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Synthesis and mesomorphic properties of 4′-n-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylic acids

Jian Xun Wen*, Min Quan Tian and Qi Chen
Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032 (China)

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Abstract

4′-n-Alkoxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylic acids have been prepared by the oxidation of polyfluorophenylacetylenes with potassium permanganate as oxidant in alkaline 1,4-dioxan/water solution. The mesomorphic behavior of these new compounds was studied by means of polarizing microscopy. The results show that they exist either as enantiotropic or monotropic nematic liquid crystals. The effect of lateral polyfluoro substitution has also been studied.

Introduction

Polyfluorobenzoic acids and 4′-n-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylic acids are important intermediates for the preparation of various liquid crystals [1, 2], which could provide highly potential materials for image-displaying and information transmission in the future. Hence, it is of great significance to develop convenient methods for the synthesis of such compounds. The oxidation of alkynes is one of the most convenient methods for the preparation of carboxylic acids [3]. However, little work has been done on the synthesis of fluoro-aromatic acids using this method. We have previously reported the synthesis of substituted polyfluoro-aromatic acetylenes by nucleophilic substitution on 1-pentafluorophenyl-2-trimethylsilylacetylene [4, 5]. In this paper, a convenient method for the preparation of 4′-n-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylic acids is reported, together with the mesomorphic properties of these novel fluorinated compounds as studied by polarizing microscopy.

Results and discussion

The synthesis of 4′-n-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylic acids is shown in Scheme 1.

The starting material (compound **1**) was prepared by the method reported previously [6]. Nucleophilic substitution of *p*-substituted phenyl magnesium bromide on compound **1** in dry THF gave compounds **2a–f** [4], from which polyfluoro-substituted biphenyl acetylenes (compounds **3a–f**) were obtained after removal of the trimethylsilyl group under the action of methanol and aqueous NaOH in acetone. Oxidation of compounds **3a–f** by potassium permanganate in alkaline 1,4-dioxan/water solution afforded the polyfluoro-substituted aromatic carboxylic acids (compounds **4a–f**).

The final products were purified by recrystallization from anhydrous diethyl ether and petroleum ether. The phase transitions of these new polyfluoro-substituted biphenyl carboxylic acids were studied using a Mettler FP52 hot stage and control unit in conjunction with an Olympus BH2 polarizing microscope, while phase identification was made possible by comparing the observed textures with those quoted in the literature [7, 8].

The transition temperatures of these new fluorinated biphenyl carboxylic acids are listed in Table 1.

Although all six new fluorinated biphenyl carboxylic acids are mesomorphic, the melting points and the relative thermal stabilities of the mesophase for these homologous compounds alter in an unusual manner with increasing the alkoxy chain length. Compounds with $n=5$, 6 and 8 exhibit only the monotropic nematic phase, while compounds with $n=7$, 9 and 10 exhibit the enantiotropic nematic phase. In addition, the odd–even effect is also abnormal, i.e. the isotropic–nematic transition temperature for the homologue containing an alkoxy group with an odd number of carbon atoms is higher than that for an even member of the series.

To explain the above unusual phenomena, it is necessary to investigate the structure of the mesogens.

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*Author to whom correspondence should be addressed.

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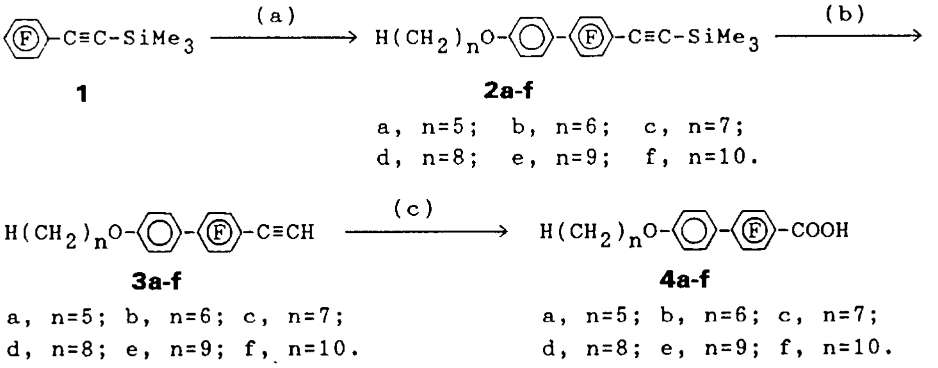
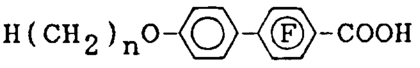


