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Intramolecular Hydrogen Bonding and Anion Binding of *N*-Benzamido-*N*′-benzoylthioureas

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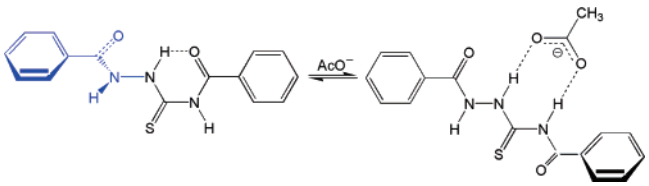

N-(*p*-Dimethylamino)benzoyl-*N*′-phenylthiourea as an *N*-acylthiourea is known to be unable to bind anions due to a strong intramolecular hydrogen bond (IHB). We show here that by inserting an amido group in the *N*′-phenyl side the newly designed *N*-benzamido-*N*′-benzoylthioureas, despite this IHB too, bind strongly to anions with binding constants on the order of 10^6-10^7 mol^{-1} L. Results suggest that potential anion receptors or organocatalysts could be developed on the basis of this framework with a wide structural diversity.

Thiourea has been a subject of intensive investigations for its performance in the construction of anion receptors via double hydrogen-bonding interaction by thioureido −NH donors.[1] This interest has recently been enhanced because of the promising progress in the thiourea-based organocatalysts again via hydrogen bonding.[2] Obviously, the hydrogen-bonding ability of the thiourea moiety is an important parameter, which in principle depends on the acidity of thioureido −NH protons and the number of binding sites. From a structural point of view, a direct means of tuning this acidity is to introduce a substituent of varied electron-donating or -withdrawing ability. *N*-Alkyl and/or *N*-aryl substitutions (such as **1**, Figure 1) have been the main choices in this regard and indeed led to great success in design and

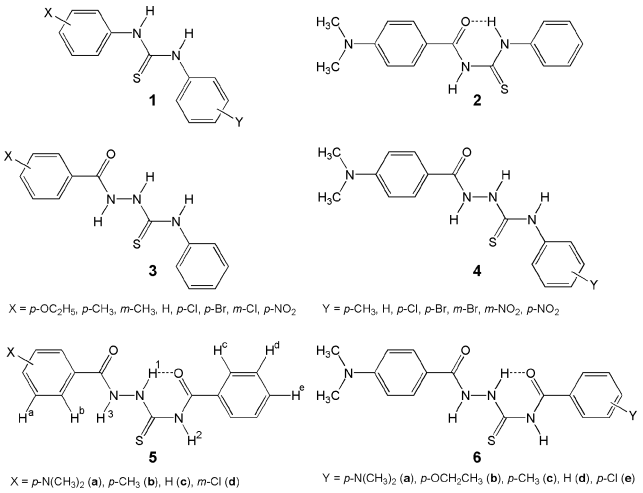

FIGURE 1. Chemical structure of thiourea-based receptors. Numbering of −NH's and aromatic protons is given in **5**.

applications of thiourea-based anion receptors.[1] In order to enhance the acidity of thioureido −NH protons and to introduce additional hydrogen-bonding sites, we have alternatively explored anion binding performance of *N*-(*p*-dimethylaminobenzoyl)thiourea (**2**, Figure 1),[3] an *N*-acylthiourea. Unfortunately, no response in its absorption and fluorescence spectra toward anions was observed. This was rationalized to result from a strong intramolecular hydrogen bond (IHB) between a carbonyl O atom and a thioureido −NH proton (Figure 1). To prevent this IHB, we extended to examine *N*-benzamidothioureas (**3** and **4**, Figure 1) by inserting an "−NH−" between the carbonyl group and thiourea moiety.[4] Compared with classical *N*-phenylthioureas **1**, *N*-benzamidothioureas **3** and **4** bearing an additional amide group showed a dramatically increased anion affinity and a more substantial spectral variation upon anion binding. This is peculiar since the thioureido −NH protons in **3** and **4** are not of higher acidity. It was concluded that this was due to anion binding induced N−N conformation change and the resultant intramolecular charge transfer (ICT) in the anion binding complex. Inspired by and attempting to clarify the possible contribution of this additional amide group in

