Intra- and Intermolecular Hydrogen Bonds in Pyrrolylindandione Derivatives and Their Interaction with Fluoride and Acetate: Possible Anion Sensing Properties

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Supporting Information

ABSTRACT: The series of push-pull compounds containing the pyrrole ring as a donor and the 1,3-indandione derived moieties as the acceptor unit were synthesized, and strong intramolecular hydrogen bonding in their molecules was studied. In the presence of fluoride and acetate anions their solutions undergo color changes. It was shown by NMR, UV-vis, and quantum chemical calculations including AIM analysis that all these compounds undergo solvent-assisted rupture of the intramolecular hydrogen bond followed by the formation of a strong intermolecular hydrogen bond with fluoride and acetate anions which finally abstract a proton from the pyrrole ring. The insensitivity of the studied compounds to other anions (Cl, Br, HSO_4 , PF_6) is consequence of the instability of the corresponding hydrogen-bonded complexes.



INTRODUCTION

Pyrrolylidene derivatives of 1,3-indandione 1 and 3 (Scheme 1) possess strong intramolecular N–H···O hydrogen bonds in nonpolar solvents and are able to form intermolecular hydrogen bonds with polar basic solvents.¹ Strong H-bonding is witnessed by large low-field ¹H NMR shift of the H-bonded proton (>13 ppm), similar to those in structurally close model compounds 5,² which were shown by X-ray analysis to have a short N···O distance of 2.60–2.62 Å.³ Note that ¹H NMR chemical shifts of the H-bonded proton in compounds 5 agree satisfactorily well with the correlation of geometric and NMR parameters described in ref 4. In spite of the absence of X-ray data for 1, its NMR behavior allows for a conclusion about the presence of strong hydrogen bonding in this and similar compounds.

Recently, we have found that solutions of these compounds in different organic solvents (DMSO, acetonitrile, dichloromethane) undergo color change in the presence of fluoride ion.⁵ This may be indicative of the rupture of the intramolecular hydrogen bond N–H…O followed by formation of intermolecular hydrogen bond or deprotonation and appearance of the anion with more extended π -conjugated system.



The present work reports on the study of intramolecular hydrogen bond in extended series of compounds 1-4 both theoretically, using DFT calculations and topological AIM

analyses, and experimentally using NMR and UV-visible spectroscopy. The choice of the objects of research was based on the fact that, in comparison with the parent compound 1, compound 2 has an extended conjugation system, and compounds 3 and 4 contain substituents with stronger electron withdrawing ability than the carbonyl oxygen atom and higher ability to charge delocalization. Taking into account the color change induced in solutions of these compounds by fluoride and acetate anions, one can consider them as potential optical sensors. The special classical study of sensing properties was not accomplished here, but in order to understand their nature, the intermolecular complexes with various anions were calculated. The relevant research in the field of sensing anions for these and similar compounds is underway now.

Pyrrole-based anion receptors now attract a great deal of interest that is reflected in hundreds publications and reviews during the past decade. Most of known anion receptors contain pyrrolic moiety incorporated into macrocycle (expanded porphyrins and their heteroatomic analogues, porphyrinogens, calix(4)pyrroles like 6,^{6–10} bipyrroles and linear oligopyrroles such as prodigiosin analogue 7 and its derivatives,¹¹ dipyrrolylquinoxalines 8,¹² numerous amide- and urea-function-alized pyrroles 9,¹³ and some derivatives of indole 10 and carbazole.^{14,15} Their activity as anion sensors is based mainly on hydrogen bonding toward most anions and, in the case of

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strongly basic anions, like fluoride, on deprotonation of the pyrrole NH group.



The derivatives **6a**–**c** modified by electron acceptor substituents¹⁰ strongly bind various anions (Cl⁻, AcO⁻, HP₂O₇^{3–}) because of formation of several hydrogen bonds. Binding of the fluoride ion is also based on hydrogen bonding at low ratios $[F^-]/[6]$, but at higher concentrations of the base the deprotonation of the substituted (activated) pyrrole motif takes place. Indole derivatives **10a**–**c** undergo deprotonation under the action of anions, but **10a** is distinguished by its high selectivity toward fluoride, whereas other compounds show approximately equal responses to F^- , AcO⁻, and HP₂O₇³⁻ ions.¹⁵ It was explained by lower NH acidity of the former

compound, compared with the indandione or tricyanoethylene derivatives.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Synthesis of compounds 1 and 3, their physical properties, and their spectra are described in ref 1.

