A Conformational Study of 5,10,15,20-Tetraalkyl-22\(+\),24\(+\)-porphyrindiium Salts (Dication Salts)

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Porphyrins, Steric Strain, Porphyrin Dications, Crystal Structure, Conformational Analysis, 22,24-Dihydroporphyrins

N-protonation of 5,10,15,20-tetraalkylporphyrins with n-butyl, isobutyl, isopropyl, 1-ethylpropyl or tert-butyl substituents yields the respective 22,24-dihydroporphyrins (22\(+\),24\(+\)-porphyrindiium salts) that exhibit highly nonplanar conformations. Depending on the steric demand of the meso substituents, the free base porphyrins have planar to moderately ruffled macrocycles (primary or secondary alkyl residues) or are severely ruffled (tertiary alkyl residues). X-ray crystallographic studies show that protonation of porphyrins with «-Bu (2), i-Pr (3) or EtPr (4) substituents leads to steric congestion of the core resulting in symmetric, saddle distorted macrocycles as evidenced by average displacements of the C\(_\beta\) positions from the mean plane ranging from 0.79 to 1.01 Å. The structures observed for these porphyrin diacids are very similar in distortion mode and degree of nonplanarity to 5,10,15,20-tetraaryl-22\(+\),24\(+\)-porphyrindiium salts and to 2,3,7,8,12,13,17,18-octaalkyl-5,10,15,20-tetraarylporphyrins. In contrast, protonation of the highly ruffled 5,10,15,20-tetrakis(tert-butyl)porphyrin results in a switch of the conformational distortion mode. The dication 6 shows both saddle distortion (C\(_\beta\) displacements ~1.3 Å) and ruffling of the macrocycle (C\(_m\) displacements of approx. 0.48 Å). Thus, the need to accommodate four N-H units in the porphyrin core with its associated out-of-plane tilting of the pyrrole rings and the steric strain induced at the meso carbon atoms results in a highly nonplanar porphyrin with mixed distortion modes.

Introduction

The investigation of nonplanar porphyrins continues to attract the attention of porphyrin chemists due to the significant biological relevance conformationally distorted porphyrins possess [1,2]. At present there is an expanding body of work indicating that ‘conformational control’ of tetrapyrole-based enzymatic reactions is of prime importance for the physiochemical fine-tuning of processes like electron transfer [3] or light harvesting and charge separation in photosynthesis [4]. Numerous modeling studies have been performed in the last decade mostly involving symmetric, highly (peripherally) substituted porphyrins such as 5,10,15,20-tetraaryl- or 2,3,7,8,12,13,17,18-octaalkyl-5,10,15,20-tetraarylporphyrins [1,5–7]. As porphyrin nonplanarity can be induced not only by peripheral meso or \(\beta\) substitution but via core substitution of the pyrrole nitrogen atoms as well, we and others have been interested in the structural and conformational effects of both core and peripheral substitution [8–10]. Appropriate model compounds can be prepared quite easily by protonation of peripherally highly substituted free base porphyrins, yielding 22\(+\),24\(+\)-porphyrindiium salts (porphyrin diacids). Thus, we wanted to perform a comparative structural analysis of the

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porphyrin acids of all representative porphyrins currently employed in biomimetic studies on the conformational flexibility of porphyrins. Four different classes of peripherally substituted free base porphyrins have been used in studies on porphyrin nonplanarity: 5,10,15,20-tetraarylporphyrins, whose free base conformation ranges from planar to moderately ruffled [11]; 2,3,7,8,12,13,17,18-octaalkylporphyrins with a planar conformation [12]; 2,3,7,8,12,13,17,18-octaalkyl-5,10,15,20-tetraarylporphyrins, with severe saddle distortions [5a]; and 5,10,15,20-tetraalkylporphyrins, with conformations ranging from planar to severely ruffled [5b,6,7]. Several structures had been reported in the literature for the diacids of the first three classes: 1 [10,13], 7 [10,14,15] and 8 [15,16] and recently we reported here a comparative analysis of 5,10,15,20-tetraaryl-22,24-dihydro-, 2,3,8,12,13,17,18-octaaalkyl-22,24-dihydro-, and 22,24-dihydro-2,3,5,7,8,10,12,13,15,17,18,20-dodecasubstituted porphyrin diacids [17]. One of the results of that study was, that all porphyrin diacids bearing meso aryl substituents exhibited a severe saddle distortion. Saddle distortions are characterized by significant displacements of the \( \text{C}_b \) positions from the mean plane (approx. 1–1.5 Å) while the meso carbon atoms remain in the plane of the macrocycle [18]. In all cases, core protonation led to a significant increase in overall distortion compared to the respective free base porphyrins.

