

Star-branched non-covalent complexes between carboxylic acids and a tris(imidazoline) base

Arno Kraft^{a†} and Roland Fröhlich^b

^a Institut für Organische Chemie und Makromolekulare Chemie II, Heinrich-Heine-Universität Düsseldorf, Universitätsstr. 1, D-40225 Düsseldorf, Federal Republic of Germany

^b Institut für Organische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstr. 40, D-48149 Münster, Federal Republic of Germany

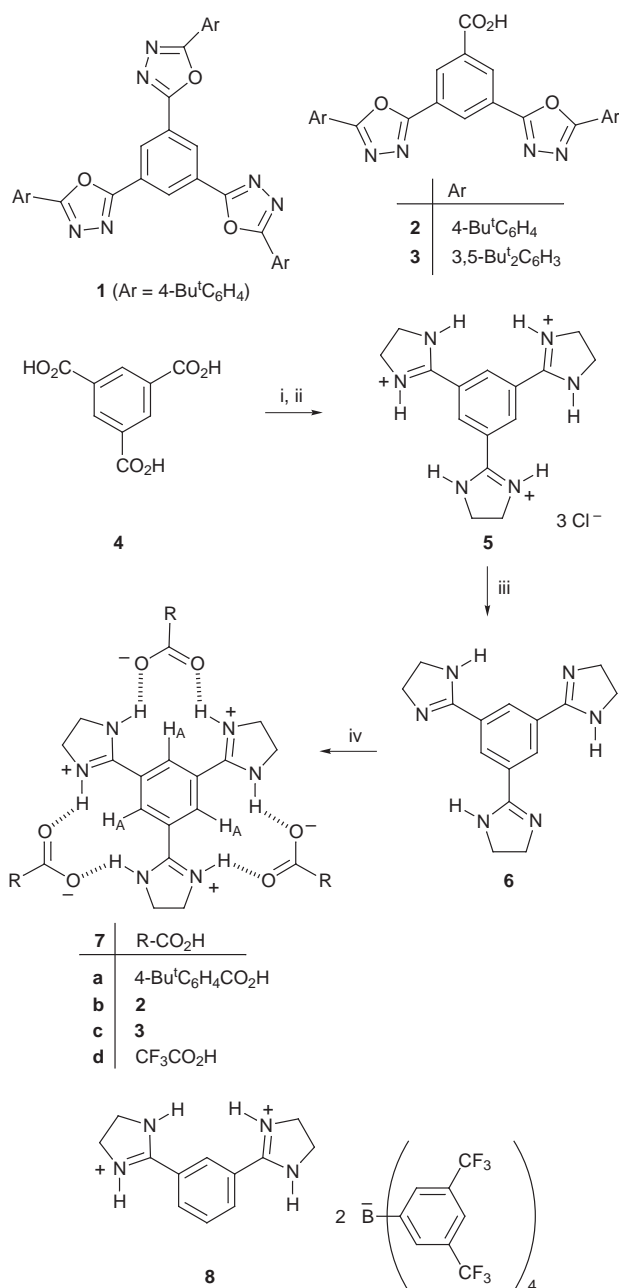
Simple dissolution of 3:1 mixtures of aromatic carboxylic acids with suitable solubilising groups and tris(4,5-dihydroimidazol-2-yl)benzene **6** gave branched hydrogen-bonded assemblies **7** that were soluble in chlorinated and aromatic solvents.

Although Nature has perfected the controlled formation of stable hydrogen-bonded aggregates in water, self-assembly of well-defined, non-covalently bonded, high-molar-mass complexes in solution still remains a challenge for chemists.¹ Self-assembly by non-covalent interactions is an elegant approach to many kinds of large defined molecules, circumventing time-consuming chemical syntheses that are often accompanied by enormous purification problems. This can also become crucial in the design of new materials. For example, diaryl-substituted 1,3,4-oxadiazoles have lately received considerable interest as potential electron-transporting materials in electroluminescent devices based on fluorescent dyes and polymers.^{2,3} Amongst these, branched structures such as **1** and dendrimers with ≥ 3 oxadiazoles per molecule have the particular attraction of being highly soluble in organic solvents and of forming stable, amorphous, thin films.^{3,4} It would be much simpler if such compounds were obtained through an assembly process from smaller components. For this, the non-covalent interaction between carboxylic acids and amidine bases looked very attractive.⁵ We decided to use cyclic amidine derivatives which are easier to prepare than unsubstituted amidines and which were already the subject of X-ray crystal structure studies by Hosseini and co-workers who showed that dicarboxylic acids and bis(tetrahydropyrimidine)s or bis(imidazoline)s self-assemble to hydrogen-bonded sheets and networks in the solid state.⁶

