# STUDY OF COMPARATIVE TRANSMISSION CAPACITY OF C–N BOND BY $^{19}$F NMR METHOD

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During a systematic quantitative study of the transmission capacity (TC) of binuclear bridge groupings (BBG), containing the atoms of the heavy nontransition metals of type $-M-X-$ (M = Sn, Hg; X = $CH_2$, $N(SO_2Ph)$) [1, 2], it was established that the indicated BBG have the property of a high electron conductance. In harmony with this, the question arose of whether the observed property is specific for organometallic systems or whether it can also be manifested in purely organic compounds. In addition, since a study of the TC of the BBG Hg–N was run on model systems of type $ArHgN(SO_2Ph)C_6H_4F$-4 , it seemed of interest to ascertain what effect the $PhSO_2$ group exerts on the TC of nitrogen-containing BBG.

In the present paper, in order to solve the set problems, we synthesized two series of compounds of type $ArCH_2NHC_6H_4F$-4 (Ia–*l*) and $ArCH_2N(SO_2Ph)C_6H_4F$-4 (IIa-*l*), where Ar = 4-$Me_2NC_6H_4$ (a), 4-$MeOC_6H_4$ (b), 4-$MeC_6H_4$ (c), Ph (d), 4-$FC_6H_4$ (e), 4-$ClC_6H_4$ (f), 3-$ClC_6H_4$ (g), 3-$FC_6H_4$ (h), 3-$CF_3C_6H_4$ (i), 3,5-$Cl_2C_6H_3$ (k), 3,4,5-$Cl_3C_6H_2$ (*l*), determined the $^{19}$F chemical shifts (δF) in them using dilute $CHCl_3$ solutions (Table 1). For a quantitative estimate of the comparative TC of the BBG $CH_2$ –NH we made a correlation of the δF in compounds of the (I) series with the literature data on the δF for the corresponding $ArCH_2-C_6H_4F$-4 (III) [3] in $CH_2Cl_2$ and $ArCH_2CH_2C_6H_4F$-4 (IV) [4] in $C_6H_6$, which is expressed by Eqs. (1) and (2).

$$\delta F\ (I) = 0{,}78\ \delta F\ (III) + 11{,}81;\ S_\rho = 0{,}09;\ S = 0{,}07;\ r = 0{,}971 \tag{1}$$

$$\delta F\ (I) = 1{,}20\ \delta F\ (IV) + 10{,}23;\ S_\rho = 0{,}11;\ S = 0{,}05;\ r = 0{,}970 \tag{2}$$

The fact that the value of the slope tangent of Eq. (1), which expresses the linear correlation between the δF in (I) and in (III), is somewhat less than one is evidence that the transition from (III) to (I) is accompanied by a much smaller decrease in the TC of the bridge system when compared with that when going from (III) to (IV) [2]. In harmony with Eq. (2), the TC of the BBG $CH_2$ –N is higher than the TC of the BBG $CH_2$ –$CH_2$.

Further, on comparing the TC of benzylamines (I) and their N-benzenesulfonyl derivatives (II) (Eq. (3)) it proved that their TC are

$$\delta F\ (I) = 0{,}98\ \delta F\ (II) + 14{,}98;\ S_\rho = 0{,}03,\ S = 0{,}05,\ r = 0{,}995 \tag{3}$$

practically the same, i.e., the addition of an acidic grouping to the nitrogen atom has no effect on the TC of the C–N bond.

TABLE 1. δF Values for (I) and (II) in $CHCl_3$ Relative to the Pseudoinner $C_6H_5F$ (ppm)

| Compound index | δF (I) | δF (II) | Compound index | δF (I) | δF (II) |
|---|---|---|---|---|---|
| a | 15,20 | 0,25 | q | 14,47 | −0,53 |
| b | 14,93 | −0,06 | h | 14,50 | −0,50 |
| c | 14,94 | 0,01 | i | 14,26 | −0,71 |
| d | 14,86 | −0,18 | k | 14,02 | −0,97 |
| e | 14,52 | −0,45 | l | 13,79 | −1,19 |
| f | 14,56 | −0,53 | | | |