Scheme 1. (a) p-$H(CH_2)_nO-C_6H_4-MgBr$, THF, reflux; (b) CH_3OH/CH_3COCH_3, $NaOH/H_2O$, RT; (c) $KMnO_4/NaOH$, 1,4-dioxan/H_2O, reflux.

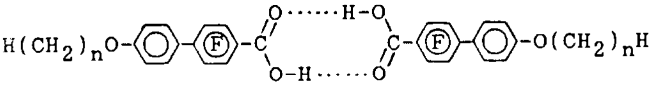
TABLE 1. Phase transition temperatures (°C)[a] of 4'-n-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylic acids



n	C→N	N→I	I→N	N[b]	N→C
5	147.3[c]	–	147.0	22.2	124.8
6	143.8[c]	–	143.3	19.0	124.3
7	134.3	152.2	150.0	31.0	119.5
8	129.0[c]	–	128.3	15.3	113.0
9	144.1	152.0	149.3	26.8	122.5
10	130.7	153.6	148.0	27.0	121.0

[a] C, crystal; N, nematic; I, isotropic.
[b] The temperature ranges of the nematic phase were determined from data obtained during the cooling process.
[c] The phase transition at this temperature is C→I.

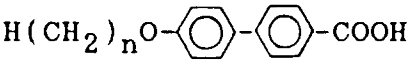
Because of the intermolecular hydrogen bonding effect of the carboxylic group, the 4'-n-alkoxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylic acids dimerize to form the following structure [9]:



Such association preserves the linearity of the molecule and increases the molecular length, thus the breadth-increasing effect caused by the polyfluoro substitution of the phenyl is counterbalanced by the length-increasing effect stemming from dimerization of the carboxylic acid. As a result, intermolecular attractions are maintained at such a high level that these fluorinated biphenyl carboxylic acids are mesomorphic. However, polyfluoro substitution of the biphenyl destroys the coplanarity of the two phenyl rings [10, 11], so that the interplanar angles may differ from one substituted biphenyl carboxylic acid to another due to the differing effect of the n-alkoxy chain. These effects not only lead to the irregular changes in the melting points and in the relative thermal stabilities of the nematic phase in this series of fluorinated compounds, but also give rise to unusual variations in the isotropic nematic transition temperatures.

According to work carried out by Gray *et al.* [12], 4'-n-alkoxybiphenyl-4-carboxylic acids exhibit highly stable mesophases (see Table 2). It is found that the polyfluoro substituted biphenyl carboxylic acid has a lower melting point and a much lower mesophase stability than the unsubstituted compound. In our opinion, lateral polyfluoro substitution of the biphenyl increases the molecular width and destroys the coplanarity of the two phenyl rings. Consequently, the lateral intermolecular attractive forces are greatly diminished and the thermal stability of the mesophase, especially the relative thermal stability of the smectic phase, is much more depressed. On the other hand, the fact that lateral polyfluoro substitution decreases the phase transition temperatures of the liquid crystal compound also provides a direction for further studies on the synthesis of low-temperature liquid crystals.

TABLE 2. Phase transition temperatures (°C)[a] of 4'-n-alkoxybiphenyl-4-carboxylic acids [12]



n	C→S	S→N	N→I	S[b]	N[b]
5	227.5	229.5	275	2	45.5
6	213	243	272.5	30	29.5
7	194.5	251	265.5	56.5	14.5
8	183	255	264.5	72	9.5
9	176	256.5	258.5	80.5	2
10	172.5	256.5	257	84	0.5

[a] C, crystal; S, smectic; N, nematic, I, isotropic.
[b] Mesophase length.

