chloroform–ethyl acetate); ^{1}H NMR (CDCl$_3$) δ 4.80 [s, 1 H, H-1 (α-anomer)], 4.75 [d, 1 H, $J_{1,2}$ = 4.4 Hz, H-1 (β-anomer)], 4.10–4.25 (m, 2 H, H-2, H-3), 3.7–3.99 (m, 3 H, H-4, H-5,5$_a$), 3.40 (s, 3 H, OCH$_3$), 1.04–1.1 (m, 28 H, (CH$_3$)$_2$CH). Anal. Calcd for $C_{18}H_{38}O_6Si_2$: C, 53.16; H, 9.42. Found: C, 53.02; H, 9.47.

Methyl 2-*O*-Acetyl-3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-β-D-arabinofuranoside (15). By the same procedure as described for **11**, 81 mg (0.2 mmol) of methyl 3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-α,β-D-arabinofuranosides (**14**) was acetylated with 0.2 mL (2 mmol) of acetic anhydride in 4 mL of dry pyridine to yield 63 mg (70%) of the β-acetate **15** (the only anomer isolated): $[\alpha]^{22}{}_D$ −54.9° (*c* 1, chloroform); R_f 0.50 (chloroform); GC/MS (k' = 32.8), m/z (relative intensity) 417 (4, M − OCH$_3$), 405 (4, M − (CH$_3$)$_2$CH), 345 (4), 291 (12), 277 (100), 116 (30), 43 (19, (CH$_3$)$_2$CH); ^{1}H NMR (CDCl$_3$) δ 5.16 (dd, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 5.3 Hz, 1 H, H-2), 4.77 [d, 1 H, H-1 (β-anomer)], 4.31 (ψt, $J_{2,3} = J_{3,4}$, 1 H, H-3), 3.92–4.02 (m, 3 H, H-4, H-5,5a), 3.38 (s, 3 H, OCH$_3$), 2.1 (s, 3 H, CH$_3$CO), 1.0–1.1 (m, 28 H, (CH$_3$)$_2$CH). Anal. Calcd for $C_{20}H_{40}O_7Si_2$: C, 53.53; H, 8.99. Found: C, 53.70; H, 9.06.

Methyl 2-Chloro-2-deoxy-3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-α-D-ribofuranoside (17). A 203-mg (0.5-mmol) sample of methyl 3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-α,β-D-arabinofuranosides (**14**) was transformed to 172 mg (81%) of methyl 2-chloro-2-deoxy-3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-α-D-ribofuranoside (**17**) via the triflate **16**, following the procedure described under **13-C**: $[\alpha]^{22}{}_D$ +11.6° (*c* 1, chloroform); R_f 0.71 (8:2 chloroform–toluene); GC/MS (k' = 18.7), m/z (relative intensity) 381 (28, M − (CH$_3$)$_2$CH), 349 (16), 321 (39), 249 (100); ^{1}H NMR (CDCl$_3$) δ 5.08 (d, $J_{1,2}$ = 4.0 Hz, 1 H, H-1), 4.39 (ψt, $J_{2,3} = J_{3,4}$ = 6.4 Hz, 1 H, H-3), 4.30 (dd, J = 6.3 Hz, H-2), 4.08 [m, (width 15 Hz), 1 H, H-4], 3.96 [m, 2 H, (AB of ABX, $J_{5,5a}$ = 12.6 Hz, $J_{4,5}$ = 3.0 Hz, $J_{4,5a}$ = 5.4 Hz), H-5,5a], 3.50 (s, 3 H, OMe), 1.03–1.08 [m (4 lines), 28 H, (CH$_3$)$_2$CH]. Anal. Calcd for $C_{18}H_{37}ClO_5Si_2$: C, 50.85; H, 8.77. Found: C, 50.97; H, 8.77.

1,3,5-Tri-*O*-acetyl-2-chloro-2-deoxy-α,β-D-ribofuranoses (5). 1,3,5-Tri-*O*-acetyl-2-chloro-2-deoxy-α,β-D-ribofuranoses (**5**) were obtained in 89% yield (62 mg) from the acetolysis of 100 mg (0.24 mmol) of methyl 2-chloro-2-deoxy-3,5-*O*-(tetraisopropyldisiloxane-1,3-diyl)-α-D-ribofuranoside (**17**), performed in a similar fashion as described for **13**. The spectroscopic, chromatographic and optical rotation {$[\alpha]^{22}{}_D$ +35.8° (*c* 1, chloroform)} data were found to be identical with those obtained for the product from the acetolysis of **3**. (For a comparison of ^{1}H NMR spectra, see Figure 1.)

Acknowledgment. J. B. Tunac and F. A. MacKellar and their respective microbiology and physical chemistry groups at Warner-Lambert/Parke-Davis are thanked for the valuable contributions to this work. The technical assistance of S. Stampwala in carrying out early aspects of this work is acknowledged. F. Parker of the University of Michigan is thanked for the 360-MHz NMR spectra. E.S. thanks the Graduate School, University of Alabama, for support as a Graduate Council Research Fellow. A portion of this work was supported in part by Contract NO1-CM-37614 awarded to Warner-Lambert/Parke-Davis by the National Cancer Institute.

A ^{13}C NMR Study of Electronic Effects in the Hydrogen Bonding of Trifluoroacetic Acid with Substituted Benzenes, 1- and 2-Substituted Naphthalenes, and 9-Substituted Anthracenes in Chloroform

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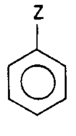
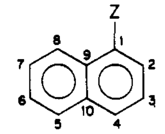
Received August 23, 1984

Considerable changes are produced in the ^{13}C chemical shifts of monosubstituted benzenes, 1- and 2-substituted naphthalenes, and 9-substituted anthracenes bearing the COCH$_3$, CO$_2$CH$_3$, CHO, OCH$_3$, and CN substituents on titrating with trifluoroacetic acid in deuteriochloroform. These shift displacements are interpreted in the light of electronic and steric effects associated with the formation of hydrogen bonds.

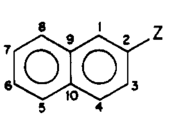
Titrating the weak bases, **1**–**4**, with trifluoroacetic acid (hereafter TFA) in deuteriochloroform causes considerable displacements of their ^{13}C NMR signals as a result of hydrogen bonding. In a previous paper[1] methods were described for using such changes in shift to calculate the values of equilibrium constants corresponding to the formation of various hydrogen-bonded aggregates. It is the purpose of the present work to try to gain some insight into the electronic and steric factors associated with the formation of hydrogen bonds in these systems through a more detailed analysis of their ^{13}C NMR shifts.