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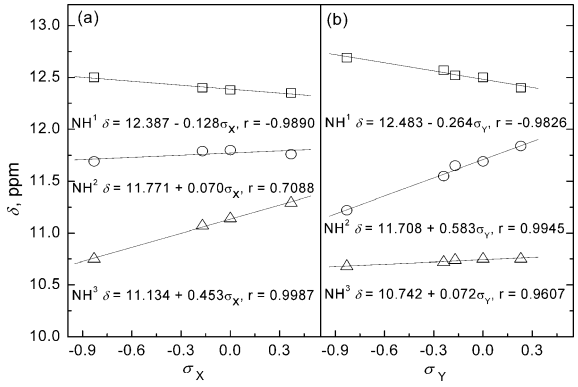

FIGURE 2. Chemical shifts of −NH protons in DMSO-d_6 versus Hammett constant of substituent X in **5** (a) and Y in **6** (b). For numbering of −NH protons, see Figure 1 for **5**.

promoting anion binding of thiourea-based receptors, we envisaged to insert an amide group into **2**-like *N*-acylthioureas to have *N*-benzamido-*N*′-benzoylthioureas (**5** and **6**, Figure 1). By doing so, the acidity of the thioureido −NH protons and the number of hydrogen-binding sites in **5** and **6** are also made higher than those in **3** and **4**, favoring not only anion receptor designing but organocatalyst development as well. Certainly, an IHB characteristic of *N*-acylthioureas such as **2** was expected for **5** and **6** that may prevent anion binding of multiple hydrogen-bonding nature.[3,4] Indeed, the crystal structure of **5c** confirmed the existence of this IHB.[5] We report here that **5** and **6**, despite the existence of such a strong C═O···HN IHB, do show in their absorption spectra sensitive response toward model anions AcO^-, F^-, and $H_2PO_4^-$ with elevated binding affinity by up to 1 order of magnitude than that of **3** and **4**.

^{1}H NMR signals of −NH protons in **5** and **6** in DMSO-d_6 were found at lower field than those of **3** and **4**. This is likely due to the IHB in **5** and **6** depicted in Figure 1 and the additional carbonyl group. Figure 2 shows that the chemical shifts of the −NH protons in **5** and **6** vary linearly with the Hammett constant (σ) of substituent X or Y. The slopes of the chemical shift of $-NH^1$ against $\sigma_{X(Y)}$ are both negative, confirming that the $-NH^1$ proton is indeed involved in an IHB (Figure 1).[4,6] It is also noted that the slope of −0.264 versus σ_Y is more negative than that of −0.128 versus σ_X. This means that, with varying X or Y from electron-donating to -withdrawing, the $-NH^1\cdots O{=}C$ IHB is weakened and substituent Y in **6** exerts a slightly stronger influence on this IHB. The linear slopes of the chemical shifts of $-NH^2$ and $-NH^3$ protons in **5** against σ_X are 0.070 and 0.453, while those in **6** versus σ_Y are 0.583 and 0.072, respectively (Figure 2). These slopes are comparable to those of **3** of 0.0977 and 0.463[4d] and of **4** of 0.523 and 0.125,[3] respectively. Substantially different slopes in the two sets of NMR data of non-hydrogen-bonded $-NH^2$ and $-NH^3$ protons in **5** and **6** again probe the twisted conformation of the N−N single bond that stops to some extent the electronic communication of the substituent effect, a character prevailing in neutral hydrazines[7,8] and reported for **3**[4d] and **4**.[3] It could be similarly expected[3,4]