Experimental

Infrared (IR) spectra were recorded on a Shimadzu IR-440 spectrophotometer using KBr pellets for solids or liquid films. ^1H NMR spectra with TMS as the internal standard and ^{19}F NMR spectra with trifluoroacetic acid (TFA) as the external standard were recorded on a Varian EM 360L spectrometer (60 MHz) or an FX-90 Q spectrometer (90 MHz). For ^{19}F NMR spectra, high field is taken as positive. Mass spectra were recorded on a Finnigan 4021 spectrometer.

Compounds **2a–f** and **3a–f** were synthesized using the nucleophilic reaction reported previously [4]. The ^1H NMR and ^{19}F NMR data for **2a–f** and **3a–f** are given below.

1-Trimethylsilyl-2-[4-(4-n-pentyloxyphenyl)-2,3,5,6-tetrafluorophenyl-acetylene (**2a**): Yield, 53.1%. ^1H NMR (CCl_4/TMS) δ: 0.10 (s, 9H, $Si(CH_3)_3$); 0.77 (t, 3H, $J=5.0$ Hz, CH_3); 0.97–1.99 (m, 6H); 3.68 (t, 2H, $J=6.0$ Hz, OCH_2); 6.85 (AA'BB', 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 59.45 (m, 2F, F_{arom}); 66.75 (m, 2F, F_{arom}) ppm.

1-Trimethylsilyl-2-[4-(4-n-hexyloxyphenyl)-2,3,5,6-tetrafluorophenyl]acetylene (**2b**): Yield, 54.8%. ^1H NMR (CCl_4/TMS) δ: 0.11 (s, 9H, $Si(CH_3)_3$); 0.78 (t, 3H, $J=5.0$ Hz, CH_3); 0.97–1.95 (m, 8H); 3.72 (t, 2H, $J=6.0$ Hz, OCH_2); 6.95 (AA'BB', 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 59.56 (m, 2F, F_{arom}); 66.87 (m, 2F, F_{arom}) ppm.

1-Trimethylsilyl-2-[4-(4-n-heptyloxyphenyl)-2,3,5,6-tetrafluorophenyl]acetylene (**2c**): Yield, 65.7%. ^1H NMR (CCl_4/TMS) δ: 0.13 (s, 9H, $Si(CH_3)_3$; 0.79 (t, 3H, $J=5.0$ Hz, CH_3); 0.97–1.87 (m, 10H); 3.83 (t, 2H, $J=6.0$ Hz, OCH_2); 7.00 (AA'BB', 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 59.67 (m, 2F, F_{arom}); 67.00 (m, 2F, F_{arom}) ppm.

1-Trimethylsilyl-2-[4-(4-n-octyloxyphenyl)-2,3,5,6-tetrafluorophenyl]acetylene (**2d**): Yield, 58.7%. ^1H NMR (CCl_4/TMS) δ: 0.15 (s, 9H, $Si(CH_3)_3$); 0.79 (t, 3H, $J=5.0$ Hz, CH_3); 0.98–1.89 (m, 12H); 3.80 (t, 2H, $J=6.0$ Hz, OCH_2); 7.01 (AA'BB', 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 59.43 (m, 2F, F_{arom}); 66.80 (m, 2F, F_{arom}) ppm.

1-Trimethylsilyl-2-[4-(4-n-nonyloxyphenyl)-2,3,5,6-tetrafluorophenyl]acetylene (**2e**): Yield, 53.1%. ^1H NMR (CCl_4/TMS) δ: 0.17 (s, 9H, $Si(CH_3)_3$); 0.80 (t, 3H, $J=5.0$ Hz, CH_3); 1.00–1.90 (m, 14H); 3.78 (t, 2H, $J=6.0$ Hz, OCH_2); 7.02 (AA'BB', 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 59.20 (m, 2F, F_{arom}); 66.60 (m, 2F, F_{arom}) ppm.