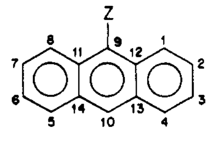
1a, Z = COCH$_3$
b, Z = CO$_2$CH$_3$
c, Z = CHO
d, Z = CN
e, Z = OCH$_3$



2a, Z = COCH$_3$
b, Z = CO$_2$CH$_3$
c, Z = CHO
d, Z = CN
e, Z = OCH$_3$
f, Z = NO$_2$
g, Z = SCH$_3$



3a, Z = COCH$_3$
b, Z = CO$_2$CH$_3$
c, Z = CHO
d, Z = CN
e, Z = OCH$_3$
f, Z = NO$_2$



4a, Z = COCH$_3$
b, Z = CO$_2$CH$_3$
c, Z = CHO

Earlier studies have shown[2,3] that the ^{13}C chemical shifts of carbonyl and methoxy substituents in aromatic systems are not the same for the in-plane as for the out-of-plane geometries. Therefore, differences in the average conformations of many of the basic substituents of the series **1**–**4** in solution may be readily recognized by observing the relative positions of their ^{13}C resonances. As seen in Table I the carbonyl shifts of formyl, acetyl, and methyl carboxylate substituents, as well as the methyl shifts of these

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Table I. ^{13}C Chemical Shifts[a] of the Substituents of Substituted Benzenes, 1, 1- and 2-Substituted Naphthalenes, 2 and 3, and 9-Substituted Anthracenes, 4, in Deuteriochloroform

	Z				
compd	CH_3O	CN	CHO	$COCH_3$	CO_2CH_3
1	55.08	118.83	192.24	198.06, 26.54[b]	167.09, 52.02[b]
2	55.44	117.76	193.41	201.71, 29.91[b]	167.97, 52.06[b]
3	55.31	119.17	192.18	197.94, 26.59[b]	167.19, 52.12[b]
4[c]	63.10	117.14[d]	192.75	204.35, 33.79[b]	170.02, 52.51[b]

[a] In parts per million downfield from tetramethylsilane; 0.5 M solutions. [b] The shift of the methyl resonance. [c] From ref 23. [d] The shift for a saturated solution of the base, about 0.3 M.

groups, are nearly identical for benzenes **1** and 2-substituted naphthalenes **3**, in both of which the substituents are believed to lie within the aromatic planes.[2a,4,5] For **2** and **4**, however, for which out-of-plane conformations have been reported,[4b,6,7] these shifts appear further downfield. Such differences in chemical shift are accounted for by differences in electron density at the carbons of these substituents, a lowering of electronic charge being associated with diminished electron delocalization from the aromatic rings for those groups which are rotated out of the molecular plane.[2,8] Larger torsional angles should then give rise to more downfield ^{13}C chemical shifts and this is clearly the case for **1a–c–4a–c** as demonstrated by the series of carbonyl shifts 198.1, 197.9, 201.7, and 204.4 ppm of the methyl ketones **1a**, **3a**, **2a**, and **4a**, respectively, the magnitudes of which follow the order of increasing torsional angles reported for the acetyl substituents of these bases in solution:[2a,4b,6a] 0°, 0°, 31°, 80°. The same qualitative trends are noted for the methyl resonances of **1a–4a** and for the carbonyl shifts of the esters and aldehydes **1c–3c**.

The methyl ethers **1e**, **2e**, and **3e** exhibit "normal" methoxy chemical shifts of about 55 ppm,[3c] typical of coplanar aryl methoxy conformation.[7,9] In **4e**, however, the methoxy substituent is clearly out-of-plane because its resonance is shifted to lower field by 8 ppm. A torsional angle of 86° has been reported[7] for this group.

Conformational variations of this sort are of interest in a study of hydrogen bonding because they could affect the basicity of the electron pair donor and hence the strength of the hydrogen bond.[10] They might also have a bearing on the orientation of the proton donor in the hydrogen bonded complexes.

Results

For each solution in the titration of bases **1–4** with TFA in deuteriochloroform equilibria, 1a,b apply.

$$B + A \overset{K_1}{\rightleftharpoons} B{\cdot}A \tag{1a}$$

$$B + A_n \overset{K_n}{\rightleftharpoons} B{\cdot}A_n \tag{1b}$$

Here B, A, and A_n are molecules of base, TFA monomer, and acid polymer, respectively, and BA and BA_n are molecules of the corresponding hydrogen-bonded complexes. The mole fraction, f, of base in complexed forms, BA and BA_n, is

$$f = (\delta - \delta_B^\circ)/\Delta_n \tag{2}$$

where η_B° and δ are the measured chemical shifts of one of the ^{13}C resonances of the base dissolved in deuteriochloroform and in deuteriochloroform plus TFA, respectively, and Δ_n is the change in the shift associated with a change of solvent from deuteriochloroform to neat TFA at the same base concentration.

For each base the ^{13}C resonance chosen to monitor the extent of acid–base complexing is that of a carbon atom far removed from the complexing site but one having a substantial hydrogen-bonding shift, Δ_n. This is the shift of carbon 4 in benzenes **1** and in 1-substituted naphthalenes **2** and of carbons 6 and 10 respectively in 2-substituted naphthalenes **3** and 9-substituted anthracenes **4**. These resonances are assumed to have the same shift in both the hydrogen-bonded forms, BA and BA_n, and to be otherwise insensitive to the changing solvent throughout the titrations. These assumptions are supported by the values of pK_1 (eq 1a) calculated[1] for benzenes **1**, which correlate linearly with those of pK_{HB}, the corresponding equlibrium constant for 1:1 complex formation with *p*-fluorophenol in carbon tetrachloride.[11] Such a correlation also implies that there is no significant formation of hydrogen-bonded ion pairs in these solutions,[11] a fact confirmed by the absence of the peak at 1668 cm^{-1} for the trifluoroacetate anion[12] in the infrared spectra of the acid–base solutions. The increases by about 15 cm^{-1} in the stretching frequencies of the cyano substituents and the 20–60 cm^{-1} decreases in those of the carbonyl bonds on titrating carbon tetrachloride solutions of the respective bases with TFA also are of a magnitude quite typical of hydrogen bond formation.[13,14]