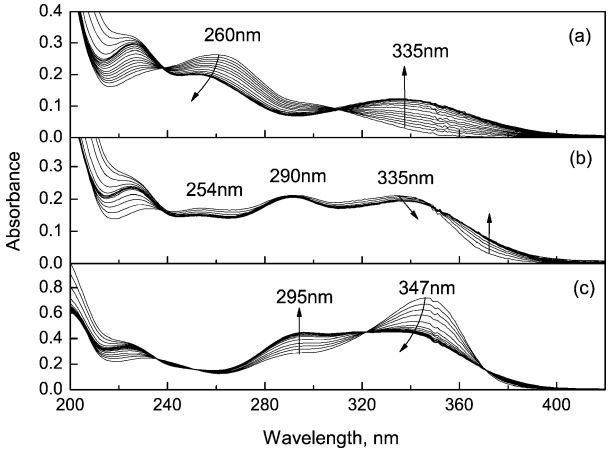

FIGURE 3. Absorption spectra of (a) **5c** (1.00×10^{-5} mol L^{-1}), (b) **5a** (8.76×10^{-6} mol L^{-1}), and (c) **6a** (1.30×10^{-5} mol L^{-1}) in MeCN in the presence of increasing concentration of AcO^-.

that no absorption signal change would be observed upon anion binding to the thiourea moiety in **5** and **6** as it is decoupled from the *N*-benzamido chromophore signal reporter. The intercepts of the aforementioned linear correlations for **5** and **6** are respectively higher than those of **3** and **4**, indicating the expected higher acidity of these non-hydrogen-bonded −NH protons in **5** and **6**.

It was previously reported that, due to such a strong NH···O═C IHB in **2**, no response toward an anion in both its absorption and fluorescence spectra in acetonitrile (MeCN) was observed.[3] The absorption spectra of **5** and **6**, however, do show a sensitive response to anions (Figure 3). Note that the observation of isosbestic points in the titration traces points to the formation of well-defined anion binding complexes which are later shown to be in 1:1 stoichiometry by Job plots. Molecules in **5** and **6** can be divided into three subgroups on the basis of their spectral characteristics. The first group includes **5b**−**d** without substituent *p*-$N(CH_3)_2$, whose absorption maxima are at ca. 260 nm, originating from the benzamide chromophore. With increasing AcO^- concentration, the absorbance at 260 nm of **5b**, for example, decreases while a new band at 335 nm develops (Figure 3a). The second group includes **5a** and **6b**−**e**, which bear one *p*-$N(CH_3)_2$. When AcO^- is introduced, their absorption spectra, which peaks at 290 and 335 nm (Figure 3b) due to the charge-transfer chromophore *p*-(dimethylamino)-benzamide (DMABA),[3,4e] undergo relatively minor variations by a decrease in the absorbance at maximum and an enhancement in absorption between 350 and 400 nm. **6a** is in the third group, which contains two *p*-$N(CH_3)_2$ and shows its absorption maximum at 347 nm (Figure 3c). This is longer than that with one DMABA chromophore (335 nm, **5a** and **6b**−**e**), which is presumably assigned to *J*-aggregates[9] of two DMABA chromophores with a *J*-splitting of 0.26 eV.[10] In the presence of AcO^-, the absorption shifts to blue at 335 nm and the absorbance at 347 nm decreases and a new band at 295 nm appears (Figure 3c). It is also found that with **5b**−**d** the new

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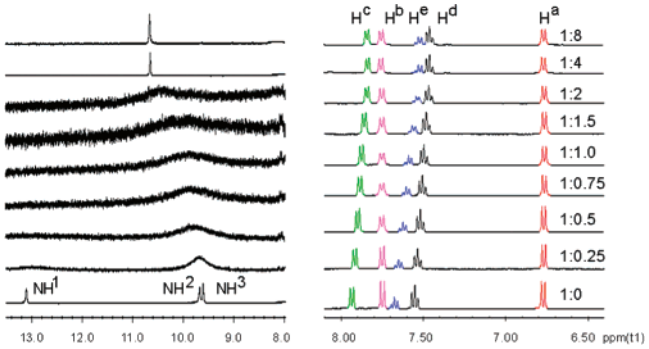