2-((1H-Pyrrol-2-yl)methylene)-5,6-benz[f]-1,3(2H)-in**dandione (2).** 5,6-Benz[*f*]-1,3(2*H*)-indandione (0.324 g, 1.65 mmol) and 1H-pyrrole-2-carbaldehyde (0.157 g, 1.65 mmol) were suspended in 10 mL of acetic acid, and 3 drops of concentrated HCl were added under vigorous stirring. Then the mixture was refluxed for 45 min and cooled to room temperature. The reaction mixture was poured into 50 mL of water, the precipitate formed filtered, dried, and purified by column chromatography with dichloromethane as an eluent to give 0.32 g (70%) of 2 as an orange solid. Mp 212-214 °C. Anal. Found, %: C 79.33; H 4.22; N 5.20. C18H11NO2. Calcd, %: C, 79.11; H, 4.06; N, 5.13. ¹H NMR, δ, ppm, CDCl₃: 13.49 bs, 1H, NH; 8.42 s, 1H and 8.41 s, 1H - H-4, H-9; 8.09 m, 2H, H-5,H-8; 7.83 s, 1H, ==CH; 7.69 m, 2H, H-6, H-7; 7.46 m, 1H, H-5'; 7.14 m, 1H, H-3'; 6.67 m, 1H, H-4'. ¹³C NMR, δ, ppm, CDCl₃: 191.67, 190.38, 136.70, 136.34, 136.17, 135.93, 133. 90, 131.97, 130.52, 130.33, 128.92, 127.36, 123.48, 123.32, 114.80.

(*Z*)-2-((1*H*-Pyrrol-2-yl)methylene)-[1,2'-biindenylidene]-1',3,3'(2*H*)-trione (4). To the suspension of [1,2'-biindenylidene]-1',3,3'(2*H*)-trione (bindone) (0.32 g, 1.16 mmol) in 4 mL of acetic anhydride at 60 °C was added 1*H*-pyrrole-2-carbaldehyde (0.11 g, 1.16 mmol). The mixture was stirred overnight and cooled. The precipitated dark-violet solid was filtered, washed with cold acetic anhydride, and dried. Yield 0.31 g (76%). Mp 240–242 °C. Anal. Found, %: 78.43; H, 3.64; N 3.72. C₂₃H₁₃NO₃. Calcd, %: C, 78.62; H, 3.73; N, 3.99. ¹H NMR, δ, ppm, CDCl₃: 13.48 bs, 1H, NH; 8.84 d, 1H, H-10; 8.00 s, 1H, H-6; 8.00 (overlapped), 1H, H-20 or H-17; 7.96 d, 1H, H-17 or H-20; 7.85 d, 1H, H-13; 7.81 m, 2H, H-18, H-19; 7.69 t, 1H, H-11; 7.63, t, 1H, H-12; 7.53 m, 1H, H-5; 7.12 m, 1H, H-3; 6.58 m, 1H, H-4. ¹³C NMR, δ, ppm, CDCl₃: 192.55, 190.83, 189.42, 163.23, 143.12, 141.75, 140.77, 139.49, 139.42,

Table 1. Selected B3LYP/6-311(d,p) Optimized Geometric Parameters (in Å) for Compounds 1–4 in Gas Phase and DMSO Solution (PCM Model)



	gas				DMSO			
compd	O…H–N	C6-C7	C7–C9	C5-C6	O…H−N	C6-C7	C7–C9	C5-C6
1	1.797	1.370	1.487	1.411	1.826	1.374	1.482	1.407
2	1.781	1.372	1.488	1.409	1.812	1.376	1.482	1.407
3	1.754	1.383	1.468	1.408	1.783	1.387	1.462	1.404
4	1.759	1.381	1.465	1.409	1.796	1.385	1.459	1.405

137.99, 134.57, 132.98, 131.66, 131.11, 130.08, 128.53, 123.25, 122.95, 122.69, 120.52, 114.66.

Calculations of the optimized geometries, total energies, and free energies of compounds 1-4, their anions, and their Hcomplexes in the gas phase and solution were performed at the DFT level of theory using B3LYP potential and 6-311(d,p) basis set. Solvent effects were taken into account using the polarizable continuum model (PCM) and supermoleculepolarizable continuum model (SM-PCM) with DMSO as a solvent. No restrictions were imposed on the geometry optimization. All calculated minima were checked by frequency calculations; no imaginary frequencies were found. Simulation of the proton transfer between the pyrrolyl part of 1B and the acetate anion was performed by scanning the N…H distance for the fixed N…O distance of 2.60 Å. The AIM analysis was performed at the MP2/6-311++G(d,p) level of theory. Chemical shifts were calculated with the GIAO method at the B3LYP/6-311(d,p) optimized geometry. All computations were performed with the Gaussian 09 program package.¹⁶

UV-vis spectra for 1×10^{-4} M solutions of pure compounds 1, 2, 4 in acetonitrile and with addition of Bu₄NF were recorded on a Perkin-Elmer Lambda 35 UV/vis spectrometer for the molar ratio compound/Bu₄NF from 1:1 to 1:200.

