Colorimetric Fluoride-Anion Sensor Based on Intramolecular Hydrogen Bonding and Enol–Keto Tautomerization of a Phenothiazine Derivative

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A colorimetric sensor for fluoride ions based on a new sensing mechanism is reported. The colorimetric sensor contains an isomerizable *enol–keto* moiety as the recognition site and phenothiazine as chromogenic center. A color change visible to the naked eye is observed upon addition of fluoride ions to the solution of sensor **1** in aprotic solvents such as $CHCl_3$ and MeCN. The sensor shows no colorimetric response for other halide ions. Enol-keto tautomerization is proposed to be responsible for the anion sensing of **1**, based on UV/VIS absorption, ^{1}H-NMR, and single-crystal structure analysis.

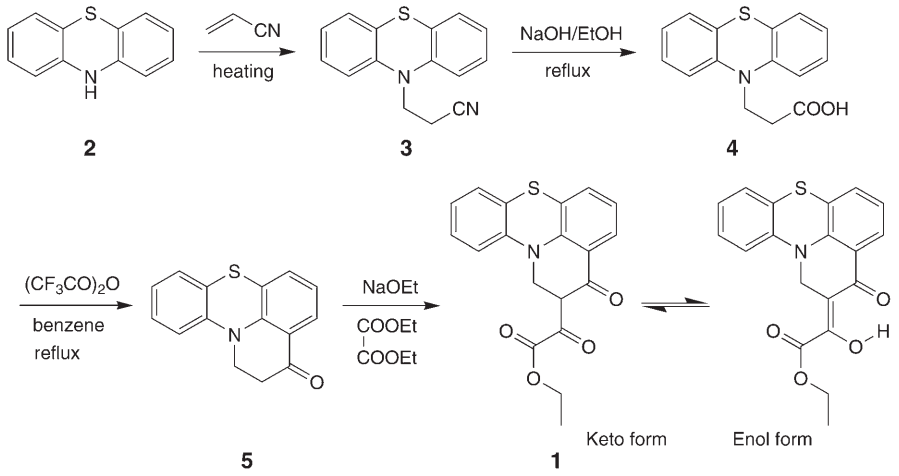
Introduction. – Synthetic molecular sensors for anions have received considerable attention in recent years. Many synthetic receptors have been reported, especially for fluoride anions [1–29], in which various binding and sensing mechanisms are employed, such as H-bonding [18–24][28], binding-induced perturbation of π-conjugation of sensor molecules [25–27], or the catalysis effect of F^- to trigger a chemical reaction [29]. The development of a fluoride sensor is especially challenging due to the importance of this anion with respect to health, environment, and security. Herein, we report an F^- chemosensor based on a new sensing mechanism, the enol–keto tautomerism of a 1,3-diketo phenothiazine derivative. The sensor exhibits a distinct color change in the presence of fluoride anions, and shows no response to the other halide ions. The sensor also gives response to acetate (AcO^-) and dihydrogenphosphate ($H_2PO_4^-$) ions.

In our continuing effort to develop novel fluorophores and chromophores for chemosensors [24], we synthesized compound **1** (*Scheme 1*). Although this compound has been described several decades ago [30], no structural data were available. Thus, the full characterization of **1** was carried out (^{1}H-NMR, MS, and single-crystal structure analysis).

Results and Discussions. – Compound **1** is not fluorescent, possibly due to the quenching effect of the carbonyl groups (nonemissive $n \rightarrow \pi^*$ transition). However, an unexpected dark red color is observed for **1**, as the precursor **5** is a light yellow powder and the conjugation of **1** is limited. Our study proposes that this color is due to the enol–keto tautomerism of **1** [31].

Single crystals of **1** are obtained by evaporation of a solution of **1** in CH_2Cl_2. The single-crystal analysis reveals an intramolecular H-bonding and formation of an enol

Scheme 1. *Synthesis of Enol* **1**



structure (*Fig. 1*). The C(16)–O(2) and O(1)–C(13) bond lengths are 1.326 and 1.256 Å, respectively (*Table 1*). Thus, they are between typical C=O (1.20 Å) and C–O bond lengths (1.41 Å). Furthermore, the C(14)–C(16) and C(13)–C(14) bond length are 1.365 and 1.453 Å, respectively, also between typical C–C (1.54 Å) and C=C bond

