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Short communication

C–F···HO hydrogen bond in 8-fluoro-4-methyl-1-naphthol

Hiroyuki Takemura[a,*], Risako Ueda[a,1], Tetsuo Iwanaga[b,2]

[a] Department of Chemical and Biological Science, Faculty of Science, Japan Women's University, Mejirodai 2-8-1, Bunkyou-ku, Tokyo 112-8681, Japan
[b] Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1 Ridaicho, Okayama 700-0005, Japan

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ABSTRACT

The 8-fluoro-4-methyl-1-naphthol forms the intermolecular bifurcated HB, OH···(F, HO) in the crystal. This is quite contrasting to the reported results of the *ab initio* calculations. On the contrary, the intramolecular hydrogen bond in solution was confirmed by ^{1}H, ^{13}C, and ^{19}F NMR spectra.

1. Introduction

In previous reports, we have proved that the fluorocarbon unit (C–F) has a relatively strong affinity toward metal cations [1], and the main attractive force is a result of a cation–dipole interaction. By analogy of this fact, the C–F unit is expected to be a proton acceptor in the hydrogen bond (HB) system. Actually, such HBs C–F···HX (X=O and N) are estimated and observed by the *ab initio* calculations [2] or physicochemical technique such as microwave [3], gas-phase UV and IR [4], laser-induced fluorescence [5], REMPI [6], rotational spectrum [7], and gas-phase electron diffraction [8]. Based on these studies, the HBs have proved to be a weak interaction, and the stability energy has been considered to be at most several kcal mol^{-1}. Therefore, the HBs are rarely observed and hard to detect in an actual system. Nevertheless, several examples of C–F···HX (X=O and N) HBs were found by crystallographic analyses and/or NMR spectroscopy, but the HBs are not ubiquitous [9].

We tried to detect such weak interactions by simple techniques, which are familiar to organic chemists, and succeeded in observing the C–F···HO HB of 9-fluoro-18-hydroxy-[3.3]metacyclophane using the NMR and IR spectra, and X-ray crystallographic analysis [10]. The cyclophane system is a good model for this purpose because the geometry of the F and O atoms is adequate and these atoms are spatially close to each other but are separated by many σ bonds. However, because such a system is a special one, we then planned to make the C–F···HO HB system using a simple structure like the 1-fluoro-8-naphthol **1** [11]. By applying the structure of the proton sponge, 1,8-bis(*N*,*N*-dimethylamino)naphthalene [12], the O, H, and F atoms can form a six-membered ring and it is energetically the most favored geometry to form the HB.

Rozas et al. carried out the *ab initio* calculations (B3LYP/6-31G**) of several phenols, vinyl alcohols, and naphthols containing compound **1** (Fig. 1). The optimized structure of $\mathbf{1}_{cis}$ forms C–F···HO HB in which ∠O–H···F = 141.2°, d(OH···F) = 185.6 pm, and d(O–H) = 96.8 pm [13]. The ν_{OH} vibration was calculated to be 3799 cm^{-1}. On the other hand, $\nu_{OH} = 3819\ cm^{-1}$ and d(O–H) = 96.7 pm of $\mathbf{1}_{trans}$ were estimated which were slightly less stable than $\mathbf{1}_{cis}$ by 3.93 kcal mol^{-1}. After their report, we planned to synthesize the 8-fluoro-1-naphthol and its reference compound, 5-fluoro-1-naphthol, in order to estimate the C–F···HO HB by simple experiments.

2. Results and discussion

2.1. Synthesis

We attempted the synthesis of 8-fluoro-1-naphthol **1** according to Schlosser's report [14]. They described the addition of furan to 2-fluorobenzyne which produced the 1,4-epoxy-1,4-dihydronaphthalene. It was then hydrolyzed by acid to afford 8-fluoro-1-naphthol and 5-fluoro-1-naphthol in a 17:83 ratio. However, in our experiments, the former 1,8-derivative was not isolated

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[*] Corresponding author. Tel.: +81 3 5981 3664; fax: +81 3 5981 3664.
E-mail addresses: takemurah@fc.jwu.ac.jp (H. Takemura), iwanaga@chem.ous.ac.jp (T. Iwanaga).