¹H and ¹³C NMR spectra were recorded on a Bruker DMX-500 spectrometer at working frequencies of 500.13 MHz (¹H) and 125.1 MHz (¹³C). ¹H and ¹³C NMR chemical shifts are reported in parts per million relative to TMS.

RESULTS AND DISCUSSION

Theoretical Calculations. Evidently, the anion sensing properties of the studied compounds are determined by their ability to form intermolecular $N-H\cdots B$ hydrogen bond after the rupture of the intramolecular $N-H\cdots O=C$ hydrogen bond and 180° flip of the 2-pyrrolyl group. Therefore, theoretical and experimental investigation of both types of hydrogen bonding in compounds 1-4 is a key point of the present study.

Geometry. Most important geometric parameters of compounds 1–4 in the vicinity of the N–H…O=C hydrogen bond are shown in Table 1. The H…O distance in compounds 1 and 2 is 0.04 Å longer than those in 3 and 4, indicating a stronger hydrogen bond in the latter compound. The order of the O –H…N bond lengths in Table 1 $(3 \ge 4 > 2 > 1)$ coincides with the order of the H-bond energies as determined from the AIM analysis (vide infra, Table 3).

Table 2. Wiberg Bond Indices Calculated for Trans-Conformers of Molecules 1–4



Table 3. Properties of the BCP (NH···O) and Hydrogen Bond Energies $E_{\rm HB}$ in the Cis-Conformers 1A-4A in Gas Phase and DMSO Solution (B3LYP/6-311G** Optimized Geometry)

compd	$ ho(\mathbf{r})^a$	$ abla^2 ho({f r})^a$	$E_{\rm HB}^{\ \ b}$					
Medium: Gas								
1	3.71	12.33	10.3					
2	3.86	12.64	10.9					
3	4.06	13.69	11.9					
4	4.06	13.52	11.8					
Medium: DMSO Solution (PCM) (ε = 46.7)								
1	3.97	11.76	9.3					
2	3.57	12.06	9.8					
3	3.81	13.16	10.9					
4	3.70	12.74	10.5					
Medium: DMSO Solution (SM + PCM) (ε = 46.7)								
1	2.44	8.85	5.9					
2	2.50	9.11	6.1					
3	2.74	10.41	7.0					
4	2.62	9.79	6.6					

^{*a*}MP2(full)/6-311++G^{**} calculated electron density [$\rho(\mathbf{r}_c)$, a.u.] and its Laplacian [$\nabla^2 \rho(\mathbf{r}_c)$, a.u.], in BCP (O…HN). ^{*b*}The H-bond energy [E_{HB} , kcal/mol].

At the same time, neither the Mulliken (-0.385, -0.391, -0.387, -0.391) nor the electrostatic charges (-0.517, -0.531, -0.499, -0.513) on the H-bonded carbonyl oxygen atoms in compounds 1–4, respectively, correlate with the corresponding



Figure 1. Structure of cis- and trans-complexes of 1-4 with DMSO (see Table 4).

hydrogen bond lengths from Table 1. Moreover, judged from the chemically reasonable electrostatic charges, the carbonyl groups in 3 and 4 seem to have a somewhat lower basicity which is in apparent contradiction with the shorter hydrogen bond in these molecules. To remove this discrepancy, one should keep in mind that the strength of the hydrogen bond $N-H\cdots O=C$ depends also on the acidity of the NH group in the same molecule. We tried to estimate the NH acidity by calculating the Wiberg bond indices of the N-H bond in the absence of interaction of the NH proton with the carbonyl oxygen, that is, for the trans-conformers (Table 2).

However, although these indices correctly reproduce the increase of NH acidity by transferring a molecule from the gas phase to DMSO solution, in both phases they are practically constant within the series. Taking into account that the NH acidity is favored not only by weakening of the N-H bond but also by extension of the conjugation system of the rest of the molecule, we have considered the geometry of the chain of conjugation between the electron donating 5-pyrrolyl group and the aromatic part of molecules 1-4. As a criterion of the degree of extension of conjugation, the difference between the C7-C9 and C6-C7 bond distances can be used. This value decreases by >0.032 Å, from ~0.12 Å for molecules 1 and 2 to \sim 0.08 Å for molecules 3 and 4. This means that the hydrogen bond in the studied compounds belongs to the resonanceassisted type,⁴ and the conjugation is more efficient and the hydrogen bond is stronger in molecules 3 and 4.