As all of the free base porphyrins utilized for these studies were either planar or saddle distorted, it remained to be seen what happens to the porphyrin macrocycle of 5,10,15,20-tetraalkylporphyrins upon N-protonation (2-6). Such porphyrins have been shown to possess significantly ruffled macrocycles when the steric demand of the meso substituent is large enough (e.g. tert-butyl or adamantyl) [5b,6,7]. Ruffled macrocycles are characterized by large displacements of the \( \text{C}_m \) positions from the mean plane (typically 0.5–1 Å), a tilting of the pyrrole rings against each other (about the \( \text{C}_b-\text{C}_b \) axis), with the N-H vectors remaining in the \( \text{N}_4 \)-plane [18].

Core protonation has to result in an out-of-plane tilting of the individual pyrrole rings as four hydrogen atoms do not fit into the central core of the macrocycle while maintaining a square-planar \( \text{N}_4 \)-unit. This has been the consistent result of most structural studies on porphyrin diacids [13]. The only alternative would be NH-pyramidalization, i.e. partial \( \text{sp}^2 \rightarrow \text{sp}^3 \) rehybridization which has only been observed for some 2,3,7,8,12,17,18-octaalkyl-22H*-24H*-porphyrindium salts [8,14a,17]. Thus, core protonation of highly ruffled free base porphyrins has to be accompanied by a conformational switch of the distortion mode. In order to address this question, the 5,10,15,20-tetraalkylporphyrin diacids 2-6 where synthesized and their structures and conformation determined by X-ray crystallographic means.

Results and Discussion

The choice of meso substituents in the target compounds 2-6 was dictated by the earlier studies on the respective free base and metallo porphyrins [5b,6,7]. These studies showed that increasing steric bulk of the meso substituents leads to increasingly ruffled macrocycles, although the relative steric effect of e.g. isopropyl versus \( n \)-butyl groups was smaller than expected [7]. Preparation of the dications was achieved easily by treatment of the respective free bases with trifluoroacetic acid (TFA) in methylene chloride. On the basis of their absorption maxima the dications prepared fall into two classes. The long wavelength absorption maxima for the ditrifluoroacetates of 2, 5, 3, 4 are 632, 633, 640, and 643 nm, respectively, while that for 6 was observed at 702 nm. As macrocycle distortion is accompanied by a bathochromic shift of the absorption maxima [1,5–8,19] this indicated quite different degrees of conformational distortion in the various diacids. The 5,10,15,20-tetraalkylporphyrin diacids 2-5 were expected to have overall similar structures with minor differences in dependence of the steric demand of the \( n \)-butyl, isobutyl, isopropyl and 1-ethylpropyl substituents. The tert-butyl derivative 6 was assumed to have a much more nonplanar conformation. The results of the different crystal structure analyses showed that a similar situation exists in the solid state. The crystal and molecular structure of [2][C\(_6\)F\(_3\)O\(_2\)]\(_2\)·2CF\(_3\)CO\(_2\)H shows a monodentate binding of two trifluoroacetate residues to each face of the porphyrin: N21-O2A 2.947 Å, N23-O2A 2.843 Å; N22-O8A 2.874 Å, N24-O8A 2.909 Å. Each of the trifluoroacetates in turn is hydrogen bonded to a trifluoroacetic acid molecule.
Table I. Structural and geometrical parameters for the porphyrin dication salts studied.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Observed range for reference compounds</th>
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<tr>
<td>[H₄TPP]⁺</td>
<td>[H₄OEP]⁺</td>
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<tr>
<td>[C₂F₃O₂]²⁻</td>
<td>[C₂F₃O₂]²⁻</td>
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<tr>
<td>N-C₃</td>
<td>1.381-1.39</td>
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<tr>
<td>C₃-C₄</td>
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<tr>
<td>C₅-C₆</td>
<td>1.35-1.370</td>
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<tr>
<td>N-C₆-C₇</td>
<td>125.0-125.9</td>
</tr>
<tr>
<td>N-C₆-C₈</td>
<td>106.1-108</td>
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<td>N-C₆-C₉</td>
<td>108-110.3</td>
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<td>N-C₆-C₁₀</td>
<td>120-125.6</td>
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<td>N-C₆-C₁₁</td>
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<tr>
<td>N-C₆-C₁₂</td>
<td>127.9-128.1</td>
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Bond lengths [Å]

