

(1-Pyridinio)perfluorophenacylide: a new stable pyridinium ylide in the enol form

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Received 29 February 2008

Accepted 6 March 2008

Online 15 March 2008

The title compound, $C_{13}H_6F_5NO$, exists in the enol form and adopts the *E* configuration about the enol double bond. It is the first example of an enol-type pyridinium ylide. The enol structure was unambiguously determined on the basis of the significantly longer C—O bond and shorter C—C bond. Intramolecular C—H···O and C—H···F hydrogen bonds are responsible for promotion of the enol form and for the stability of this compound.

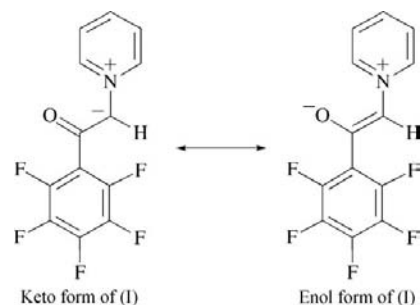
Comment

Pyridinium ylides are an important family of synthetic intermediates for a variety of organic compounds, such as indolines (Tsuge *et al.*, 1985; Kanemasa *et al.*, 1989; Zhang *et al.*, 2000; Wu & Chen, 2003; Kakehi, 2005; Xia *et al.*, 2006) and cyclopropanes (Shestopalov *et al.*, 1989; Vo *et al.*, 1997; Kojima *et al.*, 2000; Yamada *et al.*, 2007). Among the various types of pyridinium ylides, pyridinium acylmethyldes are often employed for organic synthesis because they can be readily prepared from the corresponding pyridinium salts with a base. These pyridinium ylides are generally unstable and are therefore used in reactions without isolation. However, when an electron-withdrawing group is attached to the C atom next to the pyridinium ring, the stabilization of the ylides increases significantly.

In the course of our research on the reactivity of pyridinium ylides (Yamada *et al.*, 2007), we found that the title compound, (I), is significantly stable without having an electron-withdrawing group on the C atom next to the pyridinium ring. Moreover, the X-ray structure clarifies that the equilibrium in the keto–enol tautomerism is shifted significantly to the enol form.

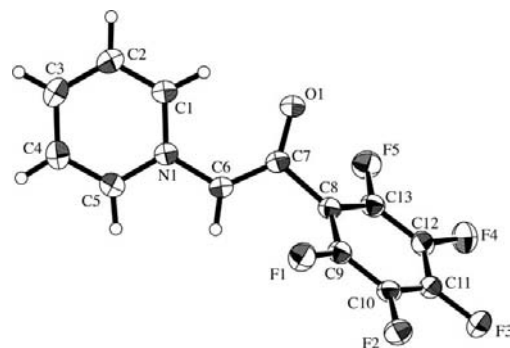
The pyridinium ring (Fig. 1) is almost coplanar with the enol plane, and the pyridinium and perfluorophenyl rings adopt the *E* configuration. The N1—C6—C7—O1 and N1—C6—C7—C8 torsion angles are 0.2 (2) and -178.72 (13)°, respectively, suggesting double-bond character for the C6—C7 bond.

Several pyridinium ylides have previously been structurally characterized, all with an electron-withdrawing group at C6 contributing to the stabilization of the anionic charge. The bond lengths around the anionic moieties of these compounds



are compared with those of (I) in Table 1. The C6—C7 distances for the reported pyridinium ylides are in the range 1.411–1.443 (5) Å, and the C7—O1 distances occur between 1.211 (3) and 1.242 Å. The C6—C7 bond length of 1.3648 (19) Å in (I) is the shortest reported for a pyridinium ylide and is also much shorter than the general Csp^2-Csp^2 bond length (Allen *et al.*, 1987). It is, however, very close to that of the $Csp^2=Csp^2$ bond of a classic enol tautomer (Allen *et al.*, 1987) and is also close to the reported value of 1.360 (13) Å for the C=C double bond in lithium 3,3-dimethyl-1-buten-2-olate [Cambridge Structural Database (CSD, Version 5.28; Allen, 2002) refcode DETRAV (Laube *et al.*, 1985)]. In contrast, the C7—O1 distance of 1.257 (2) Å is the longest among those reported and is intermediate between a C=O double bond and a C—O single bond. The relatively shorter N1—C6 distance of (I) is also in agreement with the sp^2 character of atom C6. These observed bond lengths strongly suggest that this pyridinium ylide exists in the enol form. It is important to note that when the perfluorophenyl ring was replaced with a phenyl ring, the ylide became unstable and could not be isolated. Therefore, the perfluorophenyl ring determines the stability of the pyridinium ylide.