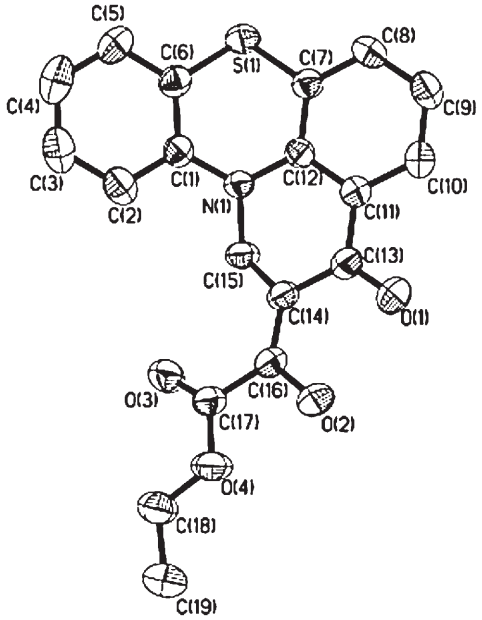


Fig. 1. *ORTEP View of the single-crystal structure of* **1**. Arbitrary atom numbering. Thermal ellipsoids are drawn at the 30% probability level; the H-atoms are omitted for clarity.

Table 1. *Selected Bond Lengths* [Å], *Bond Angles* [°], *and Dihedral Angles* [°] *of Compound* **1**

Bond length		Bond angle		Dihedral angle	
C(16)–O(2)	1.326	C(15)–C(14)–C(16)	126.7	C(10)–C(11)–C(13)–O(1)	10.7
C(17)–O(3)	1.196	C(13)–C(14)–C(16)	118.4	O(1)–C(13)–C(14)–C(16)	2.9
C(16)–C–(17)	1.502	C(13)–C(14)–C(15)	114.6	O(2)–C(16)–C(14)–C(13)	0.6
C(14)–C(16)	1.365			O(3)–C(17)–C(16)–C(14)	– 4.9
C(13)–C(14)	1.453			C(17)–C(16)–C(14)–C(13)	177.2
C(14)–C(15)	1.512				
O(1)–C(13)	1.256				

lengths (1.34 Å). The bond angles C(15)–C(14)–C(16), C(13)–C(14)–C(16), and C(13)–C(14)–C(15) are 126.7, 118.4, and 114.6°, respectively. The dihedral angle O(1)–C(13)–C(14)–C(16) and O(2)–C(16)–C(14)–C(13) are 2.9 and 0.6°, respectively. Thus, the partial structure O(2)–C(16)–C(14)–C(13)–O(1) is almost planar. These data reveal that a coplanar structure of the two carbonyl groups and an intramolecular H-bond due to the presence of an enol structure is highly possible [17].

We propose that enol–keto tautomerization of **1** exists as well in solution, particularly in the presence of H-bond-forming solvents such as MeOH or H_2O. More evidence for the enol structure is also shown by ^{1}H-NMR spectroscopy (*Fig. 2*).

The ^{1}H-NMR spectrum of **1** in $CDCl_3$ shows the CH_2N signal at δ 5.27 as a *s* (*Fig. 2,a*), which indicates that there are no H-atoms at C(d) (*Fig. 2*). In addition, a *s* appears at δ 15.53, a typical enol H-signal. Therefore, these NMR data also support the enol structure of **1**. Furthermore, we found that the tautomerization of the intramolecularly H-bonded enol form can be effected by the addition of protic solvents, such as MeOH, to the solution of **1** in aprotic solvents. In the ^{1}H-NMR spectrum of **1** in $CDCl_3$/CD_3OD (*Fig. 2,b*), two sets of peaks can be observed. For example, a new *t* appears at δ 1.40. We propose that this *t* is due to the ester Me(a′) group of the keto form. The H-atoms at C(c′) of the keto form appear as an *AB* system (with $J_{AB} = 13.6$ Hz), since these H-atoms, next to a center of chirality, are diastereotopic. The signal of the H-atom at C(d′) is not observed, due to the H/D exchange in the presence of CD_3OD. In the presence of CD_3OD, a *ca.* 1:1 ratio of the enol and keto form is rapidly established according to the integration of the respective signals.

In agreement with the ^{1}H-NMR behavior of **1**, we assume that its color may be due to the intramolecular H-bonding of its enol structure, which is an auxochrome and has a comparably strong acidity. It has been proposed that an extended H-bond can induce a red-shift of the UV/VIS absorption [17]. Both the single-crystal structure and ^{1}H-NMR study of **1** indicate that the intramolecular H-bonding and enol–keto tautomerization of this phenothiazine derivative exist and that the equilibrium can be shifted by protic H-bond-donor solvents such as MeOH.