[1] Tel.: +81 3 5981 3664; fax: +81 3 5981 3664.

[2] Tel.: +81 86 256 9779.

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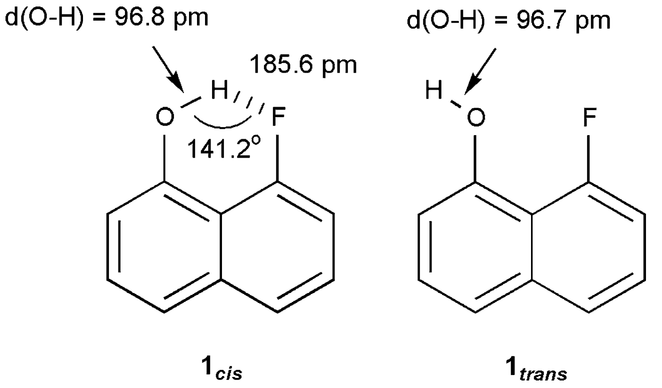


Fig. 1. Optimized structures of 8-fluoro-1-naphthol **1** (*cis* and *trans*) calculated by Rozas et al.

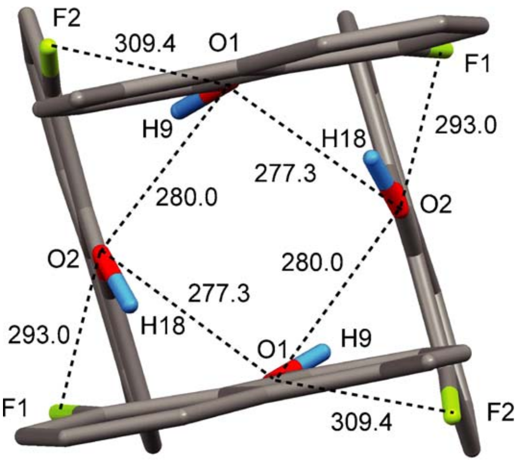


Fig. 2. Hydrogen bond pattern of tetrameric 8-fluoro-4-methyl-1-naphthol **2**. Interatomic distances are indicated in pm.

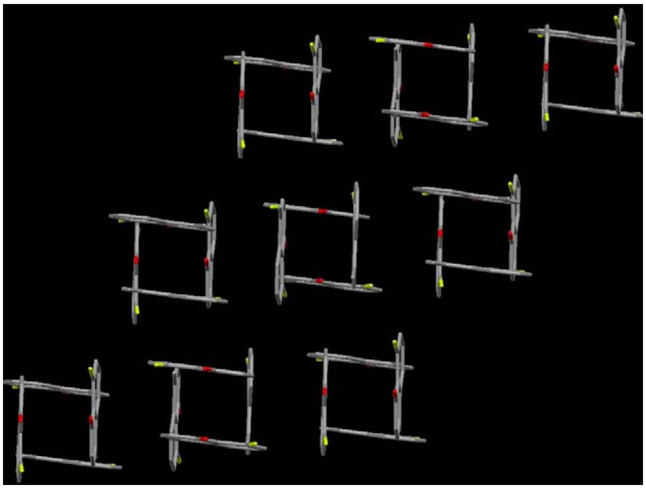


Fig. 3. Molecular packing diagram of **2**.

