

Synthesis and Crystal Structure of 4-Cyano-3-fluorophenyl-3-(4-hexoxy-3-methoxyphenyl)acrylic Acid Ester

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In present study, 4-cyano-3-fluorophenyl-3-(4-hexoxy-3-methoxyphenyl)acrylic acid ester was synthesized through the esterification of 2-fluoro-4-hydroxybenzotrile and 3-(4-hexoxy-3-methoxyphenyl)acrylic acid ester (4-hydroxyfurelic acid) using *N,N'*-dicyclohexyl-carbodiimide (DCC) as esterifying agent. The structure of the this compound was characterized using IR and ¹H NMR spectra and X-ray crystallography. The compound crystallizes in the triclinic system, space group P-1, with cell dimensions of $a = 7.461(2)$, $b = 11.781(3)$, $c = 13.801(4)$ Å, $\alpha = 96.153(4)$, $\beta = 93.117(4)$, $\gamma = 100.207(5)^\circ$, $V = 1183.7(6)$ Å³ and $Z = 1$.

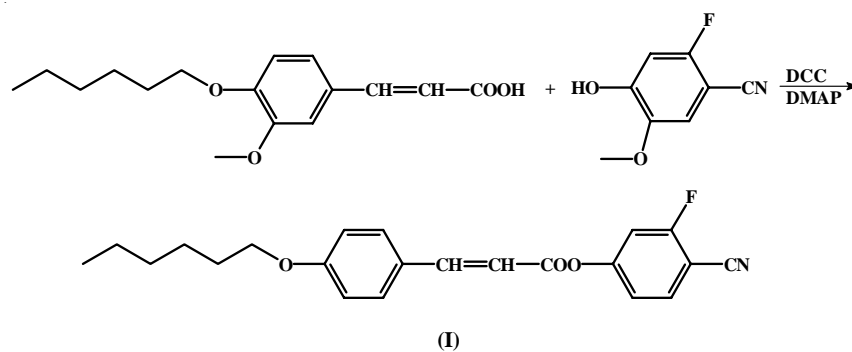
Key Words: Synthesis, Crystal structure, 4-Cyano-3-fluorophenyl 3-(4-hexoxy-3-methoxyphenyl)-acrylic acid ester.

INTRODUCTION

Liquid crystals are a category of substances whose properties are between that of liquids and that of crystals under specific conditions. Liquid crystal compounds have been shown to yield easily well-controlled organized monolayers^{1,2} and multilayers³⁻⁵ at the air-water interface. Their organization at the air-water interface depends on the liquid crystal (LC) molecule-LC molecule interactions and the LC molecule-aqueous subphase interactions as well as the compressing state of the film. As electronically display materials, liquid crystals process prominent advantages⁶⁻⁸.

Recently, fluoro-substituted liquid crystals is an interesting subject because these liquid crystals generally exhibit excellent properties⁹⁻¹¹ compared with the corresponding unsubstituted compounds, such as low viscosity, high voltage mean retention, high specific resistance, and so on. To study the effect of lateral substitution on liquid crystals incorporating F and CN groups in a terminal position, we synthesized 4-cyano-3-fluorophenyl 3-(4-hexoxy-3-methoxyphenyl)-acrylic acid ester. The fluorine atom was chosen as the lateral substituent, because fluoro-substituted liquid crystals generally exhibit nematic-isotropic transition temperature only a little below those of the corresponding compounds with a hydrogen

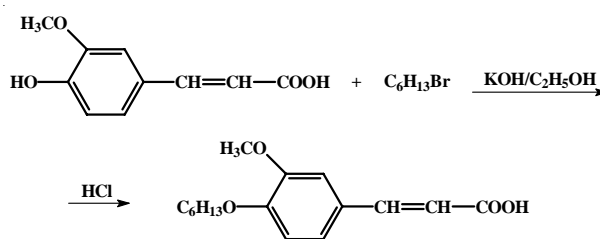
atom in place of the fluorine atom¹². The synthetic route is described as follows:



EXPERIMENTAL

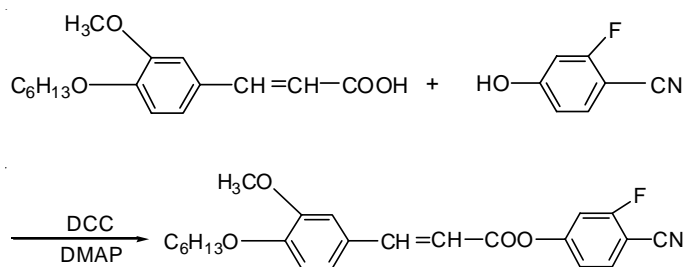
All the reagents were obtained commercially, and used without further purification. Tetrahydrofuran (THF) and pyridine (Py) were dried immediately before use. Melting points were measured on a WRR melting point apparatus, with the thermometer uncorrected. Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer with KBr tablets. ¹H NMR spectra were recorded on a Rigaku JNM-ECP 600 spectrometer using DMSO-*d*₆ as solvent, and as internal standard used was TMS.

