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Short communication

The close interaction of a C—F bond with a carbonyl π–system: Attractive, repulsive, or both?

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ABSTRACT

We have synthesized a molecule containing a close interaction between a C—F bond and the π–orbitals of a ketone carbonyl group. Our studies have revealed that there is a combination of attractive and repulsive forces at play: the ketone's IR stretching mode is blue-shifted, the carbonyl is bent away from the fluorine atom, and electron deformation density maps show some significant distortion of the fluorine atom's electron density distribution. Finally, binding of the ketone to an aluminum-based Lewis acid deshields the fluorine nucleus. IR and NMR spectroscopy, single crystal X-ray crystallography, and quantum mechanical calculations were used to investigate this unusual interaction.

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1. Introduction

Noncovalent interactions are critical to understanding the relationship between chemical structure and reactivity, and can influence events in unusual and initially unpredictable ways. In respect to its noncovalent interactions, fluorine has always been in a class by itself, even when compared to the other halogens. Its small size, high electronegativity, relative lack of polarizability and tendency for monovalency allow it to alter a molecule electronically while having a lesser impact on shape and conformation. One way to understand the properties of these fluorinated molecules is to study their noncovalent interactions with common functional groups [1].

One example of a noncovalent interaction that has been studied extensively is the halogen bond [2,3], which is characterized by the halogen atom serving as a Lewis acid towards a suitable donor [4,5]. This situation creates an electropositive pocket on the halogen, called the "σ–hole," to which the donor is attracted [4]. Halogen bonding interactions are known to affect binding and conformation in the active sites of catalysts [6]. However, due to the small size and high electronegativity of fluorine atoms, its σ–hole is observed in very few cases [7]. However, it is possible that a different type of interaction could produce a structure similar to a σ–hole on a fluorine atom, such as electron-electron repulsion. In this work, we report on compound **1**, which contains a close interaction between fluorine and a ketone C=O π–system. Somewhat similar interactions between a nitrogen atom and a ketone have been previously reported [8]; in the present case, there exists evidence of interactive character between the fluorine and ketone carbonyl, but it differs from that in a halogen bond, but does apparently involve a σ–hole – like region on the fluorine atom. In addition, intermolecular F···C=O short contacts have been observed in crystal packing, but these interactions have not been investigated in depth and differ from the interaction in this work in that in those cases the fluorine atom is unambiguously in contact with only the carbon atom [9]. We have previously synthesized **1** as an intermediate while making other compounds in our previous works [10] (see Supporting information, SI), and only recently recognized that it is an interesting species in its own right; thus it has not been a focus of our investigations until now.

2. Results and discussion

2.1. Molecular geometry

Compound **1** (Fig. 1) prominently features a fluorine atom positioned in proximity and directed towards the keto-carbonyl functional group. The crystal structure of **1** shows short F1–C14 and F1–O4 distances of 2.4417(3) Å and 2.7042(3) Å, respectively (standard uncertainties have been experimentally derived from the MoPro refinements) (Fig. 2). When compared to control **2**, (Fig. 2), the ketone carbonyl is significantly bent away from the fluorine (C1–C14–O4 angle is 114.75°), suggesting that the fluorine's presence has a notable impact on the molecule's overall geometry.

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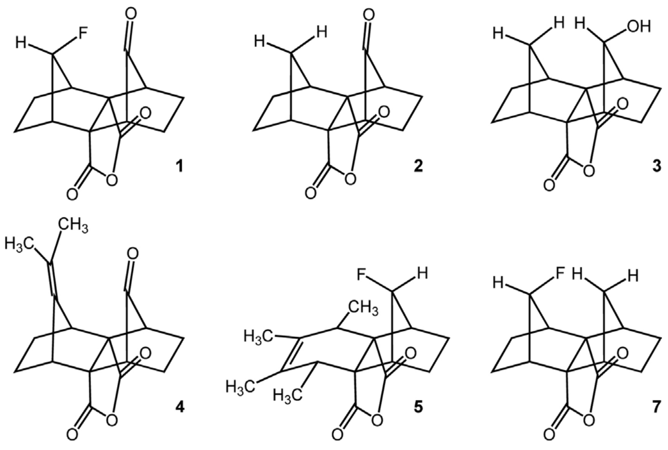

Fig. 1. Compound **1** and various control molecules.

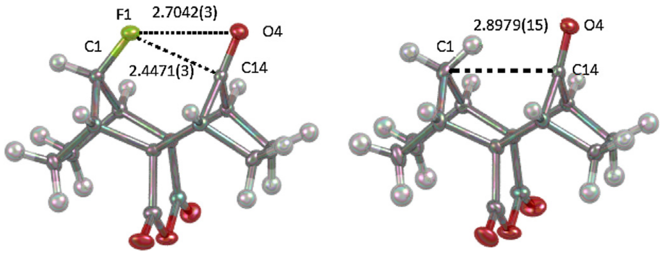

Fig. 2. Displacement ellipsoid plot (50% probability level) of **1** (left) and **2** (right) at 110(2) K. Interatomic distances are given in angstroms.