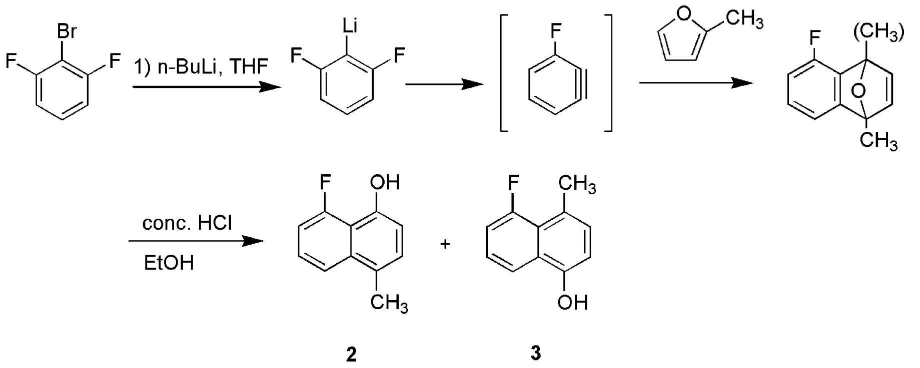
despite repeated experiments, and only the 1,5-derivative was obtained. In order to overcome this problem, 2-methylfuran was chosen as a diene because it was expected that the introduction of a methyl group cause steric repulsion between the CH_3 group and F atom. The Diels-Alder addition between the 2-fluorobenzyne and 2-methylfuran afforded a mixture of epoxides, which was hydrolyzed with conc. HCl in ethanol. As expected, a mixture of the 1,8-derivative **2** and 1,5-derivative **3** was obtained and each was separated in 18.6% and 24.1% yields, respectively (Scheme 1). Characterization of each compound was achieved by ^{1}H, ^{13}C, ^{19}F NMR, FABMS, and elemental analyses. In the FABMS spectra, the molecular peak of **3** was easily observed, but, on the other hand, that of **2** was weak ($M^+ = 176$, 17%) and the main peak ($M^+ = 350$, 36%) corresponded to the oxidatively coupled dimer molecule (probably the 2,2′-binaphthol derivative).

2.2. Crystallographic analysis

A single crystal of the 1,8-derivative **2** suitable for a crystallographic analysis was obtained from cyclohexane. On the contrary, the analysis of the 1,5-derivative could not be carried out because it formed cotton-like fine needles. Initially, the intramolecular hydrogen bonded structure similar to the results of Rozas et al. was anticipated. However, the actual structure was a tetrameric intermolecular one which was bound by characteristic intermolecular HBs to make #-shaped structure as can be seen in Figs. 2 and 3. Recently, Bonnet-Delpon and co-workers reported this type of molecular packing although it is not an OH···F HB [15]. The tetrameric structure could be divided into two units. Following discussion is based on the unit (a) in Fig. 4 because detailed HB characters around H9 and H18 are similar to each other.

In the actual structure, each OH proton was directed outward, i.e., it is the *trans* structure. An OH proton is shared by the O and F atoms of another molecule and forms the OH···OH, OH···F bifurcated HB. The structure was unexpected, but very interesting. As Desiraju and Steiner mentioned in their textbook, the three-centered HB (bifurcated HB, XH···A_1, A_2) keeps its planarity because HB has almost an electrostatic nature [16]. Thus, the sum of the bond angles $\angle$X–H–A_1 + X–H–A_2 + A_1–H–A_2 tends to be 360°. Actually, the sum of the angles around the H9 (center of the bifurcated HB) in the structure (a) of Fig. 4 is 359.2° and satisfies this principle.

Clearly, there is an OH···OH HB because the distances, $d(O_1\cdots O_2) = 280$ pm and $d(H_9\cdots O_2) = 203$ pm, are shorter than



Scheme 1. Synthetic reaction scheme of 8-fluoro-4-methyl-1-naphthol **2** and 5-fluoro-4-methyl-1-naphthol **3**.