A three-star branched structure would result when acids such as **2** or **3** (readily obtained by palladium-catalysed carbonylation of the corresponding aryl iodides)⁴ were combined with, e.g. a 1,3,5-trisubstituted benzene containing three amidine substituents such as tris(imidazoline) **6**. Although melt condensation of benzene-1,3,5-tricarboxylic acid (**4**) and imidazolidin-2-one was reported to give **6** in modest yield,⁷ a modified imidazoline synthesis⁸ in solution proved to be more reliable. Hydrochloride **5** was prepared analogously in a single step from **4** and ethylenediamine in boiling ethylene glycol under acid catalysis (Scheme 1). Treatment with aqueous NaOH and sublimation gave the free base **6** in high purity.[‡]

Salt formation resulted from simple dissolution of a 1:3 mixture of **6** and various carboxylic acids in warm CHCl_3 -EtOH.⁹ Upon standing, the salts **7** crystallised from concentrated solutions (usually after evaporation of some of the CHCl_3), and one recrystallisation provided analytically pure samples.[‡] It was surprising to note that salts obtained from acids with solubilising groups (such as *tert*-butyl derivatives of benzoic acid, **2** or **3**, but not benzoic acid or acetic acid) and **6** are remarkably soluble in non-polar organic solvents, viz CHCl_3 (**7b**: 40–50 mg cm^{-3} , **7a,c**: >100 mg cm^{-3}) or toluene, although **6** is insoluble in all common non-acidic organic

solvents and, for example, acid **2** dissolves only sparingly in CHCl_3 (< 1 mg cm^{-3}) or EtOH.



Scheme 1 Reagents and conditions: i, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \cdot 2\text{HCl}$, TsOH, ethylene glycol, reflux, 3 h; ii, HCl; iii, NaOH, 64%; iv, RCO_2H (3 equiv.), EtOH- CHCl_3 , reflux, 56–87%

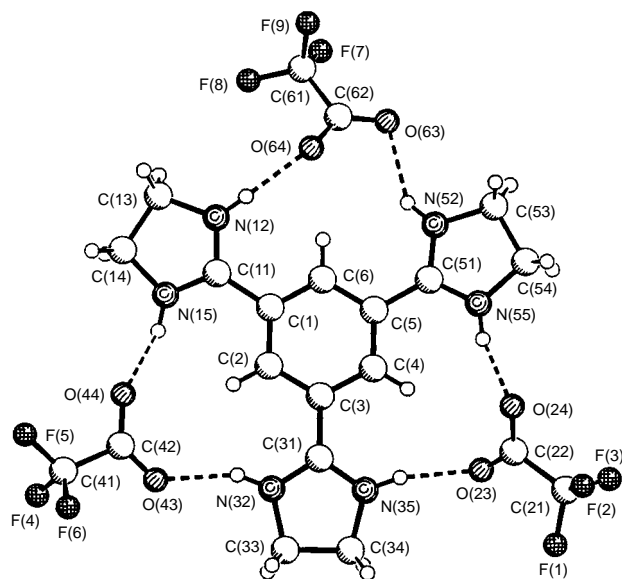


Fig. 1 Crystal structure of **7d**

The ^1H NMR spectra of **7a–c** in CDCl_3 show a broad singlet for the hydrogen-bonded imidazoline NH at δ ca. 13. The core's aromatic protons H_A give rise to a diagnostic singlet at an unusual chemical shift of δ ca. 10.1. Addition of a polar cosolvent shifts the H_A signal up-field, and in neat $[\text{D}_6]\text{DMSO}$ the corresponding resonance is observed at δ ca. 8.5. Such a difference of $\Delta\delta$ ca. 1.6 for an aromatic proton signal cannot be explained by protonation of **6** alone or simple solvent effects, and must be attributed to the fact that, in the complex, H_A experiences considerable steric pressure. Polar solvents (DMSO, MeOH) cause the complexes to dissociate, whereas in a non-polar solvent each carboxylate forms hydrogen-bonds to two imidazoline NH units, with all non-polar groups facing the outside, probably similar to Hosseini's self-assembled structures.⁶ This is further illustrated by the crystal structure of model complex **7d** for which the deviation from C_3 -symmetry may be either a consequence of crystal packing effects or an indication that the third carboxylate is less strongly bound than the remaining two (Fig. 1).§

A 1 : 3 stoichiometry of the **6**-carboxylic acid complexes was supported by Job's method of continuous variation. Dilution experiments showed that the ^1H NMR chemical shifts of complexes **7a–c** in CDCl_3 remain unchanged over a concentration range of 10^{-1} to 3×10^{-5} mol dm^{-3} ($\Delta\delta < 0.1$) although the core signals show some line-broadening below 10^{-3} mol dm^{-3} . ^1H NMR dilution studies of **8** and tetrabutylammonium benzoate in CDCl_3 - CD_3OD (97 : 3) gave an association constant of 990 ± 230 $\text{dm}^3 \text{mol}^{-1}$ for the formation of a simple 1 : 1 complex. Self-association can be excluded unless, as initial experiments have shown, the acid component contains additional functional groups capable of hydrogen bonding, e.g. amide groups. Although complexes **7a–c** dissociated during column or gel-permeation chromatography (with CH_2Cl_2 as eluent) and mass spectrometry (chemical ionization, fast atom bombardment or matrix-assisted laser desorption/ionisation), vapour-pressure osmometry allowed us to determine the number-average molar mass M_n in solution at concentrations > 5 mmol dm^{-3} : 830 g mol^{-1} (against benzil or **1** as standard) for **7a**, 1810 g mol^{-1} for **7b**, both in CHCl_3 at 30 °C, and 2400 g mol^{-1} (against benzil or polystyrene 2000 as standard) for **7c** in toluene at 50 °C. All M_n values are close to the calculated values of 817, 1850 and 2187 g mol^{-1} , respectively, and provide evidence that the complexes are not dissociated under these conditions.