FIGURE 4. Traces of ^{1}H NMR titration of **5a** in CD_3CN of −NH protons and aromatic −CH protons. [**5a**] = 15 mmol L^{-1}, and concentration ratio of **5a** to F^- is given in the figure. For numbering of −NH and aromatic protons, see Figure 1 for **5**.

absorption band in the presence of an anion appears at longer wavelength with decreasing electron-donating X, thereby suggesting the charge-transfer character of this new band as was shown in the case of **3**.[4d] Spectral variation profiles of **5** and **6** in the presence of F^- and $H_2PO_4^-$ are similar to those of AcO^-, whereas Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, and ClO_4^- exert no influence on the absorption spectra (Figure S1, Supporting Information). It is therefore likewise concluded that the anion binding mode and its consequence with **5** and **6** are similar to those with **3** and **4** and that anion binding is of multiple hydrogen-bonding nature and anion binding induces a conformation change in the N−N single bond that establishes electronic communication of the anion binding site with the chromophore in the anion binding complexes.[3,4] As an IHB exists in **5** and **6** that would, in principle, prevent multiple hydrogen-bonding interaction with anions, breaking of this IHB is assumed to occur upon anion binding.

Interaction of anions with **5** and **6** was further probed by ^{1}H NMR titrations in CD_3CN. Figure 4 shows, as an example, NMR traces of **5a** titrated by F^-. Similar profiles were found with AcO^- and $H_2PO_4^-$. It is evident in Figure 4 that the signal of $-NH^1$ at 13.10 ppm disappears upon F^- titration, while those of $-NH^2$ and $-NH^3$ at 9.69 and 9.62 ppm mix and shift downfield to 10.66 ppm. In the case of AcO^- and $H_2PO_4^-$, they mix and finally disappear. These observations indeed report the breaking of C═O···HN IHB in **5a** upon anion addition and the hydrogen-bonding interaction of **5a** with F^-. Accordingly, the signal of aromatic proton H^b in the *N*-benzamido moiety shows a slight downfield shift, whereas those of protons H^a in the *N*-benzamido moiety and H^c, H^d, and H^e in the *N*′-benzoyl moiety undergo various degrees of upfield shifts.

Job plots indicate a 1:1 stoichiometry in anion binding to **5** and **6** in MeCN. Anion binding constants of **5** and **6** were obtained by nonlinear fittings[11] of their absorbance variations against anion concentration (Table 1). Comparing data compiled in Table 1 with those of **3**[4d] and **4**,[3] it is obvious that the binding constants of **5** and **6** at 10^6-10^7 mol^{-1} L are higher, by up to 1 order of magnitude, than those of **3** and **4**. It is interesting to note that the AcO^- binding constants of **5** and **6** depend very little on X or Y in both pure MeCN and 5% H_2O−MeCN in which the binding constants are 2 orders of magnitude lower than those in pure MeCN (Table S1, Supporting Information).

TABLE 1. Anion Binding Constants of 5 and 6 in MeCN

	K_a, 10^6 mol^{-1} L		
	AcO^-	F^-	$H_2PO_4^-$
5a	7.02 ± 2.23	2.23 ± 0.59	0.271 ± 0.032
5b	6.53 ± 1.26	5.49 ± 0.32	0.725 ± 0.12
5c	9.72 ± 1.99	3.62 ± 0.64	1.17 ± 0.23
5d	13.6 ± 6.3	4.23 ± 1.12	0.598 ± 0.047
6a	6.90 ± 1.13	3.18 ± 0.73	0.304 ± 0.018
6b	16.7 ± 4.2	8.93 ± 2.99	0.962 ± 0.327
6c	4.56 ± 0.75	4.73 ± 1.03	0.975 ± 0.497
6d	7.02 ± 2.23	2.23 ± 0.59	0.271 ± 0.032
6e	19.6 ± 3.7	3.67 ± 0.54	1.16 ± 0.62