In a typical halogen bond, the electropositive σ–hole of the halogen coordinates to an electronegative atom. In **1**, the closest electron-rich atom is the ketone oxygen, but the angle about fluorine formed by the C—F bond and ketone oxygen is *ca.* 131°. This is far off from favored 180° "head-on" halogen bond angle, which suggests of course that classical halogen bonding does not occur. Predictably, no obvious evidence for halogen bonding between F and O can be observed in the crystal structure; in contrast to the classical case, the fluorine atom in **1** is aimed at the carbonyl carbon. The tilting of the ketone away from the fluorine atom could also suggest that the F···O interaction may have repulsive character. However, fluorine is most likely presenting an alternate bonding mode between its lone pairs and the electropositive ketone carbon, as a nucleophilic attack frozen in time. This "attack" could also be responsible for the ketone's tilt. Such halogen lone pair–electropositive atom interactions typically have bond angles between 90° and 120°, which fits the 104.6° angle between C1, F1, and C14 [11]. In the ^{13}C NMR spectrum of **1**, the ketone carbon shows a 6.6 Hz coupling to fluorine. This fairly weak coupling suggests that repulsion between the C=O π orbital (which has greater amplitude on oxygen) and fluorine's lone pairs counteracts donation from said lone pairs into the C=O π* antibonding orbital (which has greater amplitude on carbon).

2.2. Infrared spectroscopy

As halogen bonding or any Lewis acid/base pairing affects bond strength, IR spectroscopy should be informative. The C=O stretch of **1** is found at approximately 1785 cm^{-1}, which unfortunately coincides with the analogous anhydride stretches, so we were unable to observe it in isolation. Therefore, to judge the strength of fluorine's perturbation on the ketone properly, a control molecule was needed. As a general statement, one of the greatest difficulties in chemistry is finding appropriate controls for experiments, since to change a part of a system is to change the whole, and observable attributes are generated from multiple interdependent phenomena.

A control was synthesized in the form of **2**, which differs from **1** in that the fluorine is replaced with a hydrogen atom. Alcohol **3** was made as previously reported, and oxidized with PCC to yield **2** (Fig. 1) [12,13]. Its C=O stretching frequency was found at 1762 cm^{-1}. However, it is possible that the *in*-hydrogen in **2** also perturbs the carbonyl. A crystal structure of **2** was obtained that reveals a C1–C14 distance of 2.8979(15) Å (Fig. 2); the two H atoms attached to C1 were placed at calculated positions and refined using a riding model as X-ray crystallography cannot determine them accurately. The C1–C14 distance in **2** is shorter than the C1–C14 distance in **1** (3.1002(4) Å), which indicates that the presence of the fluorine atom in **1** imparts some strain in the molecule. As the cage structure splays open to a greater extent in **1** than in **2** to accommodate the larger fluorine atom, the forced overlap of these groups must be larger, and fluorine should perturb the ketone to a greater extent than the hydrogen.

To gauge the effect the *in*-hydrogen has on the ketone in **2** we decided to employ a second control, with no perturbing atom. Thus we turned to our previously reported olefin **4** (Fig. 1) [14]. Its ketone IR stretch is found at 1764 cm^{-1}, which is 21 cm^{-1} red-shifted compared to **1**. Looking at a calculation of the molecule's vibrational modes at ωB97XD/6-311+G**, it does not appear that its C=O stretch is strongly coupled with the olefin C=C stretch, so it should serve as a good control for an unperturbed ketone in this type of system. As this value is very similar to that of **2** (blue-shifted by only 2 cm^{-1}), it appears that the impact of hydrogen on the C=O stretch is small. Thus, the presence of fluorine is likely the cause of the relative blue shift observed in the C=O stretch of **1**.

2.3. Molecular modeling calculations

Molecular modeling calculations were used to gain a better understanding of the strength of the F···C (carbonyl) interaction. The vibrational modes were computed while fixing the F···C (carbonyl) distances in **1** and the H···C (carbonyl) distances in **2** at values between 2.0 and 3.0 Å (Fig. 3). We chose to run the calculations at the ωB97XD/6-311+G** level of theory, as it has a reputation for correctly predicting dispersion effects [15]. We conducted these calculations using Gaussian 09, and equilibrium molecular coordinates of the structures are available in the SI [16]. The calculated C=O frequency of **1** has its maximum near the fully optimized distance of 2.46 Å. Compound **2** has a maximum frequency at a much greater distance, around 2.7–2.8 Å, while unconstrained optimization gives a distance of 2.28 Å. The blue shift in **1** that occurs on approach from afar can be explained by bond compression, which does not occur in **2**. However, at a certain point, the interaction comes to be dominated by nucleophilic attack of the fluorine on the carbonyl carbon, which red-shifts the C=O stretch; perhaps not coincidentally, the optimized distance lies around the point at which one factor begins to override the other, indicating that both play roles.

2.4. Electron deformation density experiments

We performed an X-ray diffraction experiment at subatomic resolution (maximum resolution at 0.40 Å), and obtained the static deformation electron density map data for **1** (Fig. 4). Initial observations show that the C—F bond seems to have some superficial similarities to a halogen bond. It is evident that there is a large pocket of high electron density on fluorine's side of the C—F bond, and its electron density is being pushed away from the

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