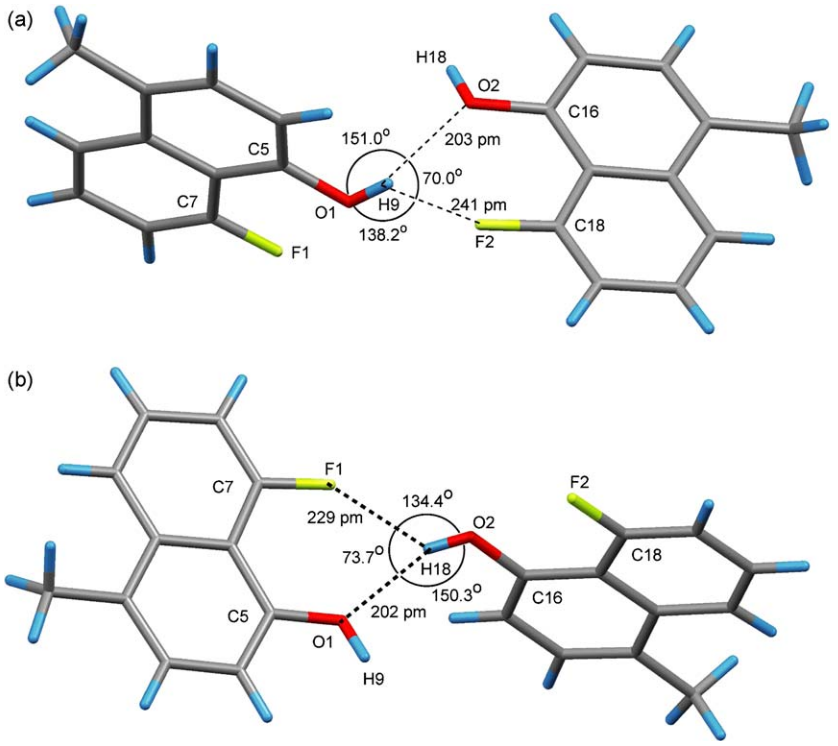


Fig. 4. Bifurcated hydrogen bond pattern (a) and (b) of 8-fluoro-4-methyl-1-naphthol **2** in the tetrameric structure.

the sum of the van der Waals radii of two O atoms (304 pm) or the O and H atoms (272 pm). It is known that the XH···A_1, A_2 (three-centered HB) distances are longer than that of the two-centered HB, XH···A, and therefore, these values in the case of **2** are short enough. In the general weak HB system, the angles $\angle$X–H–A are usually in the range of 180–120° [15], and the angle $\angle O_1–H_9\cdots O_2$ is within the range (151.0°). On the other hand, the distances between the O(1) and F(2) atoms is $d(O_1\cdots F_2)$ = 309 pm which is 10 pm longer than the sum of the van der Waals radii of the O and F atoms (299 pm). However, the distance, $d(H_9\cdots F_2)$ = 241 pm, is much shorter than that of the F and H atoms (267 pm), and the angle $\angle O_1–H_9\cdots F_2$ = 138.2° is also reasonable. In the case of unit (b), $d(O_2\cdots F_1)$ = 293 pm is comparable to the sum of the van der Waals radii of the O and F atoms, and $d(O_{18}\cdots F_1)$ = 229 pm is much shorter than the values described above.

Accordingly, C–F···HO HB is also evident in this case by considering that it is a bifurcated HB.

Because the theoretical calculations by Rozas et al. discussed an intramolecular HB system, we could not compare their results with the actual structure of **2**. In the case of **2**, the bond distance of proton donor $d(O_1–H_9)$ = 85.0 pm is slightly longer than that of the proton acceptor $d(O_2–H_{18})$ = 83.4 which can be considered to be the result of the HB. Although the observed values containing protons are not accurate enough because these are not a result of neutron diffraction, these are enough for the discussion. The positions of protons were determined by a difference Fourier synthesis.