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<td>Bond angles [deg]</td>
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<td>N-C₆-C₇</td>
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Structural parameters [Å and deg]

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<th>Structural parameters [Å and deg]</th>
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<td>N-C₆</td>
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Core size in Å; b average pyrrole tilt angle with the N₄ plane [deg]; c average deviation of the macrocycle atoms from their least-squares plane [Å]. d Average deviation from the N₄ plane [Å]; e see remarks in text; f two crystallographically independent molecules.

A similar situation was found in the structure of [3][C₂F₃O₂]²⁻·CF₃CO₂H·CHCl₃. Again two trifluoroacetate residues are hydrogen bonded in mononodenate fashion to each face of the porphyrin: N21-O3A 2.797 Å, N23-O3A 2.799 Å; N22-O2A 2.842 Å, N24-O2A 2.869 Å. One of the trifluoroacetates forms an additional hydrogen bond to a trifluoroacetic acid molecule of solvation (Fig. 2). (O1A-O2S 2.741 Å; disorder, shorter contacts 2.45-2.55 Å). The shortest intermolecular contacts observed were H2A-O1S = 2.332 Å. A chloroform molecule of solvation was located in the void between the macrocycle molecules. The macrocycle conformation is more nonplanar than in 2. Here the average deviation of the 24 macrocycles from their least-squares plane (d24) is 0.44 Å, compared to 0.37 Å in 2.
Exchange of the isopropyl substituents for 1-ethylpropyl residues leads only to a small increase in overall nonplanarity. Like the others, the structure of [4][C$_2$F$_3$O$_2$]$_2$·2CF$_3$CO$_2$H shows monodentate binding of two trifluoroacetate residues to each face of the porphyrin: N21-O4A 2.898 Å, N23-O4A 2.838 Å; N22-O2A 2.847 Å, N24-O2A 2.919 Å. Each of the trifluoroacetates is hydrogen-bonded to a trifluoroacetic acid of solvation (Fig. 3) (O1A-O2S 2.522 Å; O3A-O3S 2.482 Å). The conformation of 4 is very similar to that of 3 with a δ24 of 0.44 Å (Fig. 5).

All three porphyrin macrocycles exhibit more or less typical and symmetric saddle distortions, the differences in bond lengths and angles compared to the respective free base porphyrins [7] are typical for the switch planar → saddle [1], notably a decrease in the C$_a$-C$_m$-C$_a$ angles and an increase in the C$_m$-C$_a$-C$_h$ angles. Interestingly, there are no significant differences in the C$_a$-C$_m$ bond lengths; either within the series 2, 3, and 4 or in comparison to the related free base structures.