AlM Analysis. The properties of the N–H…O hydrogen bond in molecules 1–4 were studied not only by geometric criteria but also by quantum chemical topological analysis. The AIM method was used to find the bond critical point [BCP (3, -1)] of the N–H…O hydrogen bond to evaluate its energy and to identify the formation of the corresponding seven-membered



Figure 2. Solution of compound 2 in DMSO in the presence of 10 equiv of anions (from left to right): none, F^- , Cl^- , Br^- , HSO_4^- , PF_6^- , $CH_3CO_2^-$.

chelate ring as indicated by the ring critical point [RCP (3, +1)].

According to the electron density $\rho(\mathbf{r})$ values and their corresponding Laplacian $\nabla^2 \rho(\mathbf{r})$, the positive electron energy $E_{\rm e}(\mathbf{r})$, and the $\nabla^2 \rho(\mathbf{r})$ value in BCP (NH···O), the hydrogen bond (NH…O) in the molecules 1-4 both in the gas phase and in DMSO solution has medium strength (that is, fall in the range 4–15 kcal/mol, Table 3) and generally follows the order $3 \ge 4 > 2 > 1$. In agreement with the experimental data (¹H NMR, vide infra) both optimized geometry and the AIM parameters show moderate (by 1.0-1.3 kcal/mol) weakening of the hydrogen bond in terms of PCM model calculations and a larger one (by 3-4 kcal/mol) in terms of combined PCM + SM approach. Note that molecule 1 forms a bifurcate hydrogen bond with DMSO in the intramolecularly H-bonded cisconformation (complex 1A-DMSO) and an intermolecular Hbond in the trans-conformation (complex 1B-DMSO) (Figure 1).

In a recent paper¹ we have shown experimentally the existence of equilibrium between the hydrogen-bonded cisconformers and nonbonded trans-conformers of compounds **1** and **3** in polar solvents such as acetone, pyridine, and DMSO, whereas in acetonitrile and methylene chloride only the hydrogen-bonded cis-form was observed. This allowed us to conclude that cis-trans equilibrium is assisted by intermolecular complexation with a basic solvent, in particular, with DMSO. The spectral evidence was the broadening of the ¹H NMR H-3 signals and the existence of cross-peaks between H-6 on the one hand and NH and H-3 on the other hand, in 2D NOESY spectra. The same spectral features are observed for compounds **2** and **4** (Figure 11 and Figure S1).

compd	r1, Å	r2, Å	r3, Å	ΔG° , kcal/mol	A-DMSO/B-DMSO (~300 K)
1A	1.797			4.53	~100:0
1A-DMSO	1.984	2.308		0.12	55:45
1B-DMSO			1.771		
2A	1.781			5.10	~100:0
2A-DMSO	1.971	2.314		0.85	80:20
2B-DMSO			1.737		
3A	1.754			6.89	~100:0
3A-DMSO	1.929	2.246		0.67	75:25
3B-DMSO			1.711		
4A	1.759			4.87	~100:0
4A–DMSO	1.958	2.282		1.39	91:9
4B-DMSO			1.733		

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Figure 3. UV–vis spectra of compounds 1, 2, 4 in MeCN ($C = 1 \times 10^{-4}$ mol/L).



Figure 4. UV–vis spectra of compound 1 with fluoride ion in MeCN: $1/Bu_4NF = 1:0$ (1), 1:1 (2), 1:10 (3), 1:20 (4), 1:30 (5), 1:50 (6), 1:100 (7), 1:200 (8).

The H-bonded cis-conformations of compounds 1-4 are much more stable than their trans-conformations both in the

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Figure 5. UV–vis spectra of compound 2 with fluoride ion in MeCN: $1/Bu_4NF = 1:0$ (1), 1:2 (2), 1:6 (3), 1:10 (4), 1:30 (5), 1:50 (6), 1:100 (7), 1:150 (8).



Figure 6. UV–vis spectra of compound **1** with acetate ion in MeCN: **1**/Bu₄Ac = 1:0 (1), 1:1 (2), 1:50 (3), 1:200 (4), 1:400 (5), 1:500 (6), 1:600 (7), 1:700 (8), 1:1000 (9).