In the proton sponge, the 1,8-naphthalene structure is a critical requirement for its strong basicity (intramolecular HB), but the structure did not work in our case. Why does this difference occur? One of the reasons can be attributed to the poor proton acceptor character of the F atom. Thus, the intermolecular O–H···OH HB is predominant and the C–F···HO bond provides a secondary interaction. Another reason is that the lone pairs of the F atom act as a poor H acceptor. This is shown in the previous studies of the C–F···M^+ interaction, i.e., the coordination bond can be almost ignored and the main attractive force arises from a cation–dipole interaction. The lone pairs of the F atom are tightly bound by the nuclear and thus they are poor H^+ acceptor. Because the $H^{\delta+}$–dipole (C–F) interaction is the predominant attractive force, the geometry of the 1,8-position is not advantageous for this intramolecular interaction (C–F and C–OH are parallel). However, in the case of the bifurcated HB, the linearity of $H^{\delta+}\cdots$C–F is preserved. From this point of view, the HB characters of the OH···OH and the OH···F are different, i.e., the former arises from mainly electrostatic interaction but the latter is based on the cation–dipole or dipole-dipole interaction.

2.3. NMR spectra

However, in contrast to the crystal structure, the tetrameric structure is easily dissociated in the solution and intramolecular HB of **2** becomes major HB. This is clear from the result that the chemical shifts δ_{OH} of **2** are the same at the concentrations of 0.5 and 0.01 mol dm^{-3} in the ^{1}H NMR spectra. As described below, similar results were obtained in the IR spectra in the diluted solutions. Therefore, in contrast to the intermolecular HB in the crystal, the intramolecular C–F···HO HB of **2** could be observed in solution. In the ^{1}H NMR spectra, the OH signal of the 1,5-derivative **3** appeared at 5.07 ppm as a singlet, and that of the 1,8-derivative appeared at 6.90 ppm as a doublet (^5J(F,OH) = 28.4 Hz). As shown in the reports of Biamonte and Vasella [9a,j], the coupling constant of the OH signal in the HB system is reduced in the polar solvents. Namely, in the case of **2**, the coupling constant is ^5J(F, OH) = 28.4 Hz in $CDCl_3$, but it was reduced to 4.4 Hz in THF–d_8, and furthermore, it became 2.6 Hz (δ = 9.81 ppm) in DMSO–d_6. This result indicates that the intramolecular HB is broken by the solvent with high donor ability. The lower chemical shift of the OH signal of the 1,8-derivative than that of the 1,5-derivative ($\Delta\delta$ = 1.83 ppm), and the coupling with the F atom indicate the presence of C–F···HO HB in solution.

In previous studies of the C–F···M^+ interaction system, the high-field shift of the ^{19}F signal and reduction of ^1J(C, F) were the specific spectroscopic phenomena [1]. Similar features were observed in this 1,8-naphthalene system. In the ^{13}C NMR spectra, ^{1}J(C, F) of the 1,8-derivative (242 Hz) was 11 Hz smaller than that of the 1,5-derivative (253 Hz), which was a result of the interaction between the H$^{\delta+}$ and F atom as mentioned above. In addition, the ^{19}F chemical shift of the 1,8-derivative was −121.4 ppm which was ca. 8 ppm higher than that of the 1,5-derivative (−113.3 ppm). Thus, the ^{1}H, ^{19}F, and ^{13}C NMR spectral features suggest the polarization of the C–F and H–O and rearrangement of the electron density among these atoms.

2.4. IR spectra

Different from the NMR spectra, results of the IR spectra were equivocal. In the KBr, the spectra of **2** and **3** showed ν_{OH} = 3398 and 3268 cm^{-1}, respectively, and the band of **3** was somewhat broad as compared to that of **2**. Since the presence of the intermolecular HB of **3** in the crystal was speculated, the blue shift (130 cm^{-1}) of ν_{OH} of **2** should be ascribed to the weaker intermolecular bifurcated HB than that of **3**. We cannot provide a further explanation of this phenomenon because the circumstance around the OH group of **3** in the crystal is unknown. In the diluted CCl$_4$ solution (1.7–2.0 × 10^{-4} mol dm^{-3}), the IR spectra of **2** and **3** gave sharp bands at the same wavelength (3614 cm^{-1}). The shifts of these bands were the same in the concentration range of 1.0 × 10^{-3} to 2.0 × 10^{-4} mol dm^{-3}. As well as in previous studies of the 9-fluoro-18-hydroxy-[3.3]metacyclophane [10] or 2-fluorophenyl-diphenylmethanol [11], the IR spectra in solution were not useful for determining the C–F···HO HB.