1-Trimethylsilyl-2-[4-(4-n-decyloxyphenyl)-2,3,5,6-tetrafluorophenyl]acetylene (**2f**): Yield, 68.0%. ^1H NMR (CCl_4/TMS) δ: 0.19 (s, 9H, $Si(CH_3)_3$); 0.81 (t, 3H, $J=5.0$ Hz, CH_3); 1.03–1.93 (m, 16H); 3.80 (t, 2H, $J=6.0$ Hz, OCH_2); 7.03 (AA'BB', 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 59.10 (m, 2F, F_{arom}); 66.50 (m, 2F, F_{arom}) ppm.

4'-n-Pentyloxy-2,3,5,6-tetrafluorobiphenyl-4-acetylene (**3a**): Yield, 93.6%; m.p. 79.0 °C. ^1H NMR (CCl_4/TMS) δ: 0.73 (t, 3H, $J=5.0$ Hz, CH_3); 0.99–1.90 (m, 6H); 3.35 (s, 1H, $C \equiv CH$); 3.70 (t, 2H, $J=6.0$ Hz, OCH_2); 6.90 (AA'BB', 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 59.70 (m, 2F, F_{arom}); 66.70 (m, 2F, F_{arom}) ppm.

4'-n-Hexyloxy-2,3,5,6-tetrafluorobiphenyl-4-acetylene (**3b**): Yield, 94.9%; m.p. 76.5 °C. ^1H NMR (CCl_4/TMS) δ: 0.75 (t, 3H, $J=5.0$ Hz, CH_3); 0.96–1.93 (m, 8H); 3.38 (s, 1H, $C \equiv CH$); 3.76 (t, 2H, $J=6.0$ Hz, OCH_2); 6.93 (AA'BB', 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 59.65 (m, 2F, F_{arom}); 66.69 (m, 2F, F_{arom}) ppm.

4'-n-Heptyloxy-2,3,5,6-tetrafluorobiphenyl-4-acetylene (**3c**): Yield, 90.4%; m.p. 88.6 °C. ^1H NMR (CCl_4/TMS) δ: 0.77 (t, 3H, $J=5.0$ Hz, CH_3); 0.94–1.97 (m, 10H); 3.42 (s, 1H, $C \equiv CH$); 3.82 (t, 2H, $J=6.0$ Hz, OCH_2); 6.97 (AA'BB', 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 59.60 (m, 2F, F_{arom}); 66.67 (m, 2F, F_{arom}) ppm.

4'-n-Octyloxy-2,3,5,6-tetrafluorobiphenyl-4-acetylene (**3d**): Yield, 91.0%; m.p. 90.3 °C. ^1H NMR (CCl_4/TMS) δ: 0.78 (t, 3H, $J=5.0$ Hz, CH_3); 0.94–1.98 (m, 12H); 3.42 (s, 1H, $C \equiv CH$), 3.84 (t, 2H, $J=6.0$ Hz, OCH_2); 7.00 (AA'BB', 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 59.40 (m, 2F, F_{arom}); 66.50 (m, 2F, F_{arom}) ppm.

4'-n-Nonyloxy-2,3,5,6-tetrafluorobiphenyl-4-acetylene (**3e**): Yield, 88.9%; m.p. 80.9 °C. ^1H NMR (CCl_4/TMS) δ: 0.79 (t, 3H, $J=5.0$ Hz, CH_3); 0.94–1.99 (m, 14H); 3.42 (s, 1H, $C \equiv CH$); 3.86 (t, 2H, $J=6.0$ Hz, OCH_2); 7.03 (AA'BB', 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 59.30 (m, 2F, F_{arom}); 66.33 (m, 2F, F_{arom}) ppm.