Further investigations towards the use of this simple self-assembly process for the preparation of larger assemblies and

ordered supramolecular stacks, and their applicability in electroluminescent devices are in progress.

The Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft and Professor G. Wulff are gratefully acknowledged for financial support as well as Ms H. Fürtges for assistance in the preparation of starting materials.

Notes and References

† E-mail: kraft@iris-oc2.oc2.uni-duesseldorf.de

‡ All compounds were characterised by microanalysis, IR and NMR spectroscopy. Selected data for **5**: δ_{H} (300 MHz, D_2O) 4.23 (s, CH_2), 8.58 (s, C_6H_3). For **6**: mp 383–385 °C (lit.⁷ 340 °C); m/z (CI-MS, NH_3) 283, 282, 381 (53, 100, 83%, M^+), 254, 253 (58, 99), 240 (56), 224 (55). For **7a**: mp 389–390 °C (decomp.); δ_{H} (300 MHz, CDCl_3) 1.34 (s, CH_3), 4.14 (s, NCH_2), 7.41, 8.01 (AA'XX', C_6H_4), 10.12 (s, H_A), 13.0 (br s, NH); δ_{H} (500 MHz, $[\text{D}_6]\text{DMSO}$) 1.30 (s, CH_3), 3.68 (s, NCH_2), 7.49, 7.87 (AA'XX', C_6H_4), 8.45 (s, H_A). For **7b**: mp 235–240 °C/ 283 – 285 °C/i (decomp.); δ_{H} (500 MHz, CDCl_3) 1.38 (s, CH_3), 4.36 (s, NCH_2), 7.56, 8.10 (AA'XX', C_6H_4), 8.90 (3 H, t, J 1.6), 8.97 (6 H, d, $\text{C}_6\text{H}_3\text{CO}_2^-$), 10.10 (s, H_A), 12.9 (br s, NH); δ_{H} (500 MHz, $[\text{D}_6]\text{DMSO}$) 1.36 (s, CH_3), 3.80 (s, NCH_2), 7.69, 8.13 (AA'XX', C_6H_4), 8.55 (s, H_A), 8.78 (6 H, d, J 1.6), 8.85 (3 H, t, $\text{C}_6\text{H}_3\text{CO}_2^-$). For **7c**: mp 328–329 °C (decomp.); δ_{H} (300 MHz, CDCl_3) 1.42 (s, CH_3), 4.38 (s, CH_2), 7.66 (6 H, t, J 1.7), 8.03 (12 H, d, C_6H_3), 8.97 (3 H, t, J 1.6), 9.06 (6 H, d, $\text{C}_6\text{H}_3\text{CO}_2^-$), 10.16 (s, H_A), 13.0 (br s, NH). For **7d**: mp 240–242 °C (decomp.); δ_{H} (300 MHz, D_2O) 4.18 (s, CH_2), 8.50 (s, H_A).

§ X-Ray crystal structure analysis of **7d**: $\text{C}_{21}\text{H}_{21}\text{N}_6\text{O}_6\text{F}_9$, $M = 624.44$, $0.5 \times 0.3 \times 0.2$ mm (from MeOH), $a = 12.464(1)$, $b = 22.884(2)$, $c = 9.122(1)$ Å, $V = 2601.8(4)$ Å³, $\rho_{\text{calc}} = 1.594$ g cm^{-3} , $\mu = 14.21$ cm^{-1} , $Z = 4$, orthorhombic, space group $\text{Pna}2_1$ (No. 33), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 2834 reflections collected (+ h , $-k$, + l), $[(\sin \theta)/\lambda] = 0.62$ Å⁻¹, 2834 independent and 2525 observed reflections [$I \geq 2\sigma(I)$], 380 refined parameters, $R = 0.064$, $wR^2 = 0.179$, max. residual electron density 0.57 (–0.36) e Å^{-3} , Flack parameter –0.1(3), hydrogens calculated and riding. Data set were collected with an Enraf–Nonius CAD4 diffractometer. Programs used: data reduction MoLEN, structure solution SHELXS-86, structure refinement SHELXL-93, graphics SCHAKAL-92. CCDC 182/822.

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Received in Cambridge, UK, 17th March 1998; 8/02111B