The crystal structure of (I) is built up by two intramolecular C—H···O and C—H···F hydrogen bonds and two intermolecular C—H···O and C—H···F hydrogen bonds (Fig. 2 and Table 2) which are the result of the partial negative


Figure 1

The molecular structure of the title pyridinium ylide, (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

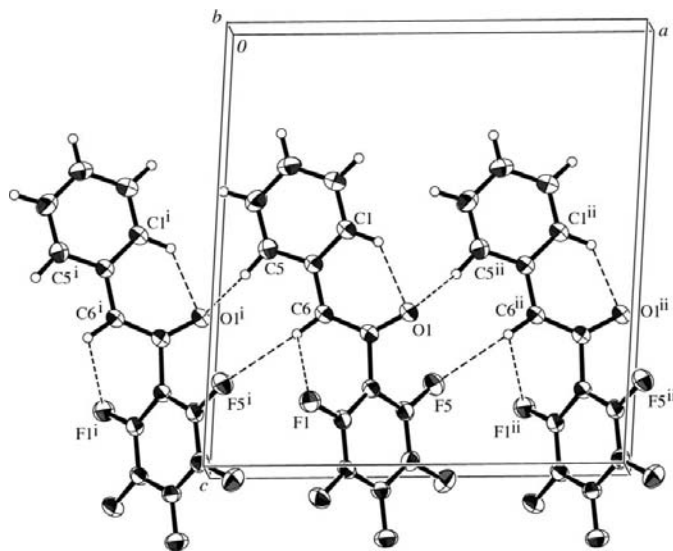


Figure 2
Part of the crystal structure of compound (I), viewed along the *b* axis. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z$; (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, z$.]

charges on oxygen and fluorine. The intramolecular C5—H5···O1 hydrogen bond results in a small C1—N1—C6—C7 torsion angle [7.7 (2)°]. The C5···O1 distance is much shorter than those of the related pyridinium ylides, suggesting a stronger interaction for this hydrogen bond. On the other hand, the C6—C7—C8—C9 torsion angle of -56.04 (19)° is the result of the attractive C6—H6···F1 interaction and electrostatic repulsion between the negatively charged O and F atoms. These hydrogen bonds promote the formation of the enol form.

Molecules of (I) in the crystal structure are linked through two weak C—H···F and C—H···O hydrogen bonds, forming chains running along the *a* axis (Fig. 2). Atoms C5 and C6 in the molecule at (*x*, *y*, *z*) act as hydrogen-bond donors *via* atoms H5 and H6 to atoms C5 and F5 in the molecule at ($x - \frac{1}{2}, -y + \frac{3}{2}, z$). There are no other significant intermolecular interactions.

In summary, the significantly longer C—O and shorter C—C bond lengths around the anionic moiety demonstrate that ylide (I) exists in the enol form. The perfluorophenyl group is responsible for the stability and promotion of the enol tautomer through intramolecular hydrogen bonds, which will provide insight into the control of keto–enol equilibrium in related systems.

Experimental

Triethylamine (75 ml, 0.53 mmol) was added to a solution of 1-[2-oxo-2-(perfluorophenyl)ethyl]pyridinium bromide (129 mg, 0.35 mmol) in CH₂Cl₂ (4 ml). The mixture was stirred at room temperature for 2 h. The product was extracted three times with CH₂Cl₂. The combined organic layer was dried over anhydrous MgSO₄ and evaporated to give (I) (95.5 mg). Recrystallization of (I) from CH₂Cl₂ gave yellow crystals suitable for X-ray crystallographic analysis (yield 96%;

Table 1

Comparison of the bond lengths (Å) in various pyridinium ylides.

Comparative data from the Cambridge Structural Database (CSD, Version 5.28; Allen, 2002).