In the absence of medium effects other than hydrogen bonding with TFA, the chemical shift, δ, of each carbon of base dissolved in deuteriochloroform with TFA is the time-averaged value of its shift in the free and associated forms, B, BA, and BA_n:

$$\delta = f_B\delta_B^\circ + f_1\delta_1^\circ + f_n\delta_n^\circ \tag{3}$$

where f_B, f_1, and f_n are the mole fractions of base, B, and of the 1:1 and polymeric complexes, BA and BA_n, respectively, and δ_B°, δ_1°, δ_n° are the chemical shifts of that carbon in each of these species. Using $f = (1 - f_B) = f_1 + f_n$, gives eq 4 from 3:

$$\Delta\delta/f = (\delta - \delta_B^\circ)/f = f_1(\Delta_1^\circ - \Delta_n^\circ)/f + \Delta_n^\circ \tag{4}$$

where Δ_1° (= $(\delta_1^\circ - \delta_B^\circ)$) and Δ_n° (= $(\delta_n^\circ - \delta_B^\circ)$) are the shifts of the carbon resonance in complexes BA and BA_n relative to its shift in the free base, B. Values of these hydrogen-bonding shifts can be obtained for each carbon of base from the slope and intercept of a plot of $\Delta\delta/f$ vs. f_1/f.

Equation 3 expands to eq 5 when nonspecific, solute–solvent, dipole–dipole interactions are included such as

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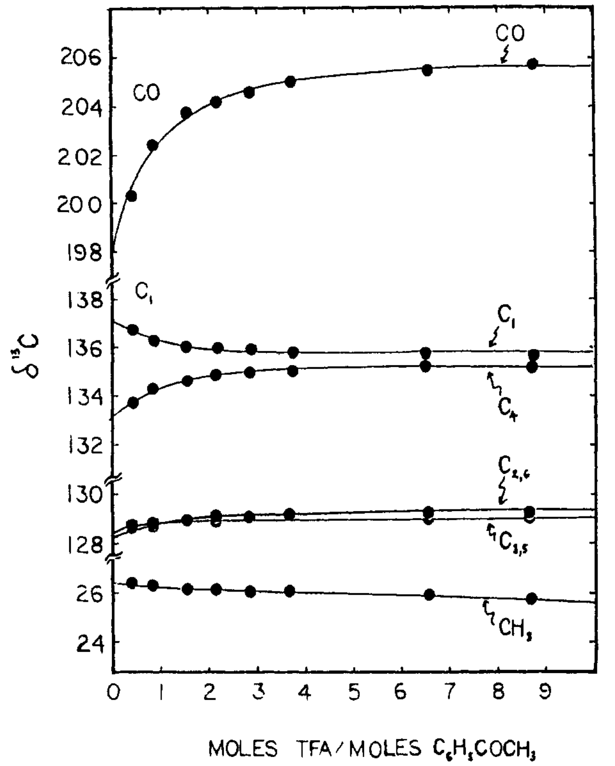

Figure 1. ^{13}C chemical shifts of acetophenone as function of the molar ratio of trifluoroacetic acid to acetophenone.

those involved in the solvation of the hydrogen-bonded complexes by the surrounding medium:[15]

$$\delta = f_B(\delta_B{}^\circ + \beta_B S) + f_1(\delta_1{}^\circ + \beta_1 S) + f_n(\delta_n{}^\circ + \beta_n S) \quad (5)$$

Here S reflects the changing polarity of the solvent system in the course of a titration and β_B, β_1, and β_n are the sensitivies of the ^{13}C chemical shifts of species B, BA, and BA_n, respectively, to the effects of solvation. If S takes the form of the Onsager modification of reaction field theory,[16] $S = (\epsilon - 1)/(2\epsilon + 1)$, and $\beta_B \sim \beta_1 \sim \beta_n \sim \beta$ in order to reduce the number of independent variables,[17,18] eq 4 becomes eq 6:

$$\Delta\delta/f = f_1(\Delta_1{}^0 - \Delta_n{}^\circ)/f + \Delta_n{}^\circ + \beta\Delta S/f \quad (6)$$

where ΔS is the change in the value of the solvent parameter in going from a solution of base in deuteriochloroform to one of base, deuteriochloroform, plus TFA. Values of $\Delta_1{}^\circ$ and $\Delta_n{}^\circ$, which now correspond to the hydrogen-bonding shifts of the complexes BA and BA_n in neat deuteriochloroform, may be obtained, together with values of β, by regression analysis of eq 6 for each carbon associated with the base being titrated.

Table II summarizes the hydrogen bonding shifts, Δ_n, of all carbon resonances of bases 1–4 and the changes in the proton resonances of the substituents which are associated with a change of solvent from deuteriochloroform to neat TFA. Values of K_1, the equilibrium constant for 1:1 complex formation, are listed as well. Although the ^{13}C chemical shifts of several of these compounds have been reported earlier,[19] they were redetermined in this study in order to insure uniform experimental conditions. Values of $\Delta_1{}^\circ$ and $\Delta_n{}^\circ$, calculated by using eq 6, are given in Tables III and IV. A typical titration curve and its linear version (eq 6) are shown for the case of acetophenone in Figures 1 and 2.

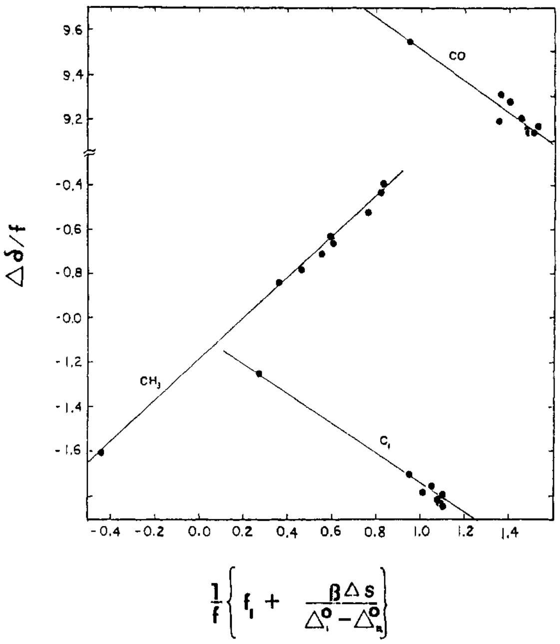

Figure 2. Correlation of $\Delta\delta/f$ with fraction of 1:1 complex and with the change in the solvent parameters, ΔS (eq 6) in the titration of acetophenone with trifluoroacetic acid in deuteriochloroform: slope = $(\Delta_1{}^\circ - \Delta_n{}^\circ)$; intercept = Δ_n.