3. Conclusion

The theoretical calculations by Rozas et al. encouraged our synthesis and prediction of the C–F···HO HB phenomenon, but the actual molecule formed a different pattern of HB. We do not suppose this difference comes from the presence of the methyl group of **2** because the methyl group is independent of the F or O atoms in the crystal. Although comparison between the results of the theoretical calculations and the observed values of the actual molecule was impossible, the formation of the C–F···HO HB of **2** both in the crystal and in solution was clearly observed. At this point, our speculation and molecular design (and also Rozas et al.) was reasonable. In the studies of this kind of HB, the crystallographic analysis and the NMR spectra are powerful tools. However, different from normal HBs, the IR spectra both in the solid and solution are not practical.

4. Experimental

4.1. General experimental procedures

Melting points: Yanaco MP-500D apparatus in Ar sealed tubes, and are uncorrected. NMR: JEOL AL-300 (300.4 MHz for ^{1}H, 75.6 MHz for ^{13}C, and 283.0 MHz for ^{19}F with TMS and CFCl$_3$ as internal references, respectively). IR: JASCO IR-FT/IR 4200 (CCl$_4$, in NaCl cells (0.1 and 0.5 mm) at 25 °C). FAB MS: JEOL JMS-SX/SX102A. Elemental analysis: the Service Centre of the Elementary Analysis of Organic Compounds affiliated with the Faculty of Science, Kyushu University. Chromatography was performed by a medium-pressure liquid chromatography system, YAMAZEN YFLC-254-GRII.

4.2. 8-Fluoro-4-methyl-1-naphthol (2) and 5-fluoro-4-methyl-1-naphthol (3)

To a flame-dried three-necked flask was added 1-bromo-2,6-difluorobenzene (3.0 g, 15.5 mmol), 2-methylfuran (7.0 mL, 77.5 mmol), and 30 mL of dry THF which was cooled to −75 °C. Under an Ar gas stream, *n*-BuLi (2.6 M, 6.0 mL, 15.6 mmol) was added and stirred for 30 min at that temperature. The mixture was then left at ambient temperature overnight. The mixture was next diluted with *n*-hexane and filtered off through alumina. The filtrate was evaporated to afford yellow oil. The oil was dissolved in 50 mL of ethanol and 15 mL of conc. HCl was then added. The mixture was heated under reflux for 20 h. After cooling, 50 mL of dichloromethane and 100 mL of water was added. The organic layer was separated and dried over MgSO$_4$. Evaporation of the solvents afforded brown oil which was chromatographed on silica-gel (*n*-hexane/CH$_2$Cl$_2$ = 8:2–5:5). Colorless granules **2** (0.51 g, 18.6%) and colorless fine needles **3** (0.66 g, 24.1%) were obtained.

