly staggered one-dimensional columns along the Miller axis [010] in the crystal (Figure 3). In general, almost organic semiconductor compounds consisting of polynuclear aromatic hydrocarbons and polynuclear heteroaromatics usually form two-dimensional herringbone molecular orientation in crystal [18, 19]. Interestingly, the orientation of the compound was not herringbone but good π - π stacking structure. This

implies that the orientation of the compound in vapor deposition thin film is similar to the stacking in the crystal. The results also strongly support the good semiconducting behaviors of the compound.

Intermolecular short contacts were listed in Table 3 and no hydrogen bonding was observed. Interestingly, cyano groups of the molecules form intermolecular short contact networks with one of aromatic protons and cyanophenyl C–H protons of the laterally adjacent molecules. Molecules were well oriented between neighbor columns via the interactions (Figure 4). Lengths of the short contacts were also shown (Å).

In addition, the circumference of the columns is crowded with the trifluoromethyl groups (Figure 4). The stability of the compound on the top contact semiconductor device against air and moisture conditions is well explained by the hydrophobicity of the trifluoromethyl groups.

4. Conclusions

The crystal structure of novel n-type organic semiconducting material 3',3'-(1,4-phenylene)bis{2'-(4''-trifluoromethyl)phenyl}acrylonitrile was determined. Its exact structure was determined via single crystal X-ray diffraction analysis using twin crystal treatment. The molecular structure of the compound was not extremely planar but slightly leaned, and the molecules stacked by π - π interaction. The molecules between the neighbor one-dimensional columns were stabilized by intermolecular CN–H short contact networks in the crystal.

Supplementary Data

CCDC no. 999008 contains the supplementary crystallographic data for the compound. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallography Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44(0) 1223-336033.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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