Discussion

The extent of proton transfer in the hydrogen bond of TFA with substituted benzenes **1** is approximately 16–26%, as estimated from the ratios of the changes produced by hydrogen bonding and protonation[20] in the shifts of C4 of these bases dissolved in carbon tetrachloride. This figure is somewhat higher than the 12–14% derived from ^{19}F chemical shift changes for hydrogen bonding of the bases with the weaker proton donor, *p*-fluorophenol, in carbon tetrachloride[11] and is about four times the value for hydrogen bonding of the bases with deuteriochloroform. In the case of **1a**, **1b**, and **1c** higher values of shift ratios are obtained by using the carbonyl shifts rather than those of any ring carbon, a difference which must be attributed to the polarizing effect of the electrostatic interaction between the proton donor and the acceptor base[10] on the bonds of proximate atoms. For all bases of this study it is also primarily the carbons near the basic site, the ipso and substituent carbons, which are found to be sensitive to the association of further TFA units with the hydrogen-bonded acid–base pair and to the effects of solvation.

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[17] At low acid concentrations, ΔS is small so that the change in chemical shifts, $\Delta\delta$, is approximately that of eq 4. Values of ΔS become significant only at high acid concentrations at which f_B is near zero. Therefore, the dependence of $\Delta\delta$ on ΔS involves primarily the proportionality constants β_1 and β_n. Since these largely depend on the polarizibility of the hydrogen-bonded solutes and the size of the solvation sphere at the hydrogen-bonded site, their values should not be too different and $\beta_1 = \beta_n$ is a reasonable approximation.

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Table II. Shift Changes,[a] Δ_n, and Equilibrium Constants, K_1,[b] for Hydrogen Bonding of Trifluoroacetic Acid with Substituted Benzenes, 1, 1- and 2-Substituted Naphthalenes, 2 and 3, and 9-Substituted Anthracenes, 4

C_i/Z	$COCH_3$	CO_2CH_3	CHO	OCH_3	CN	NO_2	other
			Benzenes, 1				
C1	−1.25	−1.21	−1.36	−1.87	−2.15	−0.24	
C2,6	1.14	0.44	1.73	1.07	0.49	0.32	
C3,5	0.62	0.50	0.60	0.60	0.35	0.37	
C4	2.57	1.59	2.79	2.76	1.52	1.44	
Z	9.55 (CO) −1.61 (0.157)[c] (CH_3)	5.01 (CO_2) 1.01 (0.096)[c] (CH_3)	6.74 (−0.157)[c]	1.00 (0.160)[c]	−1.13		
K_1	5.44	4.66	4.49	2.65	3.19	–	
			1-Substituted Naphthalenes, 2				
C1	−1.54	−0.55	−1.07	−0.87	−2.25	−1.00	−2.51[d]
C2	2.40	0.74	3.40	4.59	1.22	1.40	1.01
C3	−0.01	−0.03	0.06	0.00	−0.03	−0.15	0.06
C4	2.68	1.31	3.29	2.68	1.68	1.87	1.32
C5	0.62	0.44	0.64	0.56	0.47	0.32	0.36
C6	0.63	0.48	0.71	0.40	0.46	0.35	0.50
C7	1.01	0.53	1.19	0.92	0.70	0.82	0.50
C8	−0.71	−0.84	−0.34	−0.74	−0.66	−0.38	−0.39
C9	−0.18	−0.13	0.62	0.42	0.44	0.42	0.42
C10	0.61	0.55	0.65	0.84	0.65	0.65	0.75
Z	9.40 (CO) −1.68 (0.094)[c] (CH_3)	5.58 (CO_2) 0.96 (0.100)[c]	5.65 (−0.350)[c]	1.92 (0.080)[c]	−0.72		−1.41 (0.024)[c]
K_1	6.92	4.49	4.27	0.54	2.11	3.79	0.28
			2-Substituted Naphthalenes, 3				
C1	2.54	1.22	3.83	2.73	1.26	0.96	
C2	−1.86	−1.55	−1.20	−1.99	−2.30	−0.58	
C3	−0.40	−0.61	−0.41	−1.49	−0.48	−0.53	
C4	0.63	0.55	0.62	0.71	0.47	0.44	
C5	0.16	0.57	0.15	0.10	0.08	0.10	
C6	1.59	1.06	1.69	1.25	0.87	0.92	
C7	0.72	0.11	0.69	0.59	0.47	0.43	
C8	0.45	0.22	0.55	0.41	0.20	0.23	
C9	0.49	0.27	−0.05	0.13	1.18	0.39	
C10	1.60	1.10	1.69	1.18	0.41	1.13	
Z	9.10 (CO) −1.74 (0.050)[c] (CH_3)	4.75 (CO_2) 0.96 (0.040)[c] (CH_3)	6.22 (−0.300)[c]	0.55 (0.107)[c]	−1.05		
K_1	4.29	4.06	3.84	0.78	4.46	1.88	
			9-Substituted Anthracenes, 4				
C1,8	−1.03	−1.07	−0.82		−1.40		
C2,7	1.06	0.79	2.40		0.53		
C3,6	0.33	0.20	0.59		−0.03		
C4,5	0.35	0.32	0.79		0.03		
C9	−3.01	−2.12	−4.46		−3.79		
C10	2.04	1.45	5.95		1.26		
C11,12	0.48	0.41	2.25		0.11[e]		
C13,14	0.26	0.24	−0.41		−0.42[e]		
Z	11.54 (CO) −0.94 (0.077)[c] (CH_3)	6.21 (CO_2) 1.02 (0.130)[c]	1.92 (−1.330)[e]				
K_1	4.06	4.08	9.04				

[a] In parts per million. The shift of base in neat TFA minus its shift in deuteriochloroform. [b] In L/mol. [c] The change in the shift of the proton resonance, in parts per million for the same change of solvent. [d] These and the shift changes below are those associated with the SCH_3 substituent of **2g**. [e] The assignments of shifts may be reversed here.

For most other carbons, with the notable exception of the quarternary carbons,[21] $\beta \sim 0$ and $\Delta_1{}^\circ = \Delta_n{}^\circ = \Delta_n$ so that for these eq 6 reduces to

$$\Delta\delta/f = \Delta_n = \text{constant} \qquad (7)$$

Large variations in the values of the hydrogen-bonding shift changes, $\Delta_1{}^\circ$ and $\Delta_n{}^\circ$, for complexing of bases 1–4 as BA and BA_n, respectively, are found for the carbon resonances of the hydrogen- bonding substituents. Values range from as little as 0.2 ppm to more than 14 ppm (see Table III) but are nearly identical for bases having similar orientations of substituents in neutral solutions, benzenes 1 and 2-substituted naphthalenes 3, for which they differ by no more than 0.5 ppm, regardless of which substituent is being hydrogen bonded. This suggests that the conformations of these bases are identical in the hydrogen-bonded complexes as well.