For comparative purposes Table I lists the observed range of geometrical data for the other three classes of porphyrin diacids described in the introduction. The data are based on the structures with the following counterions: 1 – two perchlorate structures [8,10,17], a hydrogen sulfate [17], and a mixed chloride/iron tetrachloride salt [13]; 7 – a trifluoroacetate and a methyl sulfate salt [8,17], and a perchlorate salt [10]; 8 – three acetate and trifluoroacetate structures [8,17,20] and a chloride salt [17]. The planar structure [7][RhCl$_3$(CO)$_2$]$_2$ with NH-pyramidalization [14a] was omitted from this list. A comparison of the entries for 2, 3, and 4 with those for 1 shows that no significant structural differences occur between the 5,10,15,20-tetraphenylporphyrin diacids and the 5,10,15,20-tetraalkylporphyrin diacids with primary or secondary alkyl substituents.

The growing of crystals and the structural analysis of 6 proved to be difficult. Over the course of more than four years numerous attempts were made to obtain suitable crystals containing 6 and about 10 different data sets were collected. While crystallization could be achieved quite easily, a satisfactory refinement of the crystal data was often impossible due to the large number of disordered counter anions and solvate molecules. As a result of the nonplanar nature of the porphyrin macrocycles large voids are formed in the crystal which are filled with disordered solvate molecules (see below). Additionally, the propensity of 5,10,15,20-tetraakis(tert-butyl)porphyrin to react with nucleophiles limited the choice of acids to those soluble
in chlorinated solvents. Use of, for example, HClO₄ in methanol results in the formation of the 5-hydro-15-methoxy-5,10,15,20-tetrakis(tert-butyl)porphyrin dipercarbonate [6,7]. In the end, only two structures of marginal quality were obtained.

One sample crystallized in the monoclinic space group P2₁/n with two crystallographically independent molecules of 6 in the unit cell (not shown). The general composition of this sample was [6][C₂F₅O₂]₂·2CF₃CO₂H with severe disorder in both the counternions and the solvate molecules of TFA. The diprotonated macrocycles were hydrogen bonded in monodentate fashion with trifluoroacetate residues: N21-O4A 2.881 Å, N23-O4A 2.958 Å, N22-O2A 2.916 Å, N24-O2A 2.908 Å; N25-O6A 2.871 Å, N27-O6A 2.951 Å, N26-O8A 2.932 Å, N28-O8A 2.879 Å. Due to the severely disordered solvate and counternion residues the structure is of low quality and structural data are listed in Table I only for comparison.

A second monoclinic modification was found to crystallize in space group C2/c (Fig. 4). Again, two trifluoroacetate residues and two trifluoroacetic acid molecules of solvation were present per porphyrin macrocycle to yield the composition [6][C₂F₅O₂]₂·2CF₃CO₂H. Most of these residues were highly disordered, resulting in a structure with unsatisfactory R-values, albeit with much better e.s.d.'s than in the other modification described above. The counteranions were bonded in monodentate fashion with the following hydrogen bond characteristics: O4A-N21 2.897 Å, O4A-N23 2.891 Å, O2A-N22 2.892 Å, O2A-N24 2.943 Å. A very complex hydrogen-bonded network that involved six different residues of TFA and trifluoroacetate molecules was observed. In a general fashion, hydrogen bonded chains of TFA molecules in partially occupied positions were located in the grooves formed by the nonplanar porphyrin macrocycles in the crystal.

As indicated by the spectroscopic data in solution and in the solid state. Nevertheless, both modifications of 6 present a unique nonplanar conformation with significant contributions from both saddle distortion (average Cₜ displacements 1.29 Å) and ruffling (average Cₘ displacements ~0.5 Å). The geometrical and conformational parameters are very similar in both monoclinic modifications of 6. The differences in bond lengths and angles between 6 and the other tetraalkylporphyrin diacids are those expected as the result of increased nonplanarity, e.g. much wider Cₐ-Cₘ-Cₐ angles. The effect, that these angles are even wider than in derivatives of 8 is the result of the ruffling present which tends to increase the Cₐ-Cₘ bonds.