Figure 7. UV–vis spectra of compound 4 with acetate ion in MeCN: $4/Bu_4NAcO = 1:0$ (1), 1:10 (2), 1:20 (3).

gas phase ($\Delta E = 8.1$ kcal/mol for 1) and in DMSO solution (5.2 kcal/mol, PCM model). Note that these values differ from the H-bond energies estimated from the AIM analysis (Table 3), thus proving that they include not only hydrogen bond energies but also various other interactions like dipole–dipole,

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Figure 8. ¹H NMR spectra of 1 in DMSO-d₆ (a) and with 20-fold excess of Bu₄NF in 1:1 CD₂Cl₂/DMSO-d₆ mixture at 260 K (b).



Figure 9. ¹H NMR spectrum of 1 in CD_2Cl_2 (a) and in DMSO- d_6 (b) in the presence of various amounts of Bu_4NF .

electrostatic, and hydrogen bonding between C-H-3 and carbonyl in the trans-conformation.

The position of the **A**-**B** cis \leftrightarrows trans equilibrium determined by the free energy difference (ΔG°) is strongly shifted to the left in the gas phase, whereas for the complexes of the two species with DMSO (**A**-DMSO and **B**-DMSO) the concentration of the trans-conformation **B**-DMSO is substantial or even almost equal to that of the cis-conformation **A**-DMSO (Table 4).

Interaction with Anions. UV-Visible Spectroscopy Study. The addition of various anions (Cl⁻, Br⁻, HSO₄⁻, PF₆⁻, F⁻, AcO⁻) in the form of the corresponding tetrabutylammonium salts (always the same thereinafter) to the DMSO solutions of compounds 1–4 was studied. It was found that the addition of the fluoride and, to a lesser extent, acetate ion causes color change as shown in Figure 2. In all other cases neither UV-vis nor ¹H NMR spectra show any changes.

Intense long-wave absorption bands in the UV–vis spectra of solution of compounds 1, 2, and 4 in acetonitrile have maxima at 427, 451, and 345 nm, respectively (Figure 3). Addition of fluoride ion to the solutions of compounds 1 and 2 in the molar ratio from 1:1 to 1:200 results in a decrease of the intensity of these bands and appearance and increase of the intensity of the bathochromically shifted bands (457 and 492 nm) due to electronic transitions in the corresponding anions (Figures 4 and 5).

The absence of clearly defined isosbestic points in the spectra in Figures 4 and 5 points to the participation of more than two forms in the reaction of substrates 1 and 2 with Bu_4NF (e.g., the starting neutral molecule and its anion in the cis- and transconformation). The maximum at 469 nm in the spectra of compound 2 with Bu_4NF in Figure 5 may just be suggestive of

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Figure 10. Low-field (left) and aromatic (right) parts of the ¹H NMR spectra of 1 in DMSO- d_6 upon addition of 0 (a), 1 (b), 2 (c), and 5 (d) equiv of Bu₄NF.

the appearance of the trans anionic conformation in the equilibrium.

Addition of tetrabutylammonium acetate to the acetonitrile solution of compound 1 results in similar changes of the spectrum of the neutral molecule as those occurring with fluoride ion (Figure 6) except for the fact that the equilibrium is strongly shifted toward the neutral form. As a result, even with large excess of acetate ion (1:1000) the maximum belonging to the anion of compound 1 (457 nm) is displayed only as a shoulder on the long-wave wing of the band of the starting molecule.

No changes occur in the spectrum of compound 4 in acetonitrile solution with equimolar amount of acetate ion. With 10-fold excess of AcO^- (Figure 7, spectrum 2) the intensity of the band at 345 nm decreases; a larger excess of the acetate ion (Figure 7, spectrum 3) leads to a further drop in intensity of this band, an increase of intensity of the bands at 412 and 572 nm, and appearance of an absorption band at 600 nm, responsible for the green color of the solution.

The acetonitrile solution of compound 4 reacts instantly with fluoride ion, turning from light-brown to blue-green and then to red-brown.

NMR Spectroscopy Study. ¹H NMR spectra of the solutions of compounds **1**, **2**, and **4** in DMSO- d_6 upon addition of excess Bu₄NF confirm the N-deprotonation of the pyrrole ring (Figures 8, 11, and S2). The NH signal at 12.9 ppm disappears and a new triplet signal corresponding to HF₂⁻ ion arises at 16.1 ppm. Delocalization of the negative charge over the whole molecule leads to a high-field shift of all protons except pyrrolic H-3, which moves to low field by about 1.2 ppm.