CSD Refcode	N1—C6	C6—C7	C7—O1	Reference
(I)	1.4110 (17)	1.3648 (19)	1.2572 (17)	<i>a</i>
AHENAC	1.400 (2)	1.421 (2)	1.231 (2)	<i>b</i>
BCAIMP	1.4105	1.4113	1.2273	<i>c</i>
FALPAJ	1.444 (5)	1.443 (5)	1.229 (5)	<i>d</i>
FEFLEI	1.422 (4)	1.412 (5)	1.241 (4)	<i>e</i>
FOBNEQ	1.404 (3)	1.426 (4)	1.219 (3)	<i>f</i>
IZARAC	1.408 (2)	1.416 (3)	1.230 (2)	<i>g</i>
LAHLAI	1.457 (3)	1.428 (4)	1.211 (3)	<i>h</i>
PYINDB	1.4193	1.4285	1.2415	<i>i</i>
VAMQEG	1.4400 (11)	1.4105 (12)	1.2269 (12)	<i>j</i>
YARYUM	1.407 (12)	1.427 (2)	1.221 (2)	<i>k</i>

Notes: (*a*) this work; (*b*) Kolev *et al.* (2002); (*c*) Friedman *et al.* (1978); (*d*) Banks *et al.* (1986); (*e*) Uçar *et al.* (2005); (*f*) Kolev, Yancheva *et al.* (2005); (*g*) Kolev *et al.* (2004); (*h*) Bansal *et al.* (2004); (*i*) Kaminskii *et al.* (1976); (*j*) Kuhn *et al.* (2003); (*k*) Kolev, Wortmann *et al.* (2005).

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C6—H6···F1	0.94 (2)	2.72 (2)	2.994 (2)	97.7 (11)
C1—H1···O1	0.97 (2)	2.10 (2)	2.842 (2)	131.7 (15)
C5—H5···O1 ⁱ	0.97 (2)	2.39 (2)	3.240 (2)	147.3 (17)
C6—H6···F5 ⁱ	0.94 (2)	2.48 (2)	3.396 (2)	164.9 (14)

Symmetry code: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z$.

decomposition point 377 K). IR (KBr, ν , cm⁻¹): 1634 (*s*), 1570 (*m*), 1484 (*m*), 1372 (*s*); ¹H NMR (400 MHz, CDCl₃): δ 9.50 (*d*, *J* = 6.4 Hz, 2H), 7.58 (*t*, *J* = 7.2 Hz, 1H), 7.53 (*m*, 2H), 6.17 (*s*, 1H); MS *m/z*: 287 (*M*⁺, 97%), 285 (100), 120 (48), 65 (51).

Crystal data

C ₁₃ H ₆ F ₅ NO	<i>V</i> = 1131.24 (7) Å ³
<i>M_r</i> = 287.19	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>a</i>	Cu <i>K</i> α radiation
<i>a</i> = 11.5658 (4) Å	μ = 1.47 mm ⁻¹
<i>b</i> = 8.0116 (3) Å	<i>T</i> = 296.1 K
<i>c</i> = 12.2308 (4) Å	0.40 × 0.25 × 0.10 mm
β = 93.453 (2)°	

Data collection

Rigaku R-Axis RAPID diffractometer	12696 measured reflections
Absorption correction: empirical (using intensity measurements) (ABSCOR; Higashi, 1995)	2056 independent reflections
<i>T</i> _{min} = 0.592, <i>T</i> _{max} = 0.867	1825 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.047

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034	207 parameters
<i>wR</i> (<i>F</i> ²) = 0.104	All H-atom parameters refined
<i>S</i> = 1.08	$\Delta\rho_{\max}$ = 0.18 e Å ⁻³
2056 reflections	$\Delta\rho_{\min}$ = -0.16 e Å ⁻³

All H atoms were located in difference Fourier maps and refined isotropically without restraints; the C—H distances are in the range 0.926 (19)–0.98 (2) Å.

Data collection: *RAPID-AUTO* (Rigaku, 2004); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2006); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

This work was supported by a Grant-in-Aid for Scientific Research (B) (No. 17350046) from the Japan Society for the Promotion of Science.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3132). Services for accessing these data are described at the back of the journal.

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