Hydrogen bonding produces downfield shifts of the CO resonances of all bases containing the carbonyl group.[2a] Complexing of the oxygen with TFA polarizes the carbonyl bond. The result is reduced electron density at the carbon atom and deshielding of its nucleus. It has been suggested[22] that the degree of such polarization, and hence the size of the shift change, is smaller the more electronegative the atoms are which are directly bonded to the carbonyl carbon. Accordingly, the order of downfield carbonyl shifts, $\Delta_1{}^\circ$ and $\Delta_n{}^\circ$, expected for 1–4 is CH_3CO

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(21) The greater sensitivity of quarternary carbons compared to proton-bearing ones to changes in environment has been demonstrated for a series of six-membered ring heterocycles for which the temperature gradients of their ^{13}C chemical shifts were linear in the case of all CH carbons but strongly curved for quarternary carbons in identical environments. Lambert, J. B.; Vagenas, A. R.; Somani, S. *J. Am. Chem. Soc.* **1981**, *103*, 6398.

(22) Maciel, G. I. *J. Chem. Phys.* **1965**, *42*, 2746.

Table III. Changes in the Chemical Shifts of Substituent Carbons[a] for Hydrogen Bonding of Trifluoroacetic Acid with Substituted Benzenes, 1, 1- and 2-Substituted Naphthalenes, 2 and 3, and 9-Substituted Anthracenes, 4, as 1:1 Complex, BA ($\Delta_1°$), and Polymeric Complex, BA_n ($\Delta_n°$), in Deuteriochloroform, Calculated from Eq 6

	CO		CH_3			CHO	
Ci	$\Delta_1°$	$\Delta_n°$	$\Delta_1°$	$\Delta_n°$		$\Delta_1°$	$\Delta_n°$
1a	9.51	10.23	−0.27	−1.20	1c	7.38	7.86
2a	8.74	10.32	−0.80	−2.08	2c	6.37	6.56
3a	9.86	10.02	−0.54	−1.50	3c	7.30	7.41
4a	13.17	14.39	−0.28	−1.81	4c	4.28	0.97
	CO_2		CH_3			CN	
Ci	$\Delta_1°$	$\Delta_n°$	$\Delta_1°$	$\Delta_n°$		$\Delta_1°$	$\Delta_n°$
1b	4.11	4.92	1.86	1.23	1d	−1.77	−1.44
2b	4.81	6.14	1.02	−0.36	2d	−1.32	−1.35
3b	4.24	4.59	1.77	1.10	3d	−1.72	−1.94
4b	5.81	7.38	0.79	−1.04			
	OCH_3					SCH_3	
Ci	$\Delta_1°$	$\Delta_n°$				$\Delta_1°$	$\Delta_n°$
1e	0.86	0.19					
2e	2.77	1.90			2g	0.16	−1.13
3e	0.68	0.17					

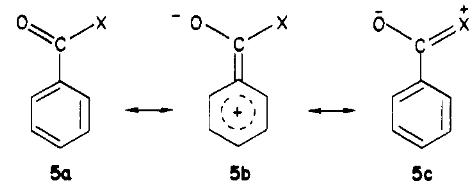
[a] In parts per million. Positive values signify a change of shift to lower field on hydrogen bond formation.

Table IV. Changes in the Chemical Shifts of Quaternary Carbons[a] for Hydrogen Bonding of Trifluoroacetic Acid with Substituted Benzenes, 1, 1- and 2-Substituted Naphthalenes, 2 and 3, and 9-Substituted Anthracenes, 4, as 1:1 Complex, BA ($\Delta_1°$), and Polymeric Complex, BA_n ($\Delta_n°$), in Dueteriochloroform, Calculated from Eq 6

	C_{ipso}		C9[b](11,12)[c]		C10[b](13,14)[c]	
compd	$\Delta_1°$	$\Delta_n°$	$\Delta_1°$	$\Delta_n°$	$\Delta_1°$	$\Delta_n°$
1a	−1.75	−1.06				
2a	−2.32	−1.88	−0.07	0.26	0.11	0.89
3a	−2.34	−2.45	−0.63	−0.01	0.93	1.30
4a	−3.34	−2.45	−0.02	0.48	−0.18	0.50
1b	−1.26	−0.24				
2b	−1.10	−0.33	−0.05	1.01	0.46	1.40
3b	−2.31	−1.93	−0.31	0.07	0.56	0.97
4b	−2.59	−1.88	0.13	0.69	−0.05	0.61
1c	−1.81	−0.67				
2c	−1.83	−1.40	0.18	0.50	−0.23	0.23
3c	−2.49	−1.51	−0.52	−0.61	1.08	1.65
4c[d]	−6.49	−9.13	2.18	1.46	−1.00	−1.74
1d	−2.18	−1.47				
2d	−2.06	−1.47	−0.01	0.33	0.18	0.75
3d	−2.66	−2.24	0.09	0.86	1.02	1.99
1e	−1.59	−0.22				
2e	−0.81	−0.64	−1.35	−0.20	0.76	1.14
3e	−5.34	−4.12	−2.08	−1.22	−1.32	−0.88
2f	−0.68	−0.42	0.51	0.75	0.13	0.79
3f	−0.61	−0.34	0.17	0.49	0.14	0.56
2g	0.80	−0.95	0.84	0.68	1.80	1.45

[a] In parts per million. Positive values signify a change of shift to lower field on hydrogen bond formation. [b] The quaternary carbons of **2** and **3**. [c] The quaternary carbons of **4**. [d] The shift changes for C1,8 of **4c** were −0.82 and −1.32 ppm for $\Delta_1°$ and $\Delta_n°$, respectively.

> CHO > CO_2CH_3. This order, though observed for substituted benzenes and naphthalenes **2** and **3**, is not followed by the anthracenes **4**. Clearly other electronic influences must be involved as well.