Dramatic changes of the ¹H NMR spectrum upon the formation of the anion deserve special consideration. Unlike neutral compound **1**, the cis-conformation of anion **1A** is unstable because of repulsive interaction between the negatively charged nitrogen and the carbonyl oxygen. On the contrary, the trans-conformation is stabilized by the C–H…O=C hydrogen bond as proved by a large low-field shift of H-3 (8.52 ppm) with respect to those of H-4 and H-5 (6.37 and 7.6 ppm, respectively):

Table 5. Geometric Parameters (in Å) of the Complexes 1-4 with Anions



		anion										
		Cl			Br			HSO ₄			AcO	
compd	r1	r2 ^a	r3	r1	r2 ^a	r3	r1	r2 ^b	r3	r1	r2 ^b	r3
$1A-X^{-}$	1.835	2.712		1.830	2.884		1.920	2.590		2.020	2.307	
$1B-X^{-}$			2.192			2.367			1.887			1.610
$2A-X^{-}$	1.823	2.680		1.820	2.865		1.899	2.573		2.017	2.338	
$2B-X^{-}$			2.190			2.358			1.782			1.576
$3A-X^{-}$	1.791	2.689		1.792	2.832		1.884	2.421		1.998	2.193	
$3B-X^{-}$			2.177			2.354			1.722			1.546
$4A-X^{-}$	1.800	2.690		1.801	2.861		1.903	2.446		2.012	2.245	
$4B-X^{-}$			2.183			2.360			1.737			1.561
1		$- > h_{-}$										

^aShort contact H-5–Cl(Br). ^bExternal component of bifurcate hydrogen bond for HSO₄ and AcO.



The B3LYP/6-311G(d,p) energy of anion 1 in the transconformation (1B) is 3.9 kcal/mol lower than that of the cisconformation.

Deprotonation of compound 1 in CD_2Cl_2 and $CDCl_3$ occurs only partially: addition of 60-fold excess Bu_4NF gives a mixture containing ~10% of the anion and ~90% of neutral 1 (Figure 9).

In DMSO- d_{6} , gradual addition of Bu₄NF (Figure 9) results in broadening and decreasing the NH signal of 1 at 12.8 ppm, which completely disappears in the presence of 3 equiv of Bu₄NF. Besides, a new signal appears at 12.0 ppm upon the addition of 0.5 equiv of Bu₄NF, reaching the maximum integral intensity with 1 equiv of Bu₄NF and disappearing also at 3-fold excess of Bu₄NF.

One can suppose that this new signal belongs to the transform of 1, hydrogen-bonded with DMSO (1B-DMSO) and existing in equilibrium with the nonbonded one (1B). The calculated NH chemical shift of 1B is 8.6 ppm, and that of 1B-DMSO is 13.2 ppm. The experimental chemical shift of 12.0 corresponds (assuming good agreement between calculated and experimental chemical shifts) to the constant of the equilibrium $1B + DMSO \Leftrightarrow 1B - DMSO$ equal to ~3, which seems quite reasonable because of the high concentration of DMSO. The addition of Bu₄NF facilitates transformation of 1A to 1B because of deprotonation of 1 by fluoride ion and free rotation about the $=C-C_{pyrr}$ bond. However, with large excess of DMSO (as a solvent) the equilibrium $1B^{-} \cdots HF + DMSO \Leftrightarrow$ **1B**-DMSO + F^- must be shifted to the right. This means that upon addition of up to 1 equiv of Bu₄NF the fluoride ion plays the role of a mediator and its complexes with 1B can be ignored (see Figure 8b). Further addition of Bu₄NF leads to deprotonation of 1B and an increase of concentration of the

more stable complex $[1B \cdots HF_2]^-$ having the calculated NH chemical shift of 18.2 ppm (see Figure 9c).

Titration of 1 with Bu₄NF in CD₃CN solution results in a similar signal appearing at 12.4 ppm, which disappears at the same excess of fluoride. However, the calculated NH chemical shift of 1B-MeCN is only 10.8 ppm (due to both a weaker coordination and the anisotropy contribution of the $C \equiv N$ bond) so that the experimental shift of 12.4 ppm cannot be obtained by averaging between 1B and 1B-MeCN, and one has to assume the presence of an additional species in the equilibrium with the NH chemical shift larger than 12.4 ppm. In our opinion, this may be complex $[1B - HF_2]^- (\delta_{NH} 18.2)$ ppm). Then the question arises: Why is it that titration with Bu₄NF in DMSO does not require invoking the hypothesis of the presence of the fluoride complex $1B^-...HF$, whereas in acetonitrile it cannot be avoided? Of course, in DMSO the complex $1B^-$... HF may also be involved in the equilibrium, but its role must be very limited because of much higher stability of the complex of 1B with DMSO than with MeCN.

