Carbonate-Selective Chromoionophores**

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Abstract: Three members of a new class of carbonate-selective ion carriers based on trifluoroacetylazobenzene were synthesized and the influence of carbonate on their UV-spectra has been studied.

Certain trifluoroacetophenones, such as 1-butyl-4-trifluoroacetyl-benzene (**1**, TFABB)[1], reversibly interact with the carbonate ion according to Scheme 1[2].

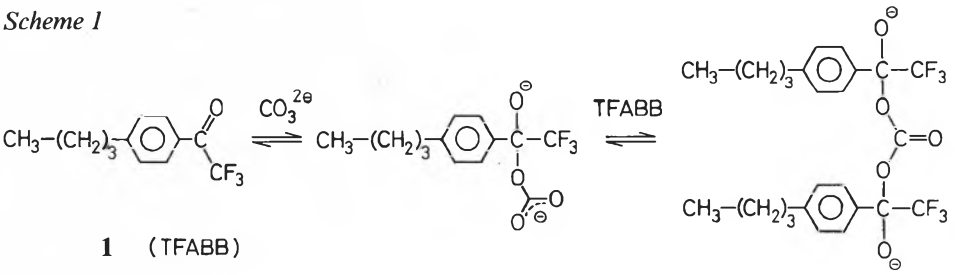
TFABB has been shown to induce remarkable carbonate ion selectivity when incorporated into solvent polymeric membranes containing classical anion exchangers[3,4] (see however[5]). Its electrochemical behaviour in membranes is consistent with the properties of neutral carriers for anions[2]. The interaction with carbonate, as indicated in Scheme 1, leads to a loss in the electron delocalization of the carbonyl group with the aromatic ring and, therefore, to an almost complete collapse of the absorption at 266 nm (λ_{max} in cyclohexane, $\varepsilon = 16200$)[2]. By replacing the butyl-substituent of the aromatic ring with a *p*-substituted benzeneazo-group, we were aiming at preparing a new class of reagents for anions. To be able to confine them to a lipophilic solvent polymeric membrane phase, rather lipophilic representatives were designed. We were hoping to obtain ionophores for carbonate undergoing a strong hypsochromic shift when interacting with this anion. If the free chromoionophore[6] would absorb visible electromagnetic radiation of $\varepsilon \geq 20000$[7] and result with carbonate in a spectrum sufficiently differenciated from the spectrum without carbonate interaction, such a component would become attractive for chemical sensors with an optical transduction (optode)[8,9]. Here we are reporting on the preparation of compounds **3** to **6** (Scheme 2) and on a preliminary study of their interaction with carbonate.

To dissolve carbonate in organic solvents we utilized $(TDMA)_2CO_3$[2] (bis(tridodecylmethylammonium)carbonate), a rather lipophilic colourless oil, that is easily soluble in most organic solvents. Unfortunately, this reagent[2] contains about 30% $HCO_3^{\ominus}$. Using Kryptofix® 222 we were unable to dissolve the necessary 0.1 to 1 mg of potassium carbonate in 25 mL diethyl ether, acetone, or hexane.

While compounds **4** and **6** showed the expected hypsochromic shift, the ester **5** was rapidly decomposed in the presence of carbonate into **3** and lauric acid respectively their salts. Due to this decomposition, analytically relevant electrochemical measurements on the ester in solvent polymeric membranes failed completely. As Table 1 shows, ethanol probably forms a hemiketal by interaction with the trifluoroacetyl-group and thus this solvent is useless for studying absoption shifts through carbonate interaction. Surprisingly, the tertiary amine **6** gave no shift in dioxane induced by carbonate interaction.

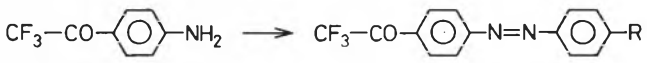
Potentiometric studies on solvent polymeric membranes with the ether **4** (40.4 wt-% PVC, 53.7 wt-% plasticizer, 2.0 wt-% TDMACl, and 3.9 wt-% **4**), which were performed as described earlier[2], indeed corroborate a response to carbonate with a slope of the electrode response of −29.35 mV in the range of 10^{-5} to 10^{-3} M (theoretical: −29.38 mV). Since membranes with only 3.9 wt-% chromoionophore **4** give optimal response to carbonate (as compared to 14.2 wt-% for TFABB), **4** seems to be even a more efficient ionophore than TFABB.