4'-n-Decyloxy-2,3,5,6-tetrafluorobiphenyl-4-acetylene (**3f**): Yield, 92.9%; m.p. 80.6 °C. ^1H NMR (CCl_4/TMS) δ: 0.81 (t, 3H, $J=5.0$ Hz, CH_3); 0.95–1.99 (m, 16H); 3.43 (s, 1H, $C \equiv CH$); 3.89 (t, 2H, $J=6.0$ Hz, OCH_2); 7.05 (AA'BB', 4H, H_{arom}) ppm. ^{19}F NMR (CCl_4/TFA) δ: 59.25 (m, 2F, F_{arom}); 66.35 (m, 2F, F_{arom}) ppm.

Preparation of 4'-n-heptyloxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylic acid (4c): typical procedure

To a solution consisting of compound **3c** (0.97 g, 2.66 mol) in 1,4-dioxan (90 ml) was added potassium permanganate (6.80 g, 43.0 mmol), sodium hydroxide (0.35 g, 8.75 mmol) and water (60 ml). The reaction mixture was refluxed with stirring for 6 h. The solvent was then removed by distillation, and sodium sulfite and 10% aqueous hydrochloric acid added with stirring until the solution was clear. The precipitate was filtered off and washed with water (small amounts of HCl being removed in this way). After drying under infrared, the crude product was recrystallized from anhydrous diethyl ether and petroleum ether to give 4'-n-heptyloxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylic acid (**4c**) as a white solid: Yield, 0.73 g (71.4%); m.p. 134.3 °C. ^{1}H NMR (CD_3COCD_3, TMS) δ: 0.29 (t, 3H, J=5.0 Hz, CH_3); 0.47–1.31 (m, 10H); 3.42 (s, 1H, COOH); 3.53 (t, 2H, J=6.0 Hz, OCH_2); 6.50 (d, 2H)/6.92 (d, 2H) (AA'BB', J=8.0 Hz, H_{arom}) ppm. ^{19}F NMR (CD_3COCD_3, CF_3COOH) δ: 65.52 (m, 2F, F_{arom}); 67.67 (m, 2F, F_{arom}) ppm. IR (KBr) (cm^{-1}): 3400; 2960; 2870; 1710; 1640; 1610; 1520; 1480; 1415; 1320; 1295; 1250; 1185; 1170; 1030; 991; 840; 720; 640; 626. MS *m/z* (rel. int.): 384 (M^+, 72.80); 286 (100.00); 242 (21.74). Analysis: Found: C, 62.20; H, 5.00; F, 19.20%. Calc. for $C_{20}H_{20}F_4O_3$: C, 62.50; H, 5.24; F, 19.7%.

The new compounds **4a**, **4b**, **4d**, **4e** and **4f** were prepared in a similar manner.

4'-n-Pentyloxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylic acid (**4a**): Yield, 47.4%; m.p. 147.3 °C. ^{1}H NMR (CD_3COCD_3/TMS) δ: 0.30 (t, 3H, J=5.0 Hz, CH_3); 0.48–1.60 (m, 6H); 3.40 (s, 1H, COOH); 3.50 (t, 2H, J=6.0 Hz, OCH_2); 6.47 (d, 2H)/6.86 (d, 2H) (AA'BB', J=8.0 Hz, H_{arom}) ppm. ^{19}F NMR (CD_3COCD_3/TFA) δ: 65.52 (m, 2F, F_{arom}); 67.85 (m, 2F, F_{arom}) ppm. IR (KBr) (cm^{-1}): 2960; 2870; 1710; 1645; 1610; 1520; 1480; 1415; 1320; 1295; 1255; 1185; 1170; 1020; 995; 840; 720; 640; 630. MS *m/z* (rel. int.): 356 (M^+, 52.35); 287 (100.00); 242 (38.41).