Thus, the ruffling present in the free base porphyrin [21] is maintained to some extent in the diprotonated species. However, protonation with its requirement for up and down tilting of neighboring N-H vectors leads to significant conformational switching and a highly saddle distorted macrocycle. Indeed, the degree of saddle distortion is much larger than in any other peripherally unconstrained porphyrin, i.e. what would be the effect of purely relieving the core steric strain and almost reaches that observed in diacids of dodeca-substituted porphyrins. Part of the peripheral substituent induced steric strain (normally resulting in ruffling) has been redistributed into saddle-type out-of-plane distortion.
In conclusion, the $22H^+,24H^+$-porphyrin diacids obtained via protonation of the respective free base porphyrins exhibit either saddle distorted macrocycles, or highly saddle distorted and ruffled macrocycles if the steric bulk of the meso substituents has resulted in significant ruffling of the free base porphyrin. Thus, in the latter case a switching of the distortion mode is observed as the result of core protonation of 5,10,15,20-tetrakis(tert-butyl)porphyrin.

**Experimental**

General experimental and instrumental techniques were as described before [22]. The free base porphyrins were prepared according to standard procedures [7] and converted to the respective porphyrin ditartrates by dissolving about 30 mmol of the porphyrin free base in 10 ml dichloromethane followed by addition of 5 ml of a solution of 5% TFA in dichloromethane. Crystals formed upon addition of either CH$_2$Cl$_2$/CH$_3$OH of CH$_2$Cl$_2$/n-hexane. As outlined earlier [17], the stability of these dications depends on the degree of distortion in the parent free base. Thus, the crystals were stored under an atmosphere of the respective acid and only dried briefly at 10 mbar at 40 $^\circ$C before analysis.

5,10,15,20-Tetrabutyl-22$H^+$,24$H^+$-porphyrindium ditrifluoroacetate ([2]/[CF$_3$CO$_2$]$_2$)

M. p. 241 $^\circ$C. - UV/vis (CH$_2$Cl$_2$ + 0.5% TFA): $\lambda_{max}$ (lg $\epsilon$) = 422 nm (5.45), 584 (4.03), 632 (4.32). - $^1$H NMR (250 MHz, CDCl$_3$, TMS): $\delta$ = 2.14 (s, 4H, NH). 1.69 (t, 12H, $^3J$ = 7.0 Hz, CH$_3$CH$_2$CH$_2$CH$_3$). 1.84 (sext, 8H, $^3J$ = 7.0 Hz, CH$_3$CH$_2$CH$_2$CH$_3$). 2.49 (quint, 8H, $^3J$ = 7.0 Hz, CH$_2$CH$_2$CH$_2$CH$_3$). 4.89 (t, 8H, $^3J$ = 7.0 Hz, CH$_3$CH$_2$CH$_2$CH$_3$). 9.27 (s, 8H, $\beta$-H).

C$_{40}$H$_{48}$N$_4$O$_4$F$_6$·2CF$_3$CO$_2$H (990.88): Calcd C
53.33, H 5.09, N 5.65. Found C 53.06, H 5.15, N 5.51%.

5,10,15,20-tetraisopropyl-22H⁺,24H⁺-porphyrindium difluoroacetate ([3][CF₃CO₂]₂)

M. p. 187 °C. – UV/vis (CH₃Cl + 1% TFA): λₘₐₓ (lg ε) = 425 nm (5.44), 589 (3.86), 640 (4.31). – ¹H NMR (500 MHz, CDCl₃, TMS): δ = 0.17 (s, 4H, NH), 2.35 (d, 2H, ³J = 7.5 Hz, CH(CH₃)₂), 5.06 (quint, 4H, ³J = 7.5 Hz, CH(CH₃)₂), 8.839, 8.841 (each s, 8H, β-H). C₃₆H₄₉N₄O₄F₆ (706.73): Caled C 54.93, H 6.51, N 4.99%. Found C 54.93, H 6.51, N 4.99%.