The color of **1** in solution is solvent-dependent. A deep red color is observed for **1** in aprotic solvents, such as THF. But in protic solvents, such as MeOH, the red color disappears and a light yellow color is observed. To establish that protic solvents can shift the enol–keto equilibrium [32][33], an UV/VIS absorption titration with progressive addition of H_2O to an acetone solution of **1** was carried out (*Fig. 3*): The absorption at 479 nm decreases on addition of H_2O to **1** in acetone, and the color of the solution changes from red to light yellow. Presumably, the *enol* form is predominant in acetone solution. By adding H_2O, a strong H-bond donor and acceptor, the intra-

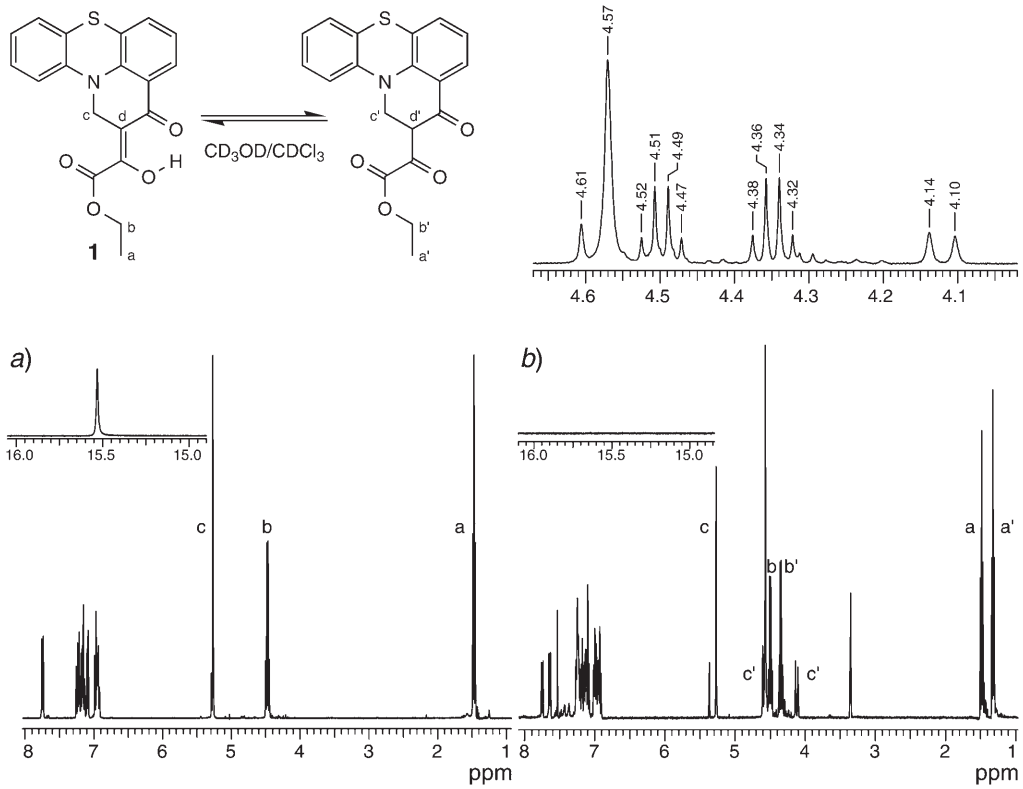


Fig. 2. *^{1}H-NMR Spectra* (400 MHz) *of* **1** a) *in $CDCl_3$ and* b) *in $CDCl_3$/CD_3OD.* Insets: structures of sensor **1** and enlargement of part of spectrum *b*.

molecular H-bonding of **1** is in competition with strong intermolecular H-bonding. Without the stabilization of the intramolecular H-bond, the enol form is thermodynamically unfavorable, and the keto form is formed, as suggested by the decrease of the enol absorption form at 499 nm, due to the extended delocalization [17], and the appearance of new absorption bands at 350 nm and 400 nm, due most likely to the keto form. No well-located isosbestic point was observed due to the dilution effect.

This result suggests that compound **1** might be used for anion sensing, as some anions, especially fluoride ions, show a comparably high basicity [5], and we anticipated that the solution of compound **1** may be used to recognize anions, such as fluoride (F^-), acetate (AcO^-), and dihydrogen phosphate ($H_2PO_4^-$).