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TABLE 2. Analytical Data and Physical Properties of Synthesized Compounds

| Compound | Yield, % | Temperature, °C |  | Found/calculated, % |  |  |
|---|---|---|---|---|---|---|
|  |  | mp | bp (p, mm Hg) | C | H | N |
| 4-$FC_6H_4N(SO_2Ph)CH_2C_6H_4N(Me)_2$-4 | 96 | 133–134<br>(heptane) |  | 65,44<br>65,59 | 5,46<br>5,52 | 7,14<br>7,29 |
| 4-$FC_6H_4N(SO_2Ph)CH_2C_6H_4OMe$-4 | 90 | 125–126<br>(methanol) |  | 64,66<br>64,67 | 4,86<br>4,89 | 3,56<br>3,77 |
| 4-$FC_6H_4N(SO_2Ph)CH_2C_6H_4Me$-4 | 94 | 101–102<br>(methanol) |  | 68,02<br>67,58 | 5,07<br>5,12 | 3,86<br>3,94 |
| 4-$FC_6H_4N(SO_2Ph)CH_2Ph$ | 96 | 115–116<br>(heptane) |  | 66,67<br>66,83 | 4,75<br>4,73 | 3,89<br>4,10 |
| 4-$FC_6H_4N(SO_2Ph)CH_2C_6H_4F$-4 | 95 | 127–128<br>(aq. acetone) |  | 63,53<br>63,49 | 4,42<br>4,22 | 4,00<br>3,90 |
| 4-$FC_6H_4N(SO_2Ph)CH_2C_6H_4Cl$-4 | 96 | 112–113<br>(heptane) |  | 60,68<br>60,71 | 4,36<br>4,03 | 3,53<br>3,73 |
| 4-$FC_6H_4N(SO_2Ph)CH_2C_6H_4Cl$-3 | 80 | 92–93<br>(heptane) |  | 60,79<br>60,71 | 4,17<br>4,03 | 3,42<br>3,73 |
| 4-$FC_6H_4N(SO_2Ph)CH_2C_6H_4F$-3 | 94 | 101–102<br>(heptane) |  | 63,42<br>63,49 | 4,35<br>4,22 | 3,93<br>3,90 |
| 4-$FC_6H_4N(SO_2Ph)CH_2C_6H_4CF_3$-3 | 89 |  | 210(3) | 57,96<br>58,67 | 3,70<br>3,70 | 4,10<br>3,42 |
| 4-$FC_6H_4N(SO_2Ph)CH_2C_6H_3Cl_2$-3,5 | 95 | 121–122<br>(heptane) |  | 56,00<br>55,62 | 3,62<br>3,45 | 3,22<br>3,42 |
| 4-$FC_6H_4N(SO_2Ph)CH_2C_6H_2Cl_3$-3,4,5 | 97 | 125–126<br>(heptane) |  | 51,22<br>51,31 | 2,94<br>2,95 | 3,24<br>3,15 |
| 4-$FC_6H_4NHCH_2C_6H_4N(Me)_2$-4 | 89 | 120–121<br>(methanol) |  | 73,71<br>73,73 | 7,02<br>7,03 | 11,49<br>11,47 |
| 4-$FC_6H_4NHCH_2C_6H_4OMe$-4 | 70 |  | 171–173<br>(2–3) | 71,97<br>72,69 | 6,32<br>6,11 | 5,61<br>6,06 |
| 4-$FC_6H_4NHCH_2C_6H_4Me$-4 | 75 | 66–67<br>(methanol) |  | 78,06<br>78,10 | 7,03<br>6,57 | 6,27<br>6,51 |
| 4-$FC_6H_4NHCH_2C_6H_4F$-4 | 49 | 48–49 | 158–163<br>(3–4) | 71,34<br>71,21 | 5,19<br>5,07 | 6,37<br>6,39 |
| 4-$FC_6H_4NHCH_2C_6H_4Cl$-4 | 17 | 50–51<br>(heptane) |  | 66,30<br>66,24 | 4,56<br>4,71 | 5,62<br>5,94 |
| 4-$FC_6H_4NHCH_2C_6H_4Cl$-3 * | 24 | 197–198<br>(ethanol) |  | 57,36<br>57,37 | 4,43<br>4,45 | 5,06<br>5,15 |
| 4-$FC_6H_4NHCH_2C_6H_4F$-3 * | 37 |  | 186–188<br>(14) | 60,79<br>61,06 | 5,05<br>4,74 | 5,46<br>5,48 |
| 4-$FC_6H_4NHCH_2C_6H_4CF_3$-3 | 65 |  | 144–145<br>(3) | 62,32<br>62,45 | 3,99<br>4,13 | 4,69<br>5,20 |
| 4-$FC_6H_4NHCH_2C_6H_3Cl_2$-3,5 * | 59 | 227–229<br>(ethanol) |  | 51,14<br>50,92 | 3,81<br>3,62 | 4,95<br>4,57 |
| 4-$FC_6H_4NHCH_2C_6H_2Cl_3$-3,4,5 | 80 | 90–92<br>(heptane–petroleum ether) |  | 50,82<br>51,26 | 3,05<br>2,98 | 4,38<br>4,60 |

*The analyses and melting points are given for the aniline hydrochlorides.