5,10,15,20-Tetrakis(1-ethylpropyl)-22H⁺,24H⁺-porphyrindium difluoroacetate ([4][CF₃CO₂]₂)

M. p. 241 °C. – UV/vis (CH₃Cl + 1% TFA): λₘₐₓ (lg ε) = 429 nm (5.49), 594 (3.88), 643 (4.37). – ¹H NMR (250 MHz, CDCl₃, TMS): δ = 0.42 (br s, 4H, NH), 1.02 (t, 24H, ³J = 7.0 Hz, CH(CH₂CH₃)₂), 2.75 (m, 16H, CH(CH₂CH₃)₂), 4.43 (quint, 4H, ³J = 7.0 Hz, CH(CH₂CH₃)₂), 8.75 (br s, 8H, β-H). C₄₃H₇₅N₄O₄F₆·2CF₃CO₂H (1055.05): Caled C 54.64, H 6.31, N 5.31%. Found C 54.93, H 6.51, N 4.99%.

5,10,15,20-Tetrakis(2-methylpropyl)-22H⁺,24H⁺-porphyrindium difluoroacetate ([5][CF₃CO₂]₂)

M. p. 270 °C. – UV/vis (CH₃Cl + 0.5% TFA): λₘₐₓ (lg ε) = 423 nm (5.40), 586 (3.78), 633 (4.24). – ¹H NMR (500 MHz, CDCl₃, TMS): δ = -1.78 (s, 4H, NH), 1.24 (d, 24H, ³J = 7.5 Hz, CH₂CH(CH₃)₂), 2.80 (quint, 4H, ³J = 7.5 Hz, CH₂CH(CH₃)₂), 4.71 (d, 4H, ³J = 7.5 Hz, CH₂CH(CH₃)₂), 9.18 (s, 8H, β-H). C₄₄H₇₇N₄O₄F₆·2CF₃CO₂H (990.88): Caled C 53.33, H 5.09, N 5.65. Found C 53.14, H 5.05, N 5.49%.

5,10,15,20-Tetrakis(tert-butyl)-22H⁺,24H⁺-porphyrindium difluoroacetate ([6][CF₃CO₂]₂)

M. p. 209 °C. – UV/vis (CH₃Cl + 1% TFA): λₘₐₓ (lg ε) = 449 nm (5.11), 702 (4.21). – ¹H NMR (250 MHz, CDCl₃, TMS): δ = 0.79 (s, 4H, NH), 2.08 (s, 36H, C(CH₃)₃), 8.00 (s, 8H, β-H). C₃₈H₉₁N₄O₄F₆·0.25CH₂Cl₂ (784.07): Caled C 61.66, H 6.23, N 7.15. Found C 62.00, H 6.52, N 7.27%.

Crystallography

Crystals were selected and mounted as described by Hope [23]. Intensity data for [2][C₃F₇O₃]₂·2CF₃CO₂H.

[3][C₂F₄O₂]₂·CF₃CO₂H·CHCl₃ and [6][C₂F₄O₂]₂·2CF₃CO₂H·HCl were collected using a Siemens R3m/V diffractometer at 126 K utilizing graphite monochromated Mo-Kα radiation (λ = 0.7073 Å). Data for [4][C₂F₄O₂]₂·2CF₃CO₂H were collected with a Syntex P2₁ instrument at 128 K using Cu-Kα radiation (λ = 1.54178 Å). Data for [6][C₂F₄O₂]₂·2CF₃CO₂H·HCl (monoclinic P2₁/n) were collected with a Siemens P4 rotating anode instrument at 130 K using Cu-Kα radiation (λ = 1.54178 Å).

During the data collections two standard reflections were measured every 198 reflections and showed only statistical variation of the intensities (<1%). The intensities were corrected for Lorentz and polarization effects. For all structures an absorption correction was applied using the program XABS2 [24], while extinction effects were disregarded. The structures were via Direct Methods [25], missing atoms and solvent molecules were located in subsequent Fourier difference maps. Refinements were carried out by full-matrix least-squares on [F²] using either the program SHELXL-93 [26a] or SHELXL-97 [26b]. Hydrogen atoms were included in calculated positions using a riding model with C-H = 0.96 Å and N-H = 0.90 Å; unless otherwise stated, all non-hydrogen atoms were refined with anisotropic thermal parameters. Details for the crystal data, data collection and refinement are given below.