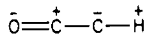


5a **5b** **5c**

Earlier studies have demonstrated[8] that carbonyl groups which are conjugated have ^{13}C chemical shifts which are upfield from those in corresponding saturated systems. Contributions from resonance structure related to **5b** and **5c**, whereby electron density is shifted to the carbonyl group from elsewhere in the molecule, should then have a shielding effect on the carbonyl resonances of **1a–c–4a–c**. Such resonance should be more important for the hydrogen-bonded complexes than for the free base, so that for bases capable of such electron delocalizations, smaller downfield hydrogen-bonding shifts might be expected. Accordingly, the shift changes of carbonyl, both $\Delta_1°$ and $\Delta_n°$ are more than 3 ppm smaller for hydrogen bonding of the planar methyl ketones **1a–3a** than for complexing of 9-acetylanthracene **4a**, in which resonance as in **5b** is inhibited by the large torsional angle of its acetyl substituents.[6a,23] Similarly, the changes in the carbonyl shifts, $\Delta_1°$ and $\Delta_n°$, of the planar esters,[9b] **1b** and **3b**, are smaller than are those of **2b** and **4b** (see Table III) in which a coplanar arrangement of aromatic rings and substituent cannot be achieved. Moreover, the shift changes of the 1-naphthoate ester **2b** are smaller than those of the anthracene derivative **4b**, by 1 ppm, in keeping with the smaller rotational angle of its substituent.[24]

The torsional angles of the formyl substituent of aldehydes **1c–4c** are all quite similar[4,6] and small, the largest being 27° in 9-anthraldehyde,[6b] so that downfield hydrogen-bonding shifts of similar magnitude might be expected for this series of bases. As seen in Table III, however, the shift changes for 9-anthraldehyde are much smaller than are those of the other aldehydes—only 4.3 ppm for formation of the 1:1 complex compared to about 7.3 ppm in the case of the planar aldehydes, **1c** and **3c**, and less than 1 ppm for complexing as BA_n. Such small hydrogen-bonding shifts are especially startling via-à-vis the 13–14 ppm downfield shifts of carbonyl in the corresponding ketone, **4a**. A very large amount of electron transfer from the aromatic rings to the substituent on hydrogen bonding of **4c** is suggested by the smallness of these shift changes and this accords with an earlier observation[23] of exceptionally strong electron attraction by the formyl group in 9-anthraldehyde. Such a substantial transfer of charge should also give rise to a stronger hydrogen bond and may be the reason why the value of the equilibrium constant, K_1, for 1:1 complex formation of **4c** (9.0 L/mol) is more than twice that for hydrogen bonding of any of the other aldehydes ($K_1 \sim 4.2$ L/mol, see Table II).

Opposing directions of ^{13}C shift changes of the carbonyl and methyl resonances, as well as downfield shifts of the methyl proton resonances (formation of BA_n, Table II), are observed for hydrogen bonding of all methyl ketones as BA and BA_n. This is as expected if the effect of the polarization of the CO bond by TFA is relayed within the substituent by the alternating inductive mechanism of Pople and Gordon,[25]



$$\overset{-}{O}=\overset{+}{C}-\overset{-}{C}-\overset{+}{H}$$

The same mode of transmission of polarization effects may account[26] for the upfield shifts of the proton resonances which accompany the deshielding of the carbonyls on

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(23) Schuster, I. I. *J. Org. Chem.* **1981**, *46*, 5110.

(24) The smaller torsional angle of the carboxylate substituent in **2b** compared to that in **4b** is inferred from the 2 ppm smaller chemical shift of its carbonyl carbon. A value of 73° has been reported for this angle in the anthracene, **4b**. See ref 7.

(25) Pople, J. A.; Gordon, M. *J. Am. Chem. Soc.* **1976**, *89*, 922.

(26) Some of the change in the shifts of the formyl hydrogen may be the result of a change in the magnetic anisotropy of the formyl group on hydrogen bond formation. However, it is difficult to predict the direction and magnitude of a shift change arising from this source.

hydrogen bonding of the aldehydes, **1c**–**4c**

$$\overset{-}{O}{=}\overset{+}{C}{-}\overset{-}{H}$$

Bellamy[27] has suggested that a change of aggregation, as from BA to BA_n (= B.A.A.$_{n-1}$), may result in a stronger hydrogen bond between the base and the base–terminal TFA unit.[28] Accordingly, a change from BA to BA_n for the methyl ketones causes their carbonyl shifts to move even further downfield and those of the methyl carbons further upfield (Table III). That these differences in shift, $\Delta_n° - \Delta_1°$, are somewhat larger for **2a** and **4a** than for **1a** and **3a** again may be a consequence of the more extensive π conjugation in the planar ketones which more effectively cancel the increase in positive charge produced at the carbonyl carbon by the strengthening of the hydrogen bond. Such leveling of the effect of stronger complexing through an increase in resonance should be substantial in the nearly all-planar aldehydes and may account for there being differences of less than 0.5 ppm in the shifts of BA and BA_n for **1c**–**3c**. In the case of 9-anthraldehyde, **4c**, for which an exceptionally large shift of electronic charge from the aromatic rings to the substituent being hydrogen bonded was postulated, the change from BA to BA_n produces, in fact, a 2.8-ppm *upfield* movement of the carbonyl resonance which leads one to infer that for this molecule there is less positive charge at the formyl carbon of the stronger complex BA_n than at that of more weakly complexed BA.

Charge alternation of the type

$$\overset{-}{O}{=}\overset{+}{C}{-}\overset{-}{O}{-}\overset{+}{C}{-}\overset{-}{H}$$

may account for the observation that both the carbonyl and OCH_3 resonances of the esters are shifted downfield on 1:1 complex formation (positive values of $\Delta_1°$, see Table III). A change in the structure of the complex, BA to BA_n, produces a further downfield movement of the CO resonance but a reversal in direction for the shift of OCH_3, which moves upfield.[29] These trends accord with progressively greater participation by the OCH_3 group in resonance such as **5c**, as more electronic charge is lost from the carbonyl carbon through strengthening of the hydrogen bond, the effects of such resonance being again transmitted inductively by the scheme of alternating charges within the substituent

$$\overset{-}{O}{-}C{=}\overset{+}{O}{-}\overset{-}{C}{-}\overset{+}{H}$$

The direct dependence of such resonance, **5c**, on the extent to which the carbonyl bond is polarized is demonstrated by the linearity of the correlation between the hydrogen-bonding shifts, both $\Delta_1°$ and $\Delta_n°$, of CO_2 and OCH_3 which is shown in Figure 3 (slope ~ –1).