Synthesis of 3-(4-(hexyloxy)-3-methoxyphenyl)acrylic acid



A mixture of 3-(4-hydroxy-3-methoxyphenyl)acrylic acid (4.85 g, 0.025 mol), 1-bromohexane (9.84 g, 0.06 mol), potassium hydroxide (2.8 g, 0.05 mol) and 95% alcohol (100 mL) is heated in a water bath at 80°C for 12 h. After being cooled, the mixture is poured into a stirred mixture of concentrated hydrochloric acid (50 mL) and ice cold water (100 mL). After about 0.5 h, the white precipitate is filtered off, washed with water, dried and recrystallized with 75% ethyl alcohol to obtain a product with constant melting point (yield 60 %).

Synthesis of 4-cyano-3-fluorophenyl-3-(4-(hexyloxy)-3-methoxyphenyl)acrylate



A mixture of 3-(4-(hexyloxy)-3-methoxyphenyl)acrylic acid (2.78 g, 0.01 mol), DCC (2.06 g, 0.01 mol), 2-fluoro-4-hydroxybenzonitrile (1.37 g, 0.01 mol) dried tetrahydrofuran (20 mL) and DMAP is stirred at room temperature for 3 h. The precipitate is filtered off and the filtrate is poured into the crushed ice (100 g). White precipitate appears and then is filtered, washed with water and dried. The crude product is purified by column chromatography on silica gel and eluted with the mixture of petroleum ether and ethyl acetate. The eluate is removed of solvent and white powder is obtained, which was recrystallized from 75% alcohol to obtain a crystal with constant melting point. $^1\text{H NMR}$: δ , 0.87 (t, proton 1), 1.30 (m, protons 2); 1.40 (m, proton 3), 1.71 (m, proton 4), 4.00 (t, proton 5), 3.84 (s, proton 6); 7.01 (d, proton 7), 7.33 (t, proton 8), 7.46 (s, proton 9), 7.60 (d, proton 10); 7.83 (d, proton 11), 6.80 (d, proton 12); 8.05 (d, proton 13).

Crystallographic Study

A suitable crystal of the title compound was mounted on a Siemens SMART 1000 CCD area-detector diffractometer. Reflection data were measured at 20°C under $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) with a graphite monochromator. Empirical absorption correction were carried out by using the SADABS¹³ program. The structure of the title compound was solved by direct methods and refined by least squares on F^2 by using the SHELXTL¹⁴ software package. All non-H atoms were anisotropically refined. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography¹⁵. Crystal data and structure refinement for the title compound were shown in Table-1. Selected bond lengths and angles were presented in Table-2. The hydrogen-bonding interaction distances were listed in Table-3.

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT PARAMETERS
FOR THE TITLE COMPOUND

Formula	C ₂₃ H ₂₄ FNO ₄
Formula weight	826.86
Wavelength (Å)	0.085
Crystal system	Triclinic
Space group	P-1
a(Å)	7.461(2)
b(Å)	11.781(3)
c(Å)	13.801(4)
α (°)	96.153(4)
β (°)	93.117(4)1
γ (°)	100.207(5)
Volume (Å ³)	1183.7(6)
Z	1
D(calc) [g/cm ³]	0.000, 1.160
F(000)	436
Mu(MoKa) [/mm]	0.087
Crystal Size (mm ³)	0.05×0.31×0.45
Temperature (K)	293
Wavelength/Å	0.71073
θ range for data collection (°)	1.8~26.1
Dataset	-9 ≤ h ≤ 6 ; -13 ≤ k ≤ 14 ; -17 ≤ l ≤ 17
R, wR	0.0832, 0.2614
S	1.02