The titration of a solution of **1** in $CHCl_3$ with fluoride ions (*Fig. 4*) reveals that the absorption at 499 nm increases on addition of 1 equiv. of F^-, and then decreases with more F^- added, whilst the absorption at 360 nm increases. A well-located isosbestic point is observed, indicating a shift of an equilibrium on addition of F^- ions. After the addition of 7 equiv. of F^-, the absorption at 499 nm has completely disappeared. Since the color of the solution changes from red to light yellow, we propose that the enol structure of **1**, which is characterized by intramolecular H-bonding, is perturbed by the

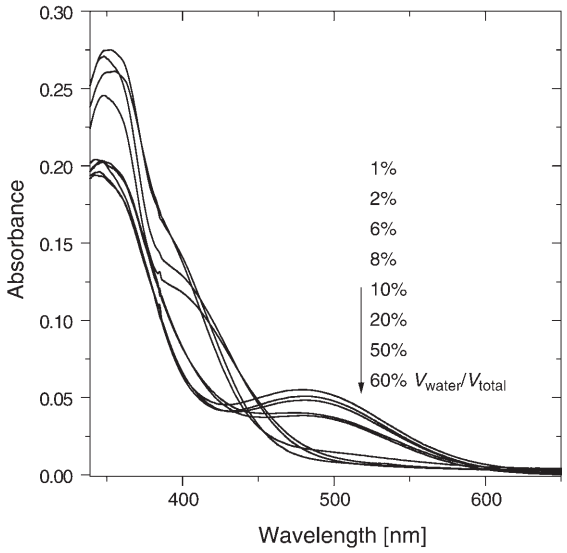


Fig. 3. *Variation of the UV/VIS absorption of* **1** *in acetone* ($3.9 \cdot 10^{-5}$ M) *by titration with* H_2O

addition of F^- and transformed to the keto structure to which the absorption at 360 nm is assigned. The association constants for the two processes, H-bonding (K_{HB}) and deprotonation (K_{DP}), of sensor **1** by fluoride ions are calculated as $K_{HB} = (2.55 \pm 2.24) \cdot 10^4\ M^{-1}$ and $K_{DP} = (6.01 \pm 0.06) \cdot 10^6\ M^{-1}$, respectively (*Fig. 4*). It is noticeable that

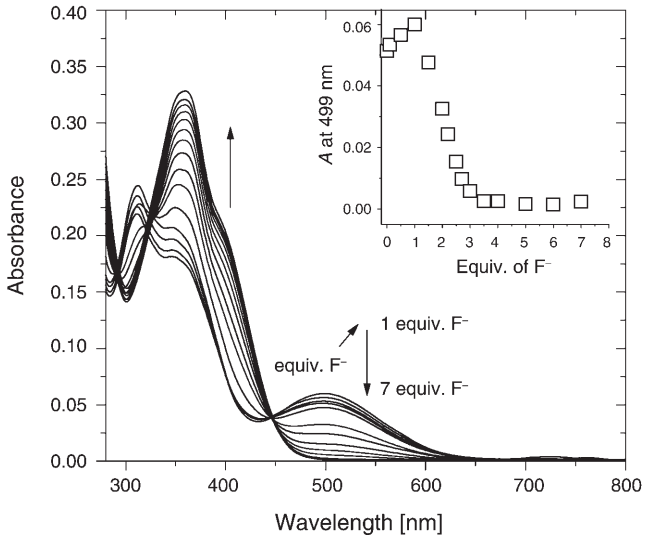


Fig. 4. *Titration of* $2.6 \cdot 10^{-5}$ M **1** *in* $CHCl_3$ *with a standard solution of* $[Bu_4N]F$, *establishing the consecutive H-bonding* (K_{HB}) *and deprotonation* (K_{DP}) *processes.* Inset: absorbance at 499 nm *vs.* number of equiv. of F^- added.

deprotonation begins significantly only after addition of 1 equiv. of fluoride. This result indicates a H-bonding and a strong tendency of deprotonation of sensor **1** because this is a acid–base reaction between the enol form of sensor **1** and the strong base F^- (yielding FHF^- in aprotic organic solvents).