Upfield shifts of the CN resonances are observed when nitriles **1d**–**3d**[30,31] complex as BA and as BA_n. As in the case of the upfield shifts of the α-carbon resonances of pyridines on hydrogen bonding,[32] such changes in shift may be attributed to higher excitation energies[33] and/or a reduction in CN bond order[34,35] in the present case arising from an increase in the contribution of the dipolar resonance form

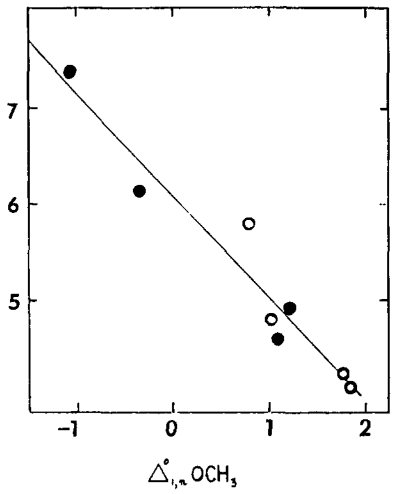

Figure 3. Correlation of $\Delta_1°$(○) and $\Delta_n°$(●) values of the carbonyl resonances with those of the OCH_3 resonances for hydrogen bonding of the methyl esters, **1b**, **2b**, **3b**, and **4b** as BA and BA_n.

$$Ar{-}\overset{+}{C}{=}\overset{-}{N}$$

on complexing of the lone pair of electrons of nitrogen[36,37] with TFA.

Hydrogen bonding of TFA with the methyl ethers, **1e**–**3e**,[38] as BA or BA_n produces downfield shifts of the methoxy carbon resonances which seem best attributed to the increase in negative charge at oxygen resulting from polarization of the oxygen–methyl bond

$$\overset{-}{H}{-}\overset{+}{C}{-}\overset{-}{O}\cdots TFA$$

as suggested by CNDO/2 calculations.[39] The shift changes, both $\Delta_1°$ and $\Delta_n°$, for hydrogen bonding of 1-methoxynaphthalene, **2e**, are more than 1 ppm larger than are those for hydrogen bonding of **1e** or **3e** (see Table III), a difference which cannot be the result of variations in the extent of aryl–methoxy resonance, since in all three ethers the substituent is believed to lie in the molecular plane.[9] That a steric effect of some sort may be involved, however, seems to be indicated by the relative positions of **1e**–**3e**, based on values of $\Delta_1°$ (and $\Delta_n°$ as well), within the following series of aromatic ethers, all of which have planar

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[27] Bellamy, L. J.; Pace, R. J. *Spectrochim. Acta* **1966**, *22*, 525, 535.

[28] The differences in the chemical shifts of BA and BA_n which are discussed here could as well be attributed to differences arising from hydrogen bonding of TFA with one (BA) vs. two (BA_n = A_m.B.A_{n-m}) lone pairs of electrons at the same basis site.

[29] Similar trends have been noted for hydrogen bonding of *n*-butyl acetate with TFA in deuteriochloroform. Begtrup, M. *J. Chem. Soc. Perkin Trans. 2* **1983**, 1609.

[30] The solubility of 9-cyanoanthracene in deuteriochloroform was too low to obtain titration data within a reasonable time period.

[31] Upfield shifts for these resonances were also observed on complexing of the nitriles with $Eu(fod)_3$ in deuteriochloroform.

[32] Schuster, I. I.; Roberts, J. D. *J. Org. Chem.* **1979**, *44*, 2658.

[33] Adams, W.; Grimison, A.; Rodriguez, G. *J. Chem. Phys.* **1969**, *50*, 645.

[34] Pugmire, R. J.; Grant, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 697.

[35] It has been suggested that the CN substituent of benzonitrile is only weakly involved in π conjugation with the aromatic ring (Fung, B. M. *J. Am. Chem. soc.* **1983**, *105*, 5713) so that there should be little change in the bond order of the aryl–CN bond on hydrogen bond formation.

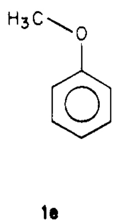
[36] The results of infrared spectral studies of several nitrile–phenol systems indicate that it is the nitrogen atom which is the electron pair donor in the RCN·HOAr aggregates (see ref 14 and Johnson, G. L.; Andrews, L. *J. Phys. Chem.* **1983**, *87*, 1852). However, recently a perpendicular hydrogen bond involving only the π electrons has been proposed for these systems on the basis of measurements of dielectric constants. (Baraton, M. I. *J. Mol. Struct.* **1971**, *10*, 231.)

[37] Nitrile carbon shifts have been found not to be sensitive to the electron density at the carbon atom. See: Tse, J. S. *Chem. Phys. Lett.* **1982**, *92*, 144. Wherli, F. W.; DeHaan, W.; Keulemans, A. I. M.; Exner, O.; Simon, W. *Helv. Chim. Acta* **1969**, *52*, 103.

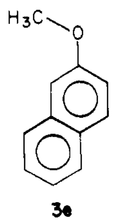
[38] The titration curves for 9-methoxyanthracene could not be determined because of the decomposition of the ether in solutions with TFA after a short period of time.

[39] Schuster, I. I. Unpublished calculations.

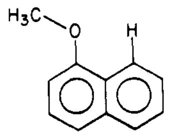
aryl–methoxy geometries (shifts of about 55 ppm for $^{13}CH_3O$) and aryl–methoxy resonance interactions of similar magnitudes as evident in the nearly identical positions of their para carbon resonances for the ethers dissolved in deuteriochloroform. A definite correlation can be seen between the magnitudes of the downfield hydrogen-bonding shifts, $\Delta_1°$, of the methoxy resonances and the size of the hydrocarbon "substituent" at the "ortho" position of these substituted "anisoles" **1**–**3e**, **6**, and **7**. Larger shift changes seem to be associated with greater bulk of the hydrocarbon moiety near the lone-pair electron orbitals (sp^2)[40] of oxygen and could be the result of a change in the average position of TFA[41] in the hydrogen-bonded complex, from in-plane to above the plane of the methoxy substituent, as the approach by the acid along the axis of the nonbonding electron pair of oxygen is blocked by progressively larger alkyl substituents. Such a structural change in the complex might well have a sizable effect on the chemical shifts of hydrogen-bonded OCH_3.