4'-n-Hexyloxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylic acid (**4b**): Yield, 45.8%; m.p. 143.8 °C. ^{1}H NMR (CD_3COCD_3/TMS) δ: 0.31 (t, 3H, J=5.0 Hz, CH_3); 0.50–1.61 (m, 8H); 3.41 (s, 1H, COOH); 3.51 (t, 2H, J=6.0 Hz, OCH_2); 6.48 (d, 2H)/6.89 (d, 2H) (AA'BB', J=8.0 Hz, H_{arom}) ppm. ^{19}F NMR (CD_3COCD_3/TFA) δ: 65.59 (m, 2F, F_{arom}); 67.79 (m, 2F, F_{arom}) ppm. IR (KBr) (cm^{-1}): 2960; 2870; 1710; 1640; 1615; 1520; 1480; 1415; 1315; 1300; 1255; 1185; 1170; 1030; 995; 840; 720; 640; 630. MS *m/z* (rel. int.): 370 (M^+, 32.46); 286 (100.00); 242 (98.41).

4'-n-Octyloxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylic acid (**4d**): Yield, 42.2%; m.p. 129.0 °C. ^{1}H NMR (CD_3COCD_3/TMS) δ: 0.35 (t, 3H, J=5.0 Hz, CH_3); 0.53–1.64 (m, 12H); 3.42 (s, 1H, COOH); 3.53 (t, 2H, J=6.0 Hz, OCH_2); 6.50 (d, 2H)/6.92 (d, 2H) (AA'BB', J=8.0 Hz, H_{arom}) ppm. ^{19}F NMR (CD_3COCD_3/TFA) δ: 65.62 (m, 2F, F_{arom}); 67.81 (m, 2F, F_{arom}) ppm. IR (KBr) (cm^{-1}): 2960; 2870; 1710; 1640; 1610; 1520; 1480; 1415; 1310; 1295; 1250; 1185; 1170; 1030; 990; 840; 720; 640; 626. MS *m/z* (rel. int.): 399 (M^+, 100.00); 286 (69.75); 242 (8.62).

4'-n-Nonyloxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylic acid (**4e**): Yield, 50.6%; m.p. 144.1 °C. ^{1}H NMR (CD_3COCD_3/TMS) δ: 0.35 (t, 3H, J=5.0 Hz, CH_3); 0.55–1.65 (m, 14H); 3.43 (s, 1H, COOH); 3.54 (t, 2H, J=6.0 Hz, OCH_2); 6.52 (d, 2H)/6.94 (d, 2H) (AA'BB', J=8.0 Hz, H_{arom}) ppm. ^{19}F NMR (CD_3COCD_3/TFA) δ: 65.62 (m, 2F, F_{arom}); 67.80 (m, 2F, F_{arom}) ppm. IR (KBr) (cm^{-1}): 2690; 2870; 1710; 1640; 1610; 1520; 1478; 1415; 1313; 1295; 1250; 1185; 1170; 1030; 991; 840; 721; 640; 626. MS *m/z* (rel. int.): 412 (M^+, 51.69); 286 (100.00); 242 (21.45).

4'-n-Decyloxy-2,3,5,6-tetrafluorobiphenyl-4-carboxylic acid (**4f**): Yield, 57.1%; m.p. 130.4 °C. ^{1}H NMR (CD_3COCD_3/TMS) δ: 0.37 (t, 3H, J=5.0 Hz, CH_3); 0.60–1.74 (m, 16H); 3.44 (s, 1H, COOH); 3.55 (t, 2H, J=6.0 Hz, OCH_2); 6.55 (d, 2H)/6.97 (d, 2H) (AA'BB', J=8.0 Hz, H_{arom}) ppm. ^{19}F NMR (CD_3COCD_3/TFA) δ: 65.67 (m, 2F, F_{arom}): 67.82 (m, 2F, F_{arom}) ppm. IR (KBr) (cm^{-1}): 2960; 2870; 1710; 1643; 1610; 1520; 1480; 1415; 1315; 1295; 1250; 1185; 1170; 1024; 991; 840; 722; 640; 626. MS *m/z* (rel. int.): 426 (M^+, 14.01); 286 (100.00); 242 (34.17).

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