On addition of F^- to the solution of **1**, the absorption band at 360 nm increases sharply. On addition of Cl^-, however, the absorption at 360 nm increases only slightly (*Fig. 5*). In general, if deprotonation cannot occur, the peak at 360 nm does not increase. *Fig. 5* infers that Cl^- cannot quench the intramolecular H-bonding. We propose that on binding of Cl^-, the dipole moment of the molecule increases, and as a result, the UV/VIS absorption is intensified.

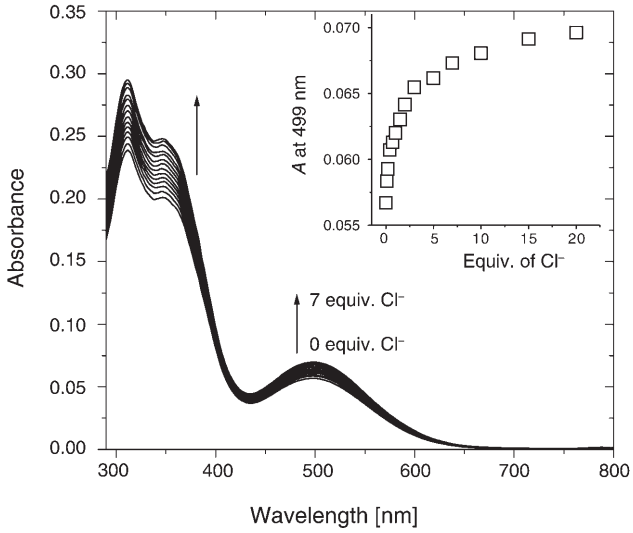


Fig. 5. *Titration of $2.6 \cdot 10^{-5}$ M* **1** *in $CHCl_3$ with a standard solution of $[Bu_4N]Cl$.* Inset: absorbance at 499 nm *vs.* number of equiv. of Cl^- added.

The binding of **1** with Br^-, I^-, AcO^-, HSO_4^-, and $H_2PO_4^-$ were also studied, revealing that **1** shows a high sensitivity and selectivity towards F^- but different sensitivities to AcO^-, and $H_2PO_4^-$ (*Table 2*). For the anions F^-, AcO^-, and $H_2PO_4^-$, two steps of recognition are observed. Firstly, there is an increase of the UV/VIS absorption on addition of these anions, then, the absorption at 499 nm decreases and correspondingly the absorption at 360 nm grows (see above). For the anions Cl^-, Br^-, I^-, and HSO_4^-, there is only a small increase of the absorptions, indicating that there is only a H-bonding process occurring, and the enol form of sensor **1** does not change to the keto form. Compared with the recognition of the other halide ions (Cl^-, Br^-, and I^-), sensor **1** is highly selective for F^-, due to the comparatively strong basicity of fluoride ions.

Much attention has been paid to colorimetric chemosensors [6][7][34–36], and it is found that compound **1** is a sensitive colorimetric sensor for F^-. With 3.5 equiv. of F^- added, the red color turns to light yellow. Similarly, on addition of AcO^- and $H_2PO_4^-$, the color of a solution of **1** turns also from red to yellow. However, a difference of the binding constant of F^-, AcO^-, and $H_2PO_4^-$ is demonstrated by the colorimetry study,

Table 2. *Stability Constants of the H-Bonding* (K_{HB}) *and Deprotonation* (K_{DP}) *of* **1** *with Several Anions*[a])

Analyte	K_{HB}[b])	K_{DP}[c])
F^-	$(2.55 \pm 2.24) \cdot 10^4$	$(6.01 \pm 0.06) \cdot 10^6$
Cl^-	$(2.15 \pm 0.93) \cdot 10^4$	–[d])
Br^-	$(2.91 \pm 1.23) \cdot 10^4$	–[d])
I^-	–[d])	–[d])
AcO^-	$(2.44 \pm 0.00) \cdot 10^6$	$(3.52 \pm 0.32) \cdot 10^5$
HSO_4^-	$(3.90 \pm 1.31) \cdot 10^4$	–[d])
$H_2PO_4^-$	$(8.90 \pm 0.14) \cdot 10^5$	$(1.57 \pm 0.16) \cdot 10^6$

[a]) In $CHCl_3$ solution. [b]) Association constant for H-bonding; in all cases, the r^2 values are higher than 0.98. [c]) Association constant for deprotonation. [d]) No reliable association constant can be determined due to the small UV/VIS absorption change.

which establishes a subtle difference of the color development on addition of the anions. Conversely, there are no color changes in the presence of 3.5 equiv. of HSO_4^-, Cl^-, or Br^-.