While substituent dependence of K_a of **5** is similar to that of **3**,[4d] it differs, however, substantially for **6** compared to **4** which showed an enhanced substituent effect on the anion binding constant.[3] The latter was previously attributed to a positive feedback of the anion binding induced N−N conformation change.[4d]

It deserves pointing out that both the chemical shifts of hydrogen-bonded $-NH^1$ and non-hydrogen-bonded $-NH^2$ protons in **6** are sensitively, despite to a varied extent, subject to Y (Figure 2b). The fact that the anion binding constants of **6** show practically no dependence on Y indicates that the observed spectral variations in **6** upon anion binding are not due to deprotonation of $-NH^2$,[12] and the positive feedback toward anion binding resulting from the anion binding induced N−N conformation change is absent with **6**. Since X or Y exerts essentially no influence on anion affinity of **5** or **6**, the aliphatic counterparts of them are expected to possess similar binding or hydrogen-bonding capacity. This offers a promising chance for creating **5**-/**6**-like thiourea-based potential organocatalysts, for example, the well-known proline derivatives[13] of **5** and **6** could well be the earlybirds of this kind.

Because of the high anion binding constants in MeCN and the concern of solvent dehydration in hydrogen-bonding-based organocatalysis, anion binding in H_2O-containing MeCN was examined. It was found that binding of AcO^- with **5d**, for example, could efficiently occur in MeCN containing up to 20% H_2O (v/v, Figure S4, Supporting Information), with K_a values of (1.36 ± 0.63) × 10^7, (5.76 ± 0.65) × 10^6, (5.90 ± 0.56) × 10^5, (1.97 ± 0.20) × 10^5, (1.51 ± 0.19) × 10^5, and (3.30 ± 0.94) × 10^4 mol^{-1} L, in MeCN containing 0, 1, 5, 10, 15, and 20% H_2O, respectively. This implies that **5** and **6** have a higher capability of competing with H_2O for anion binding, a character significant for anion receptors for practical use and for easy organocatalytic applications in organic solvents in terms of solvent dehydration.

In summary, we found that, despite the fact that no anion binding was previously observed with *N*-benzoyl-*N*′-phenylthiourea (**2**) due to a strong IHB, highly efficient anion binding occurred with the newly designed *N*-benzamido-*N*′-benzoylthioureas (**5** and **6**) bearing this IHB too. The anion affinity is

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(12) Absorption and NMR titrations of **5a** in MeCN and CD_3CN, respectively, by OH^- and F^- were carried out up to high anion concentrations. Whereas an additional "abnormal" red shift was observed in the absorption of **5a** at OH^- concentration of 40 equiv, a phenomenon ascribed to deprotonation by the highly basic anion,[1b] no such red shift was noted in the case of F^- at up to 140 equiv (Figure S2, Supporting Information). In NMR titration traces, an $-NH$ signal could be seen in the presence of up to 40 equiv of F^-, whereas it disappears when OH^- was introduced; in the aromatic proton portion, variation profiles of proton H^c start to differ at OH^- of 10 equiv (Figure S3, Supporting Information).