2; Colorless prisms (18.6%, cyclohexane): mp 71.1–72.0 °C. ^{1}H NMR (300 MHz, CDC1$_3$): δ = 7.74 (dd, *J* = 8.5 Hz, 1.0 Hz, 1H, H-7), 7.41 (dt, *J* = 8.1 Hz, 5.9 Hz, 1H, H-6), 7.25 (d, *J* = 7.1 Hz, 1H, H-2), 7.12 (ddd, *J* = 15.1 Hz, 7.7 Hz, 0.9 Hz, 1H, H-5), 6.90 (d, *J* = 28.4 Hz, 1H, OH), 6.89 (d, *J* = 7.8 Hz, 1H, H-3), 2.58 (s, 3H, CH$_3$). ^{13}C NMR (75.4 MHz, CDC1$_3$): δ = 159.8 (d, *J* = 242 Hz, C-8), 149.9 (d, *J* = 2 Hz, C-1), 135.6 (d, *J* = 4 Hz, C-10), 128.6 (s, C-3), 125.5 (d, *J* = 10 Hz, C-4), 125.3 (s, C-6), 121.3 (d, *J* = 4 Hz, C-5), 113.8 (d, *J* = 6 Hz, C-9), 111.0 (d, *J* = 3 Hz, C-2), 109.4 (d, *J* = 23 Hz, C-7), 19.3 (s, CH$_3$). ^{19}F NMR (282.2 MHz, CDC1$_3$, CFCl$_3$ as an internal standard): δ = −121.40 (m). FABMS *m*/*z* = 176.09. Anal. Calcd for C$_{11}$H$_9$OF: C, 74.99; H, 5.15. Found: C, 74.94; H, 5.25.

3; Cotton-like fine needles (24.1%, cyclohexane): mp 112.5–113.3 °C. ^{1}H NMR (300 MHz, CDC1$_3$): δ = 7.98 (d, *J* = 8.5 Hz, 1H, H-6), 7.38 (dt, *J* = 8.0 Hz, 5.0 Hz, 1H, H-7), 7.15 (dd, *J* = 13.9 Hz, 7.4 Hz, 1H, H-8), 7.07 (d, *J* = 7.6, 1H, H-2), 6.73 (d, *J* = 7.6 Hz, 1H, H-3), 5.07 (s, 1H, OH), 2.75 (d, *J* = 7.7 Hz, 3H, CH$_3$). ^{13}C NMR (75.4 MHz, CDC1$_3$): δ = 160.5 (d, *J* = 253 Hz, C-5), 149.3 (d, *J* = 6 Hz, C-1), 127.9 (s, C-3), 127.0 (d, *J* = 6 Hz, C-9), 125.6 (d, *J* = 4 Hz, C-10), 124.9 (d, *J* = 9 Hz, C-7), 124.1 (d, *J* = 14 Hz, C-4), 118.1 (d, *J* = 5 Hz, C-8), 111.6 (d, *J* = 23 Hz, C-6), 109.0 (d, *J* = 2 Hz, C-2), 22.7 (d, *J* = 13 Hz, CH$_3$). ^{19}F NMR (282.2 MHz, CDC1$_3$, CFCl$_3$ as an internal standard): δ = −113.3 (m). HRMS (FAB) Calcd for C$_{11}$H$_9$OF *m*/*z* = 176.0637, Found: 176.0634. Anal. Calcd for C$_{11}$H$_9$OF: C, 74.99; H, 5.15. Found: C, 74.89; H, 5.22

4.3. Crystallographic data of compound 2

C$_{11}$H$_9$FO, Mr = 176.18 g mo1^{-1}, colorless granule (grown from cyclohexane), size 0.40 mm × 0.40 mm × 0.40 mm, monoclinic, space group C2/c, a = 19.1675 (4) Å, b = 15.2690 (4) Å, c = 14.9014 (3) Å, V = 3373.48 (13) Å^3, Z = 16, $\rho_{\mathrm{calcd.}}$ = 1.388 M gm^{-3}, μ(Mo Kα) = 0.10 mm^{-1}, F(0 0 0) = 1472, T = 123(2) K using the ω–2θ scan technique to a maximum 2θ value of 55.0°. The diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer with Mo Kα radiation (λ = 0.71070 Å). The structure was solved by the direct method (SHELXS-97) and refined by the full-matrix least-squares (SHELXL-97). The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. A total of 13,646 reflections were collected. The final cycle of the full-matrix least-squares refinement was based on 3645 observed reflections ($I > 2\sigma(I)$) and 307 variable parameters and converged with unweighted and weighted agreement factors of R_1 = 0.0424, $R_w = 0.1080$, and *GOF* = 1.137. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.391 and −0.291e$^-$/Å^3, respectively. CCDC-709705 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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