Scheme 1



1 (TFABB)

Scheme 2



2 (TFAA) **3** R: –OH
4 –O–$(CH_2)_{11}$–CH_3
5 –OOC–$(CH_2)_{10}$–CH_3
6 –N–$(CH_2–CH_2–OOC–CH_2–CH_2–CH_3)_2$

Table 1. Change in the UV/VIS-absorption of chromoionophores due to interaction with carbonate.

Solvent	Chromoionophore 4			5			6		
	A	B	C	A	B	C	A	B	C
acetone	360 (26 000)	348 (30 900)	−12	331 (24 300)	464 (30 100)	133	452 (27 100)	408 (31 100)	−44
dioxane	373 (30 500)	368 (28 800)	−5	340 (18 700)	442 (23 000)	102	450 (31 900)	450 (31 100)	0
ethanol	349 (20 800)	348 (22 300)	0	323 (18 500)	417 (18 500)	94	407 (22 700(	407 (22 700)	0
diethyl ether	373 (30 900)	352 (31 600)	−21	335 (27 900)	465 (32 100)	130	445 (34 400)	397 (31 500)	−48
hexane	372 (32 100)	347 (29 400)	−25	335 (27 500)	439 (22 100)	104	437 (34 700)	395 (31 600)	−42

A: wavelength [nm] and molar extinction coefficient (in parentheses) without carbonate;
B: wavelength and molar extinction coefficient after 10–15 equivalents of $(TDMA)_2CO_3$ were added with the tip of a capillary to the UV-cell;
C: shift in absorption wavelength [nm] due to carbonate interaction.

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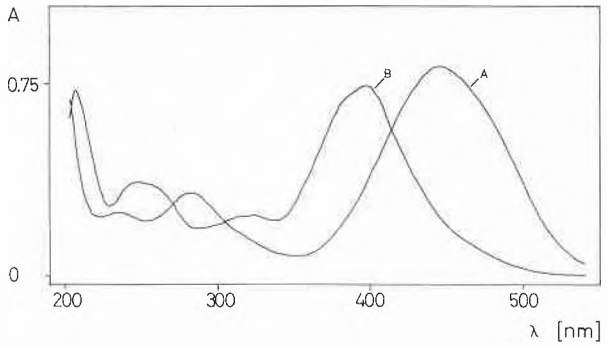

Fig. 1. UV/VIS-absorption of chromoionophore **6** *(2.38 · 10^{-5} M in diethyl ether); cf. Table 1.*

Experimental

General: All chemicals (Fluka) were reagent grade. Melting points (uncorrected) were measured on a Büchi SMP-20. IR spectra (cm^{-1}) were taken with a Perkin-Elmer PE 125, UV spectra with a Kontron Uvikon-810 spectrometer. Mass spectra were run on a Kratos AEI MS-50. ^{1}H-NMR spectra were run on either a Bruker WM-300 or a Perkin-Elmer R12B spectrometer in $CDCl_3$ with chemical shifts given in δ (ppm) from internal $(CH_3)_4Si$. Preparative flash-chromatography was performed on 230–400 mesh SiO_2 (Fluka) and thin layer chromatography (TLC) on pre-coated SiO_2 plastic plates (Macherey-Nagel).

4-Hydroxy-4'-trifluoroacetylazobenzene (**3**): A suspension of 2.84 g (15.02 mmol) *p*-trifluoroacetylanilin (**2**, TFAA)[10] in 45 mL 1 N HCl was stirred at 25 °C during 1h until everything was dissolved. The pale yellow solution was filtered through a swab and cooled in an ice bath to 5 °C. 1.03 g (14.93 mmol) $NaNO_2$ were added. After 10 min the yellow solution was poured into a solution of 1.41 g (14.98 mmol) phenol in 60 mL 1 N NaOAc. Crystals appeared after less than 5 min. After standing for 2 h, the orange crystals were collected in an Buchner funnel, washed with water (200 mL), and dried for 2 d at 40 °C which gave 3.90 g (13.25 mmol, 88%) **3** as red needles, *m.p.* 132–133 °C. This material gave correct elemental analyses and *m/z* 294 (M^+); IR ($CHCl_3$): 1715 ($COCF_3$); ^{1}H-NMR (300 MHz, $CDCl_3$): 10.50 (s, 1H, OH), 8.20–8.23 (m, 2H), 7.90–8.02 (m, 4H), 6.98–7.01 (m, 2H).