To elucidate the anion-recognition mechanism, we studied the isotope effect on the enol–keto tautomerism with the aim to establish the proposed H-bonding mechanism because the equilibrium can be shifted by H-bond-donating solvents, such as H_2O. Bondings by the H- or D-donors show different stability. Usually, D-bonds are more stable due to the smaller zero-point vibration energy (ZPVE). Thus, we thought that a different titration result will be obtained with light water and heavy water [37]. Indeed, when the solution of **1** in acetone is titrated with H_2O or D_2O (only the titration with H_2O is shown in *Fig. 6*) and the absorption of **1** at 476 nm is monitored (inset of *Fig. 6*), two linear curves with different slopes are observed which represent the best linear fitting of the experimental results. We propose that the slope of the curve is directly related to the association constant of the recognition. The free-energy changes of H- and D-bonding can be described by *Eqns. 1* and *2*, where ΔG°_H and ΔG°_D stand for the free-energy changes on binding of H_2O and D_2O molecules, respectively, to sensor **1**. The energy difference of the H-bonding of H_2O and D-bonding of D_2O is then expressed by *Eqns. 3* and *4*.

$$\Delta G^\circ_H = -RT \ln K_H \tag{1}$$

$$\Delta G^\circ_D = -RT \ln K_D \tag{2}$$

$$\Delta G^\circ_D - \Delta G^\circ_H = -RT(\ln K_D - \ln K_H) = -RT(\ln K_D/K_H) \tag{3}$$

$$\Delta\Delta G^\circ = -RT(\ln K_D/K_H) \tag{4}$$

The energy difference $\Delta\Delta G^\circ$ can thus be directly related to the slope of the curves in *Fig. 6*. With the slopes for the curves of D_2O ($-(8.8 \pm 0.40) \cdot 10^{-3}$, $r^2 = 0.99$) and H_2O ($-(4.4 \pm 0.50) \cdot 10^{-3}$, $r^2 = 0.98$) and *Eqn. 4*, one finds that D-bonding with D_2O is more stable by 1.72 kJ mol^{-1} than H-bonding with H_2O. This value agrees well with the reported value for the energy difference of the H-binding *vs.* D-binding [37]. It should