Complete details on the crystal structure investigations, including atomic coordinates, thermal parameters and complete bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK). Copies can be obtained on request by quoting the publication citation and the deposition numbers CCDC-140336 – CCDC 140340.

Crystal data for [2][C₃F₇O₃]₂·2CF₃CO₂H: Crystals were grown from CHCl₃/CH₃OH + 1% TFA, blue cube, crystal size 0.61 × 0.61 × 0.61 mm, C₄₄H₅₀F₁₂N₄O₈, FW = 990.88, tetragonal, space group P4₁, a = 15.630(4) Å, c = 19.668(10) Å, V = 4805(3) Å³, Z = 4, d calc = 1.370 Mg.m⁻³, μ = 0.124 mm⁻¹, T min = 0.93, T max = 0.93, θ max = 27.51°, 6094 reflection collected, 5683 independent reflections (R int = 0.0327), 4114 reflections with I > 2.0σ(I), 610 parameters, d I/d(θ max) = 0.830 e Å⁻³, R1 (I > 2σ(I)) = 0.0731, R1 (all data) = 0.1039, wR2 (all data) = 0.2231, S = 1.047. Disorder in trifluoroacetate and trifluoroacetic acid residues. F4A, F5A, and F7A were refined as disordered over two split positions with equal occupancy.
Crystals were grown from CHCl$_3$/CH$_3$OH + 1% TFA, green prism, crystal size 1.05 x 1.05 x 0.5 mm, C$_{39}$H$_{40}$Cl$_3$F$_3$N$_4$O$_6$, F.W. = 940.12, triclinic, space group $P_1$, $a = 11.916(4)$ Å, $b = 12.097(5)$ Å, $c = 15.917(6)$ Å, $\alpha = 87.12(3)^\circ$, $\beta = 84.96(3)^\circ$, $\gamma = 77.96(3)^\circ$, $V = 2183.6(14)$ Å$^3$, $Z = 2$, $d_{\text{calc}} = 1.430$ Mg.m$^{-3}$, $\mu = 0.297$ mm$^{-1}$, $T_{\text{min}} = 0.73$, $T_{\text{max}} = 0.86$, $\theta_{\text{max}} = 27.5^\circ$, 10524 reflections collected, 10009 independent reflections ($R_{\text{int}} = 0.0591$), 6829 reflections with $I > 2.00(I)$, 638 parameters, $\Delta/\sigma_{\text{max}} = 0.1414$, $R_1[I > 2\sigma(I)] = 0.0659$, $R_1$ (all data) = 0.0910, $wR_2$ (all data) = 0.1634, $S = 1.018$. Considerable disorder in all trifluoroacetate and trifluoroacetic acid residues.

Crystals were grown for [4]/[C$_2$F$_3$O$_2$]$_2$·2CF$_3$CO$_2$H: Crystals were grown from CH$_2$Cl$_2$/n-hexane + 1% TFA, black cube, crystal size 0.83 x 0.73 x 0.63 mm, C$_{48}$H$_{58}$F$_{12}$N$_2$O$_8$, F.W. = 1046.98, triclinic, space group $P_1$, $a = 11.775(5)$ Å, $b = 12.266(4)$ Å, $c = 20.404(8)$ Å, $\alpha = 94.30(3)^\circ$, $\beta = 98.23(3)^\circ$, $\gamma = 116.50(3)^\circ$, $V = 2578(2)$ Å$^3$, $Z = 2$, $d_{\text{calc}} = 1.349$ Mg.m$^{-3}$, $\mu = 1.444$ mm$^{-1}$, $T_{\text{min}} = 0.43$, $T_{\text{max}} = 0.52$, $\theta_{\text{max}} = 57.25^\circ$, 7412 reflection collected, 7005 independent reflections ($R_{\text{int}} = 0.0530$), 5690 reflections with $I > 2.00(I)$, 639 parameters, $\Delta/\sigma_{\text{max}} = 0.890$ e Å$^{-3}$, $R_1[I > 2\sigma(I)] = 0.0971$, $R_1$ (all data) = 0.1140, $wR_2$ (all data) = 0.2804, $S = 1.017$. Disorder in the meso substituents and for most trifluoroacetic acid and trifluoroacetic acid residues.