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even higher by up to 1 order of magnitude than that of the corresponding *N*-benzamido-*N*′-phenylthioureas (**3** and **4**) without such an IHB. Actually, an efficient anion binding could be easily observed in the presence of water of 10% by volume, for instance. The anion binding constants of **5** and **6** were found to be independent of substituent X or Y, the latter differing strikingly from that of **4**, whose anion binding showed an enhanced Y dependence. Breaking of the IHB that exists in **5** and **6** was therefore revealed to occur upon anion binding. The N−N single bond in **5** and **6** was shown to be twisted and stops electronic communication of the thiourea moiety as the anion binding site with the *N*-benzamido moiety, and the anion binding results in a conformation change in the N−N single bond that couples these two moieties. This N−N conformation change, however, shows no positive feedback to enhance the Y dependence of the anion affinity of **6**. As the *cis*-conformation of the thioureido −NH protons is required in their binding to anions or other hydrogen-bonding acceptors,[14] breaking the IHB in **5** and **6** shall also be accompanied by a rotation of the IHB involved benzamide moiety,[15] in addition to the aforementioned N−N conformation change. Whether these conformational changes contribute to the enhancement of the anion binding ability of **5** and **6** is not yet clear; it however deserves further efforts. It is interesting to note that indeed the structural difference of an additional amide group (−C(O)NH−) between **5**/**6** and **2** and between **3**/**4** and **1** appears to play a role in anion binding promotion in thiourea-based receptors. This component is thus likely useful in future development of the thiourea-based anion receptors and organocatalysts. In this connection, since both substituents X and Y do not exert influence on anion binding of **5** and **6**, more diverse structures can be developed; in particular, aliphatic counterparts of them could similarly work well in solvents not necessarily dehydrated for the sake of hydrogen-bonding interaction.

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(15) In the anion binding complex, the C═S and C═O bonds shall be unparallel. This was also indicated by the observed anion-dependent upfield shifts in the NMR signals of aromatic protons in the *N*′-phenyl rings of **6a** and **6d**. In the case of **6d** with substituent Y = H, anion induced upfield shifts become increasingly higher when the anion varies from F^- to AcO^- to $H_2PO_4^-$ of decreasing electron density, whereas with **6a** bearing a highly electron-donating Y of *p*-$N(CH_3)_2$, this anion dependence is not that much (Table S2, Supporting Information).

Experimental Section

General Procedures for Synthesis of *N*-(Substituted benzamido)-*N*′-(substituted benzoyl)thioureas. Substituted benzoic acid (3.0 mmol) was added to an excess amount of $SOCl_2$, and the solution was refluxed for 8 h. After excess $SOCl_2$ was removed under reduced pressure, benzoyl chloride was obtained. The freshly prepared chloride was slowly added to a stirred dry MeCN (5.0 mL) solution of ammonium isothiocyanate (4.5 mmol) at 0 °C followed by refluxing for 8 h. On cooling to room temperature, solid precipitate was collected and washed with dry MeCN. Filtrate was reacted under refluxing with substituted *N*-benzoylhydrazide (3.0 mmol) in MeCN for 8 h. White or light yellow solid was filtered and recrystallized three times from THF−EtOH−H_2O (6:3:1, v/v/v) to afford the corresponding crystal product.

Spectral Investigations. UV−vis spectra were recorded using a 1 cm quartz cell. ^1H and ^{13}C NMR spectra were obtained on a 400 MHz NMR spectrometer in DMSO-d_6 or CD_3CN using TMS or using residual solvent peak as an internal standard. HRMS data were recorded on a high-resolution mass spectrometer by injection of sample solution in methanol. Absorption and NMR titrations for anion binding were carried out by adding an aliquot of anion solution into the bulk receptor solution at a given concentration. Tetrabutylammonium salts of the anions were prepared by neutralization of the corresponding acids with *n*-$Bu_4N^+OH^-$.

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Supporting Information Available: Characterization data and ^1H and ^{13}C NMR spectra of **5** and **6**. Absorbance of **5** and **6** against anion concentration in MeCN and of **5d** against [AcO^-] in H_2O−MeCN. Substituent dependence of AcO^- binding constants of **3**, **4**, **5**, and **6** in MeCN and of **5** and **6** in 5% H_2O−MeCN. Absorption (MeCN) and NMR (CD_3CN) spectra of **5a** in the presence of F^- and OH^-. Anion induced upfield shifts of the NMR signals of aromatic protons in the *N*′-phenyl rings of **6a** and **6d** in CD_3CN. This material is available free of charge via the Internet at http://pubs.acs.org.

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