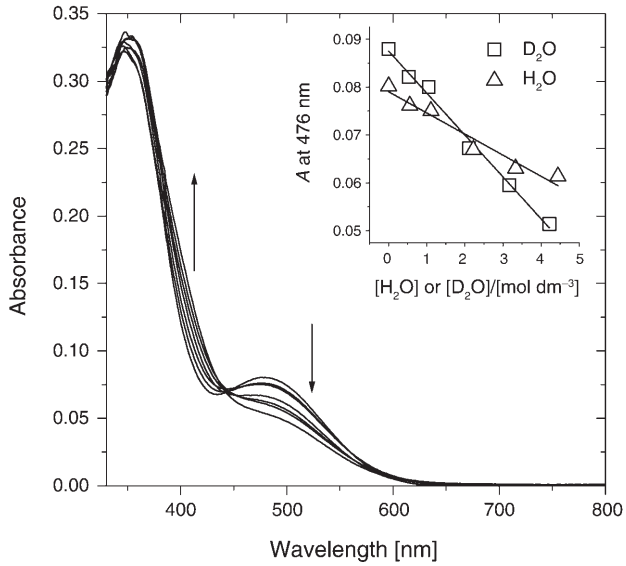


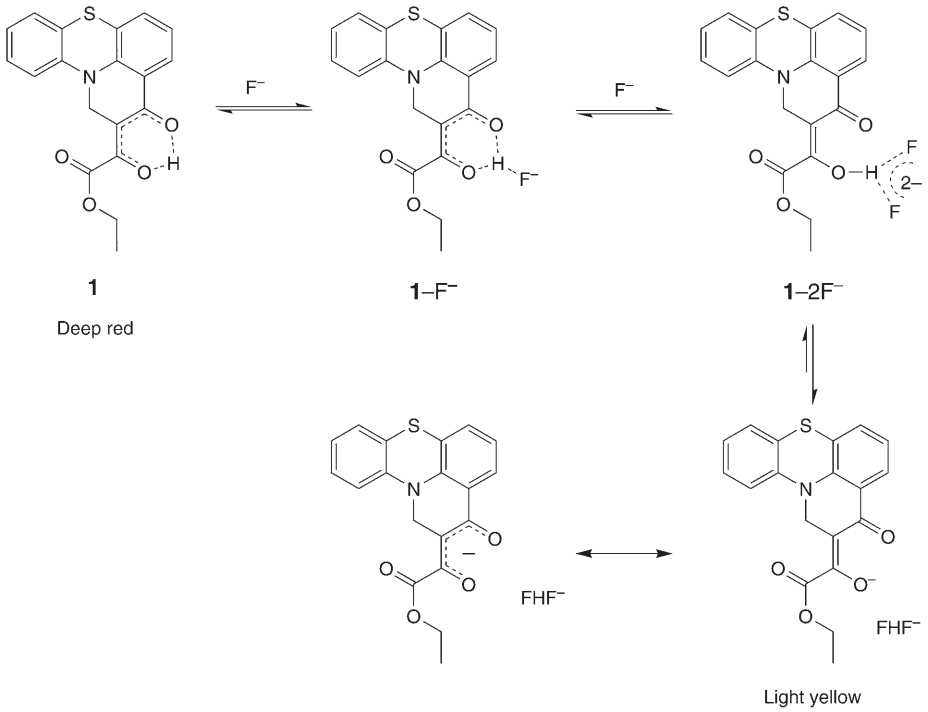
Fig. 6. *Isotope effect of the perturbation of the* enol–keto *form of compound* **1** ($3.9 \cdot 10^{-5}$ M in acetone)

be pointed out that it is highly possible that a multi-H-bonding mechanism is responsible for the shifting of the enol–keto equilibrium of sensor **1**.

Based on the above experimental results, we propose that a delocalized π-system exists in the structure of **1**, responsible for the absorption band at 499 nm and the deep red color of its solution in aprotic solvents. In the presence of low concentrations of F^-, an $OH \cdots F^-$ bond is formed (*Scheme 2*), and the dipole moment of the molecule increases, the oscillator strength of the transition increases, and the intensity of the absorption at 499 nm increases (*Fig. 4*). When more F^- ions are added, the intramolecular H-bonding (**1**–F^-) is destroyed as well as the delocalized π-system, causing the disappearance of the absorption of the delocalized enol-form at 499 nm. A similar behavior is observed for the anions AcO^- and $H_2PO_4^-$. If the basicity of the anions is not high enough to compete efficiently with the intramolecular H-bonds, it cannot destroy the H-bond-stabilized enol form, and the absorption band at 499 nm remains unchanged. The anions Cl^-, Br^-, I^-, and HSO_4^- belong to this group. In addition, for solutions of **1** in protic solvents (such as MeOH and H_2O), a mechanism similar to that outlined in *Scheme 2* is applicable.

The species distribution of the sensor–anion recognition system supports the described mechanism (*Scheme 2*). This is best examplified by the recognition of AcO^- by **1** (*Fig. 7*) (in the case of F^-, a huge error in K_{HD} is observed, due to the limited number of available data for the H-bonding process). It can be clearly seen that the H-bonded species **1**–OAc^- increases linearly on addition of AcO^- and is predominant in the solution after the addition of 1 equiv. of AcO^- ($\log[AcO^-] = \log[2.6 \cdot 10^{-5}] = -4.59$). When more AcO^- ions are added, the amount of H-bonded species decreases sharply and the deprotonated sensor $\mathbf{1}^-$ becomes dominating.

Scheme 2. *Proposed Binding Mechanism of Anions by Sensor* **1** (exemplified with F^-)



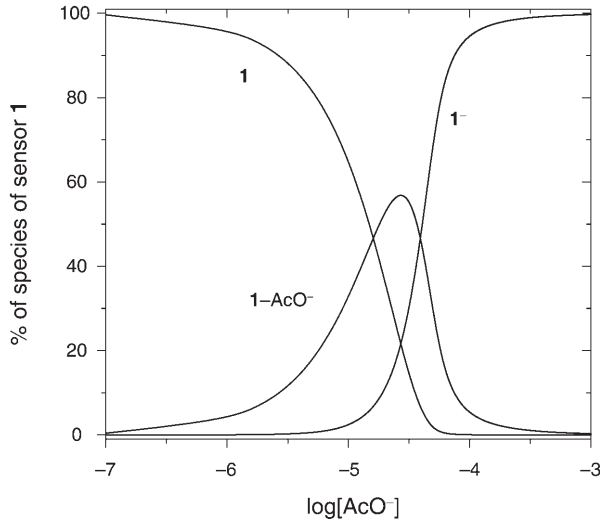


Fig. 7. *Distribution diagram of the species for sensor* **1** *with [Bu_4N]AcO* ($2.6 \cdot 10^{-5}$ M in $CHCl_3$)

Conclusion. – A new sensing mechanism of fluoride anions by intramolecular H-bonding of an enol–keto tautomerization is presented. The 1,3-diketo phenothiazine derivative **1** was found to be a sensitive and selective colorimetric sensor for fluoride ions among the halide ions. We are currently developing a fluorescent chemosensor for fluoride ions based on the described intramolecular H-bonding mechanism.