Titration of 1 in CD_2Cl_2 was not carried out because the appearance of deprotonation product is observed only at large excess of fluoride and amounts to only 10%.

The observed solvent dependence may be explained by the existence of a significant amount of the trans-conformation in DMSO (see above), its small concentration in acetonitrile, and its complete absence in dichloromethane.

The interaction of 1 with excess of $[Bu_4N]OAc$ in DMSO and acetonitrile, as was mentioned above, results in deprotonation and formation of the anion which is proved by the identity of the ¹H NMR spectra in the presence of excess of $[Bu_4N]OAc$ and Bu_4NF .

The behavior of 2 in the presence of fluoride and acetate ions in the same three solvents is similar to that of 1. The ¹H NMR spectral patterns corresponding to the pyrrole part of both anions are identical (Figures 8 and 11).

However, the spectral patterns of aromatic moieties of the two anions are different (Figure 10). Whereas the signals of four aromatic protons of anion 1 form unsymmetric ABCD

Table 6. Complex Formation Energy $\Delta E_{\rm ZP}$, Free Energy ΔG° , and Intermolecular Hydrogen Bond Energy $E(_{\rm HB})$ for Interaction of 1–4 with Snions

complex	$\Delta E_{ m ZP}$, kcal/mol	ΔG , kcal/mol	E(_{нв}), kcal/mol
1A-Cl	2.8	8.2	
1B-Cl	-1.5	5.8	5.3
1A–Br	2.6	7.9	
1B–Br	-1.3	5.1	_
1A–HSO ₄	-2.5	6.7	
1B-HSO ₄	-10.8	1.2	6.8
1A–AcO	-6.6	3.1	
1B-AcO (1B ⁻ -AcOH)	-15.9	-5.3	19.0 (25.7)
1A ⁻ -HF	-29.4	-23.3	
1B ⁻ -HF	-40.5	-33.2	33.3
2A-Cl	2.6	8.3	
2B-Cl	-1.7	4.3	5.1
2A–Br	2.5	8.0	
2B-Br	-1.6	4.3	_
$2A-HSO_4$	-2.0	7.5	
$2B-HSO_4$	-7.9	1.9	8.3
2A–AcO	-6.6	3.5	
2B-AcO (2B ⁻ -AcOH)	-40.9	-34.0	21.4 (24.1)
$2A^{-}-HF$	-16.3	-6.3	
2B [−] −HF	-29.5	-23.0	31.4
3A-Cl	2.4	7.8	
3B-Cl	-1.3	4.6	5.6
3A–Br	2.4	8.2	
3B–Br	-1.2	4.4	-
3A–HSO ₄	-3.0	7.0	
3B-HSO ₄	-11.5	-1.1	12.2
3A–AcO	-7.5	3.2	
$3B-AcO(3B^AcOH)$	-31.0	-36.6	30.9 (21.7)
3A ⁻ -HF	-16.8	-7.0	
$3B^HF$	-32.9	-25.5	23.6
4A-Cl	2.6	3.1	
4B-Cl	-1.6	4.4	5.5
4A–Br	2.4	7.7	
4B–Br	-1.5	4.3	-
$4A-HSO_4$	-2.8	7.0	
4B–HSO ₄	-12.9	-0.5	11.4
4A–AcO	-7.1	3.4	, .
$4B-AcO$ ($4B^-AcOH$)	-16.5	-5.6	22.4 (21.9)
$4A^HF$	-32.5	-25.7	
4B [−] −HF	-27.9	-35.1	30.0

spin system, the similar protons of anion 2 form symmetric AA'BB' spin system (two multiplets at 7.57 and 8.08 ppm). Besides, H-4 and H-9 of the central benzene ring give one singlet, whereas in the neutral molecule they are nonequivalent. This may be the result of fast rotation of naphthindandione moiety around the C–C bond, which in turn arises from a larger than in 1 polarization of this bond due to more electron acceptor character of the aromatic fragment.

Complexes with Anions, Their Geometry, and Energy. Interaction of 1-4 in their cis- and trans-conformations with halide (Cl, Br, F), sulfate, and acetate ions was studied by quantum chemical (DFT) calculations. The geometric and energetic parameters of the complexes are collated in Table 5 (except those with fluoride anion, which in fact are complexes of anions 1B-4B with HF) and Table 6.