1e

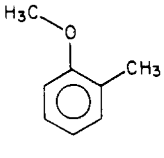


3e



2e

	1e	**3e**	**2e**
$\delta_B(OCH_3)$	55.08	55.31	55.44
$\Delta_1°(OCH_3)$	0.86	0.68	2.77
$\delta(C4)$	120.64		120.24



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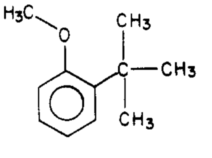

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6	**7**
55.15	55.90
2.76	4.43
120.24	120.28

The upfield movement (($\Delta_n° - \Delta_1°$) < 0, see Table III) observed for the methoxy resonances of all ethers in going from BA to BA_n accords with greater transfer of electron density from oxygen to the proton donor occuring in the more strongly hydrogen-bonded species, with the effects being transmitted inductively to the carbon atom by the alternating mode

$$\overset{+}{H}—\overset{-}{C}—\overset{+}{O}\cdots TFA$$

CNDO/2 molecular orbital calculations for the system, anisole·HF, also predict such a reversal in the trend of electron density changes at this carbon as the distance between the hydrogen-bonding atoms, oxygen and hydrogen, diminishes with concurrent lengthening of the H–F bond.[39]

The shift changes, $\Delta_1°$ and $\Delta_n°$, of the SCH_3 carbon resonance, associated with complexing of 1-(methylthio)naphthalene **2g** as BA and BA_n are more negative than are those of isoelectronic 1-methoxynaphthalene, **2e**, by approximately 3 ppm, but going from BA to BA likewise results in greater shielding of the methyl resonance.[42]

The change in the electric field of an aryl substituent undergoing hydrogen bond formation is expected to have a pronounced effect on the chemical shifts of proximate ring atoms. With a loss of electronic charge from the base to the proton donor, a shifting of electron density toward the ipso and ortho carbon atoms and away from the meta and para positions has been predicted on theoretical grounds.[43] The results of CNDO/2 molecular orbital calculations[39] suggest that increases in electron density at the peri carbons of **2** and **4** should occur as well. In the absence of significant changes in the magnetic anisotropy of the substituent on complexing with TFA, such electronic charge shifts should result in an upfield movement of the resonances of proximate carbons and in deshielding of meta and para carbon atoms. That this is, indeed, the case for bases **1**–**4** is demonstrated by the negative values of the hydrogen-bonding shifts, $\Delta_1°$ and $\Delta_n°$, of the ipso carbons (see Table IV) and Δ_n (= $\Delta_n° = \Delta_1°$) of the peri carbons, C8 of **2**, C1,8 of **4**, and of the ortho carbons, C3 of **3** (see Table II). Moreover, the shift changes of C8, C1,8, and C3 of **2**, **4**, and **3**, respectively, are all smaller than are the corresponding hydrogen-bonding shifts of the ipso carbons in these molecules as predicted on the basis of the decrease in the effects of electric fields with distance. In the case of most of the other ortho carbons—C2,6 of **1**, C2,9 of **2**, C1 of **3**, and C11,12 of **4**—the upfield hydrogen-bonding shifts, which are based on the changing electric field of the hydrogen-bonding substituent, are masked, to a greater or lesser degree, by deshielding arising from the depletion of electronic charge at these carbons as a result of resonance with the substituent being complexed.[44]

A change of complexing, BA to BA_n, produces a small amount of deshielding on the resonances of all quaternary carbons (see Table IV) the origin of which is not clear. The exceptions are the shifts of 9-anthraldehyde for which this change in hydrogen bonding produces upfield displacements of the resonances of all quaternary carbons and of C1,8 as well.

Experimental Section

Most of the bases of this study were commercial materials which were used without further purification. Those not directly available were synthesized according to standard procedures.

Titrations with TFA were performed on 0.5 M solutions of the bases in deuteriochloroform containing 5% cyclohexane as internal reference.

The ^{13}C NMR spectra were recorded at 28° with a Varian CFT-20 NMR spectrometer operating at 20.00 MHz.

Registry No. 1 ($Z = NO_2$), 98-95-3; **1a**, 98-86-2; **1b**, 93-58-3; **1c**, 100-52-7; **1d**, 100-47-0; **1e**, 100-66-3; **2a**, 941-98-0; **2b**, 2459-24-7; **2c**, 66-77-3; **2d**, 86-53-3; **2e**, 2216-69-5; **2f**, 86-57-7; **2g**, 10075-72-6; **3a**, 93-08-3; **3b**, 2459-25-8; **3c**, 66-99-9; **3d**, 613-46-7; **3e**, 93-04-9; **3f**, 581-89-5; **4a**, 784-04-3; **4b**, 1504-39-8; **4c**, 642-31-9; TFA, 76-05-1.

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[40] The hybridization of oxygen in gaseous anisole has been characterized as sp^2. Seip, H. M.; Seip, R. *Acta Chem. Scand.* **1973**, *27*, 4024.

[41] CNDO/2 molecular orbital calculations of energies of hydrogen bonding of the simple bases water and methanol predict the position of the hydrogen bond to be in the molecular plane. (Reference 10 and Kollman, P. A.; Allen, L. C. *J. Am. Chem. Soc.* **1970**, *92*, 753.) It is reasonable to assume that such a position is the preferred one for the hydrogen bond in complexes of anisole as well.

[42] It is not surprising to encounter differences in hydrogen-bonding shifts between the methylthio and methoxy substituents in view of the greater diffuseness of the electron pair engaged in hydrogen bonding in the sulfide and the limited involvement of the methylthio group in π conjugation with the aromatic rings in **2g**: $\sigma_R(CH_3S) = -0.26$ (lit. -0.32; Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1) and $\sigma_R(CH_3S.TFA) = -0.19$, compared to $\sigma_R(CH_3O) = -0.68$ (lit. -0.61) and $\sigma_R(CH_3O.TFA) = -0.50$. These values are obtained from linear correlations of the chemical shifts of 1-substituted naphthalenes in deuteriochloroform with the dual substituent parameters, σ_R and σ_I, by solving the simultaneous equations: $\delta C4 = 5.148\,\sigma_I + 13.791\sigma_R + 128.31$ and $\delta C7 = 3.777\sigma_I + 2.723\sigma_R + 126.06$.

[43] Batchelor, J. G.; Feeney, J.; Roberts, G. C. K. *J. Magn. Reson.* **1975**, *20*, 19.

[44] The shielding predicted for these ortho carbons as a consequence of the change in electric field of the substituent on hydrogen bonding is, nevertheless, evident in downfield hydrogen-bonding shifts which are, for the most part, smaller than those of the para carbons as in the case of the shift changes, Δ_n, of C2 and C4 of **1** and **2**.