Crystals were grown for [6]/[C$_2$F$_3$O$_2$]$_2$·2CF$_3$CO$_2$H (monoclinic $P_2_1/n$): Crystals were grown from CH$_2$Cl$_2$/n-pentane + 1% TFA, blue, irregular shaped crystal, crystal size 0.6 x 0.2 x 0.2 mm, C$_{88}$H$_{100}$F$_{24}$N$_8$O$_{16}$, F.W. = 1981.76, monoclinic, space group $P2_1/n$, $a = 24.182(10)$ Å, $b = 12.872(7)$ Å, $c = 31.883(13)$ Å, $\beta = 101.84(3)^\circ$, $V = 9713(8)$ Å$^3$, $Z = 4$ (2 indep. molecules), $d_{\text{calc}} = 1.355$ Mg.m$^{-3}$, $\mu = 1.078$ mm$^{-1}$, $T_{\text{min}} = 0.56$, $T_{\text{max}} = 0.81$, $\theta_{\text{max}} = 56.41^\circ$, 15431 reflection collected, 12760 independent reflections ($R_{\text{int}} = 0.0542$), 7278 reflections with $I > 2.00(I)$, 1259 parameters, $\Delta/\sigma_{\text{max}} = 0.944$ e Å$^{-3}$, $R_1[I > 2\sigma(I)] = 0.1414$, $R_1$ (all data) = 0.2045, $wR_2$ (all data) = 0.4261, $S = 1.146$. Severe disorder in the trifluoroacetic acid and trifluoroacetate residues.

Crystal data for [6]/[C$_2$F$_3$O$_2$]$_2$·2CF$_3$CO$_2$H (monoclinic $C2/c$): Crystals were grown from CH$_2$Cl$_2$/n-hexane + 1% TFA, blue block, crystal size 1 x 0.8 x 0.6 mm, C$_{44}$H$_{50}$F$_{12}$N$_4$O$_8$, F.W. = 990.88, monoclinic, space group $C2/c$, $a = 32.521(7)$ Å, $b = 12.929(3)$ Å, $c = 23.965(5)$ Å, $\beta = 101.32(3)^\circ$, $V = 9880(3)$ Å$^3$, $Z = 8$, $d_{\text{calc}} = 1.332$ Mg.m$^{-3}$, $\mu = 0.121$ mm$^{-1}$, $T_{\text{min}} = 0.89$, $T_{\text{max}} = 0.93$, $\theta_{\text{max}} = 25.00^\circ$, 9104 reflection collected, 8996 independent reflections ($R_{\text{int}} = 0.0481$), 5046 reflections with $I > 2.00(I)$, 751 parameters, $\Delta/\sigma_{\text{max}} = 1.672$ e Å$^{-3}$, $R_1[I > 2\sigma(I)] = 0.1129$, $R_1$ (all data) = 0.1629, $wR_2$ (all data) = 0.3494, $S = 1.114$. Severe disorder in the trifluoroacetic acid and trifluoroacetate residues. The trifluoroacetic acid residues of solvation form partially occupied hydrogen bonded chains, some of the residues are located on special positions and show crystallographically required disorder. Refinement of the trifluoromethyl group involving C2B, F1B, F2B, F3B required use of a strong C1B-C2B constraint, the largest shifts were observed for this group and could not be overcome completely. Six different residues of electron density were found for the two trifluoroacetate and trifluoroacetic acid residues. The residual electron density is located in the solvent region.

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