Optimized structures (PCM model, solvent DMSO) of the complexes formed by the cis-conformers 1A-4A with chloride

and bromide ions show the existence of short contacts between H-5 and halide ion (2.68-2.71 and 2.83-2.88 Å, respectively). The intramolecular N–H…O hydrogen bond length in these complexes remains the same as in free molecules. Sulfate and acetate ions form with **1A–4A** complexes possessing bifurcate hydrogen bonds with the internal components significantly longer than in the neutral precursors.

Short contacts between pyrrolic hydrogen and X⁻ of $1B-4B-X^-$ smaller than the sum of their van der Waals radii were found in all cases. AIM analysis reveals the existence of BCP in N-H…X fragment in all cases except Br⁻. The values of hydrogen bond energy of anion complexes of trans-conformers 1B-4B derived from BCP are given in Table 6.

As was mentioned above, the estimated acidity of NH hydrogen atoms is approximately the same for 1-4 (Table 2). The geometric (bond lengths) and energetic parameters of hydrogen bonds of 1B-4B with chloride anion are very close, and the same is true for geometry of bromide complexes. For acetate complexes, hydrogen bonds of 2B-4B are also very similar, both in energy $(E(_{HB}) = 21.4 - 23.6 \text{ kcal/mol}, \text{ Table 6})$ and in geometry (r3 = 1.546 - 1.576 Å, Table 5). In the case of sulfate complexes, both energies and bond lengths are quite different (6.8-12.2 kcal/mol and 1.722-1.887 Å, respectively). Because of additional hydrogen bond between carbonyl oxygen in 1B and 2B and sulfate OH group (Figure 11), the "main" hydrogen bond N-H…O became weakened and more bent. For similar complexes of sulfate with 3B and 4B additional hydrogen bond cannot be formed. It should be mentioned, however, that the calculated free energy of complexation ΔG° for all these complexes (both cis- and trans-, except transcomplexes with acetate and, in the cases of 3B and 4B, for sulfate anions) is positive, and hence, their concentration is very small. This explains the insensitivity of the studied substrates to chloride, bromide, and sulfate ions (Figure 2). The acetate complexes of 1A-4A are also unstable in spite of rather large negative ΔE values, whereas their trans-counterparts are very stable (Table 6). One can conclude that the studied pyrrole derivatives show the acetate sensing ability only being in the trans-conformation. Geometry optimization reveals a two-well potential for the hydrogen atom transfer in the acetate complexes with 1B-4B simulating the process of deprotonation: one minimum corresponds to a complex of NH-pyrrole with acetate and has the N-H bond of 1.07-1.08 Å, and the second one corresponds to a complex of pyrrolium anion with acetic acid and has the N-H distance of 1.59-1.60 Å (Figures 12 and S3). The difference of zero-point corrected energies between the two wells is 1.3 kcal/mol for 1, 1.07 kcal/mol for 2, 0.06 kcal/mol for 3, and 0.38 kcal/mol for 4 in favor of the N-H…OAc complex.

Fluoride ion abstracts the NH proton from molecules 1-4 in both the cis- and trans-conformations to form H-bonded complexes of pyrrolium anion with HF with large negative values of the total energy and free energies of complexation.

CONCLUSION

The strength of the intramolecular hydrogen bond $N-H\cdots O$ in the series of compounds 1-4, estimated as 10.3-11.9 kcal/mol in gas phase and methylene chloride solution, diminishes by about 1 kcal/mol in DMSO. This weakening paves the way to equilibrium between cis- and trans-conformers about the C-C bond supported by the intermolecular hydrogen bonding of pyrrolyl NH group with the solvent molecules. The presence of the trans-form in polar solvents facilitates complexation with



Figure 11. ¹H NMR spectra of 2 in DMSO- d_6 in the absence (a) and with 20-fold excess of Bu₄NF (b).



Figure 12. Optimized structures of 1B and 3B complexes with sulfate and acetate complexes.

fluoride and acetate anions followed by NH deprotonation of pyrrole moiety. This fact, as well as the instability of the similar complexes with other studied anions (Cl, Br, and HSO_4), allows for considering compounds 1-4 as perspective fluoride and acetate sensors. The relevant investigations of sensing properties of this series compounds and pyrrole substituted analogues are in progress, and their results will be published elsewhere.

ASSOCIATED CONTENT

Supporting Information

¹H NMR spectrum of 4 in DMSO- $d_{6^{1}}$ ¹H NMR spectrum of 4 with excess Bu₄NF, potential curve simulating proton transfer in the complex **1B**-AcO⁻, and full citation of ref 16. This material is available free of charge via the Internet at http:// pubs.acs.org.

Article

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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