4-Dodecyloxy-4'-trifluoroacetylazobenzene (**4**): A mixture of 0.50 g (1.70 mmol) **3**, 15 g (80.5 mmol) dodecanol, and 10 drops of conc. sulfuric acid (2.5 mmol) was heated for 12 h at 100 °C[11]. According to TLC (ether) a small amount of starting material remained unconsumed. The cooled mixture was purified two times by chromatography on 60 g SiO_2 using CH_2Cl_2/hexane (1:4) to give 0.42 g (0.91 mmol, 53%) of almost pure **4** as red needles, *m.p.* 72–73.5 °C. Recrystallization in a 5 mL pillglass from diethyl ether (0.17 g per mL) gave 0.35 g pure **4**, *m.p.* 73–74 °C. This material gave correct elemental analyses and *m/z* 462 (M^+); IR ($CHCl_3$): 1715 ($COCF_3$); ^{1}H-NMR (300 MHz, $CDCl_3$): 8.19–8.22 (m, 2H), 7.93–7.99 (m, 4H), 6.99–7.04 (m, 2H), 4.06 (t, 2H), 1.83 (m, 2H), 1.36–1.46 (m, 18H), 0.88 (t, 3H).

4-Lauroyloxy-4'-trifluoroacetylazobenzene (**5**): A mixture of 0.50 g (1.70 mmol) **3** and 1.00 g (4.57 mmol) lauroyl chloride in 5 mL pyridine was stirred at 5 °C. After 1 h of stirring, the red mixture was diluted with 2 mL of diethyl ether, filtered from the Py·HCl, the latter washed with 3 mL ether, and the combined filtrate rapidly chromatographed, first on 60 g SiO_2 with diethyl ether to separate from pyridine, then on 30 g SiO_2 with CH_2Cl_2/hexane (1:3) to separate from lauric acid which gave 0.35 g (0.73 mmol, 43%) **5**, *m.p.* 72–73 °C. Attempts to purify by washing with 10% HCl and 10% $KHCO_3$ gave low yields because of cleavage of the ester. Recrystallization in a 5 mL pillglass from diethyl ether (0.25 g per mL) gave 0.27 g pure **5**, *m.p.* 72.5–74 °C, as red small plates. This material gave correct elemental analyses and *m/z* 476 (M^+); IR ($CHCl_3$): 1715 ($COCF_3$); ^{1}H-NMR (300, $CDCl_3$): 8.22–8.24 (m, 2H), 7.98–8.03 (m, 4H), 7.25–7.30 (m, 2H), 2.60 (t, J = 7.4 Hz, 2H), 1.73–1.83 (m, 2H), 1.25–1.50 (m, 16H), 0.89 (t, J = 6.7 Hz, 3H).

4-Bis(2-butyryloxyethyl)amino-4'-trifluoroacetylazobenzene (**6**): To a solution of 0.50 g (2.64 mmol) TFAA (**2**) in 4 mL HOAc 0.18 g (2.61 mmol) $NaNO_2$ were added. Some N_2 was produced, and diazonium salt precipitated. After 10 min, the deep yellow suspension was poured into a solution of 0.93 g (2.77 mmol) *N,N*-bis(2-butyryloxyethyl)aniline (prepared from butyryl chloride and *N*-phenyldiethanolamine (Fluka)) and 6 mL HOAc. After standing for 3 h, the red solution was diluted with 50 mL diethyl ether, washed 3 times with water (10 mL), and evaporated which gave a brick-coulored, slowly crystalizing oil on standing. Chromatography on 60 g SiO_2 (diethyl ether as eluant) gave two fractions. The first fraction contained 1.36 g (2.61 mmol, 99%) **6** as red fine needles, *m.p.* 53–56 °C, the second fraction contained 5.1 mg (0.4%) of 4-[*N*-(2-butyryloxyethyl)-*N*-(2-hydroxyethyl)amino]-4'-trifluoroacetylazobenzene as an oil, the structure of which is consistent with its 400 MHz ^{1}H-NMR spectrum. Recrystallization of **6** from 20 mL hexane gave 1.01 g pure **6**, *m.p.* 57 °C. This material gave correct elemental analyses and *m/z* 521 (M^+); IR ($CHCl_3$): 1715 ($COCF_3$); ^{1}H-NMR (300 MHz, $CDCl_3$): 8.18 (m, 2H), 7.91–7.96 (m, 4H), 6.89 (m, 2H), 4.32 (t, J = 6.3 Hz, 4H), 3.75 (t, J = 6.2 Hz, 4H), 2,29 (t, J = 7.4 Hz, 4H), 1.58–1.70 (m, 4H), 0.94 (t, J = 7.4 Hz, 6H).

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