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Experimental Part

General. All the chemicals for the synthesis or the solvents for spectroscopies are of anal. or spectroscopic grade and were used as received without further purification. CC = Column chromatography. The binding constants were calculated with custom-written nonlinear least-squares curve-fitting programs implemented within SigmaPlot 2000 (*SPSS Inc.*). UV/VIS Spectra: *Perkin-Elmer-Lambda-35* UV/VIS spectrophotometer; titration curves were generated with Origin 5.0 (*Microcal* software). ^{1}H-NMR Spectra: *Varian-Inova* spectrometer; at 400 MHz; δ in ppm, J in Hz.

*1,2-Dihydro-3*H*-pyrido[3,2,1-*kl*]phenothiazin-3-one* (**5**). The synthesis and data of **5** are reported elsewhere [38].

*Ethyl 2,3-Dihydro-2,3-dioxo-1*H*-pyrido[3,2,1-*kl*]phenothiazine-2-acetate* (**1**). To anh. toluene (15 ml) and Na (0.45 g, 19.6 mmol) was added anh. EtOH (20 ml). After the Na was dissolved, excess toluene and EtOH was evaporated. The white residue was taken up with anh. THF, and **5** (2.0 g, 7.90 mmol) in THF (10 ml) was added. After 10 min, diethyl oxalate (2.14 g, 14.6 mmol) in THF (10 ml) was added dropwise (dark red soln.). The mixture was heated at 60° for 0.5 h. Then the solvent was evaporated, and the residue was dissolved with Et_2O (5 ml) and 10% NaOH soln. The soln. was extracted several times with benzene to remove the starting material **5**. The NaOH soln. was acidified with 10% HCl soln. to yield a reddish precipitate which was purified by CC (silica gel, CH_2Cl_2): 0.67 g (24%) of **1**. Brown powder. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.47 (*t*, *J* = 8.0, 3 H); 4.47 (*q*, *J* = 8.0, 2 H); 5.27 (*s*, 2 H); 6.92–6.99 (*m*, 2 H); 7.08 (*d*, *J* = 8.0, 1 H); 7.14–7.26 (*m*, 3 H); 7.74 (*d*, *J* = 8.0, 2 H); 15.63 (*s*, 1 H). ^{1}H-NMR ($CDCl_3$/CD_3OD, 400 MHz): 1.32 (*t*, *J* = 8.0, 3.9 H); 1.49 (*t*, *J* = 8.0, 3 H); 4.10 (*d*, *J* = 13.6, 1 H); 4.34 (*q*, *J* = 8.0, 2.5 H); 4.49 (*q*, *J* = 8.0, 2 H); 4.61 (probably *d*, *J* unavailable due to overlap, 2 H); 5.27 (*s*, 2 H); 6.91–7.02 (*m*, 4.6 H); 7.08–7.25 (*m*, 9.1 H); 7.63–7.66 (*m*, 1.3 H); 7.74–7.76 (*m*, 1 H). ESI-MS: 352.1.

X-Ray Crystallography. The single-crystal structure solution was performed with SHELXL-97 [39]. The single crystals were grown by evaporation of a CH_2Cl_2 soln. of **1**. Crystal data: CCDC No. 629375. Dark red columns. $C_{19}H_{14}NO_4S$. Space group *Cc*; $a = 22.8959(18)$, $b = 9.5515(8)$, $c = 7.5778(6)$ Å; $\alpha = 90.00$, $\beta = 101.007(3)$, $\gamma = 90.00°$; $V = 1626.7(2)$ Å^3. Reflections collected 11053; independent collections 4223 ($R_{int} = 0.0185$); final *R* indices ($I > \sigma I$): $R_1 = 0.0352$, $wR_2 = 0.0352$; *R* indices (all data): $R_1 = 0.0413$, $wR_2 = 0.0970$. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

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