TABLE-2
SLECTED BOND LENGTHS (Å) AND ANGLES (°) FOR
THE TITLE COMPOUND

F1-C3	1.342(4)	C1-C2	1.445(4)
O1-C5	1.395(4)	C8-C9	1.450(4)
O1-C8	1.372(3)	C9-C10	1.324(4)
O2-C8	1.192(4)	C10-C11	1.462(4)
O3-C13	1.358(3)	C17-C18	1.496(4)
O3-C23	1.427(4)	C18-C19	1.513(5)
O4-C14	1.356(4)	C19-C20	1.516(5)
O4-C17	1.440(4)	C20-C21	1.510(5)
N1-C1	1.141(4)	C21-C22	1.517(6)
C5-O1-C8	117.8(2)	C8-C9-C10	124.0(3)
C13-O3-C23	117.2(2)	C9-C10-C11	127.1(3)
C14-O4-C17	116.4(2)	O4-C17-C18	109.2(2)
N1-C1-C2	178.8(4)	C17-C18-C19	110.7(3)
O1-C8-O2	121.1(3)	C18-C19-C20	114.0(3)
O1-C8-C9	112.2(3)	C19-C20-C21	113.9(3)
O2-C8-C9	126.8(3)	C20-C21-C22	113.1(3)

TABLE-3
HYDROGEN-BONDING GEOMETRY (Å, °)

D-H...A	D-H	H...A	D...A	D-H...A
C9—H9...O2 ⁱ	0.9303	2.4374	3.365(4)	175.05
C10--H10...O1	0.9307	2.3402	2.714(4)	103.62
C12--H12...O2 ⁱ	0.9302	2.5637	3.483(4)	169.54
C23--H23B...F1 ⁱⁱ	0.9604	2.4360	3.384(4)	168.99

Symmetry Code: (i) = 2-x, 1-y, 1-z; (ii) = -1+x, y, -1+z

RESULTS AND DISCUSSION

Fig.1 showed the molecular structure of the compound. Packing diagram of the title compound in a unit cell was shown in Fig.2. The compound crystallizes in the triclinic system, space group P-1, with cell dimensions of $a = 7.461(2)$, $b = 11.781(3)$, $c = 13.801(4)$ Å, $\alpha = 96.153(4)$, $\beta = 93.117(4)$, $\gamma = 100.207(5)^\circ$, $V = 1183.7(6)$ Å³ and $Z = 1$.

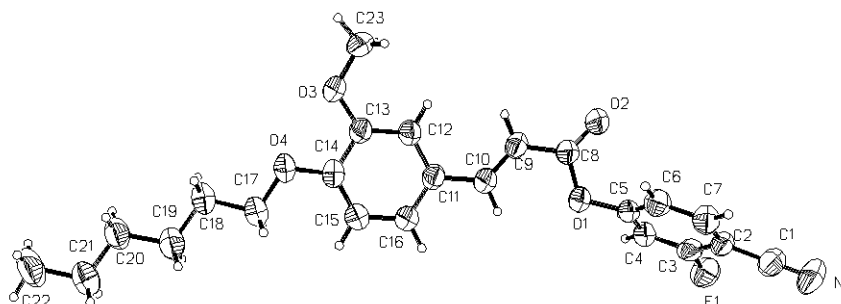


Fig. 1. Molecular structure for C₂₃H₂₄FNO₄

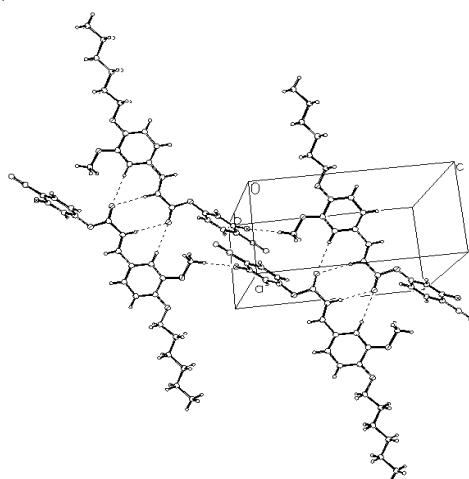


Fig. 2. View of the crystal packing down the a axis for C₂₃H₂₄FNO₄

In the nonplanar molecule, all bond lengths and angles are within normal ranges¹⁶ and comparable to the corresponding values in the related structure¹⁷. The 4-hexoxyphenyl group is essentially coplanar with the acrylate fragment, and the two benzene rings make a dihedral angle of $-67.6(1)^\circ$ with one another. The double bond shows a trans configuration, the C8-C9-C10-C11 torsion angle being $175.7(3)^\circ$. The molecules are linked into chain along the a axis by C9--H9...O2 and C12--H12...O2 hydrogen bonds. The chains are further stabilized into ribbons by C23--H23B...F1 interactions.

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