As a result, it may be concluded that the exaltation of the TC, previously observed on the example of metal-containing BBG, can also be manifested in the case of purely organic BBG, containing a heteroatom with an unshared electron pair. At the same time, it should be mentioned that, as it proved from a comparison of the TC of the BBG $HgN(SO_2Ph)$ and the TC of Hg ($\rho_{Hg(NSO_2Ph)/Hg} = 1{,}2$) [1], the above indicated property of the exaltation of the TC of mercury-containing BBG is manifested to a greater degree than for the analogous organic BBG.

## EXPERIMENTAL

The $^{19}F-\{^1H\}$ NMR spectra were obtained on an RYa-2309 spectrometer (operating frequency 84.56 MHz) at 25° using dilute solutions (concentration 0.05 mole/liter). The experimental error in measuring the $\delta F$ did not exceed ±0.01 ppm. The solvents were purified by standard procedures and were additionally distilled in a dry argon stream.

Compounds (Ia-c) were obtained by the reduction of the corresponding benzazomethines, (Ie-*l*) were obtained by alkylating the Na derivative of 4-fluoroaniline with the appropriate substituted benzyl chlorides, and (IIa-*l*) were obtained by reacting $PhSO_2Cl$ with the appropriate (I) compounds. The purity of the synthesized compounds was checked via the $^{19}F$ and $^{1}H$ NMR spectra. The constants and analysis data for the new compounds are given in Table 2.

Below are given typical examples for the synthesis of the compounds studied in this paper.

**N-(4-Chlorobenzyl)-4′-fluoroaniline (If).** To a mixture of 5 g (0.05 mole) of $Na_2CO_3$ and 19 ml (0.2 mole) of 4-fluoroaniline was added 8.05 g (0.05 mole) of 4-chlorobenzyl chloride. Then the reaction mixture was heated for 1 h at 100°, cooled, diluted with 100 ml of water, extracted with ether, dried over $Na_2SO_4$, and the ether was distilled off. Recrystallization from a heptane–petroleum ether mixture gave 2.1 g of a pale yellow crystalline compound with mp 50-51°.

**N-(4-N,N-Dimethylaminobenzyl)-4′-fluoroaniline (Ia).** A solution of 7.5 g (0.031 mole) of 4-N,N-dimethylaminophenyl-N-(4′-fluorophenyl)azomethine in 100 ml of abs. MeOH was added in drops to a suspension of 1 g (0.04 g-atom) of Mg turnings in 20 ml of hot abs. MeOH. At the end of brisk $H_2$ evolution the mixture was refluxed for 1 h, cooled, diluted with 50 ml of water, extracted with ether, dried over $Na_2SO_4$, and the solvent was removed in vacuo. The residue was recrystallized from MeOH to give 6.3 g of a pale yellow crystalline compound with mp 120-121°.

**N-(4-Chlorobenzyl)-N-benzenesulfonyl-4′-fluoroanilide (IIf).** With stirring, to 2.4 g (0.01 mole) of (If) in a mixture of 7 ml of acetone and 1 ml of pyridine was added a solution of 2.1 g (0.012 mole) of benzenesulfonyl chloride in 5 ml of acetone, after which the mixture was heated to reflux, let stand overnight, poured into 180 ml of distilled water, and the precipitate was filtered and washed with water to give 3.6 g of a compound with mp 112-113° (from heptane–pentane).

## CONCLUSIONS

1. A study was made of the $^{19}F$ NMR spectra of a number of free and N-substituted benzylanilines $ArCH_2NHC_6H_4F\text{-}4$ and $ArCH_2N(SO_2Ph)C_6H_4F$, respectively.

2. The binuclear bridge grouping $CH_2-N$ has a high transmission capacity (TC). The addition of an acidic grouping to the nitrogen atom has no effect on the TC of the C–N bond.

## LITERATURE CITED

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