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2-Amidoindole-based anion receptors

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2-Amidoindole-based anion receptors

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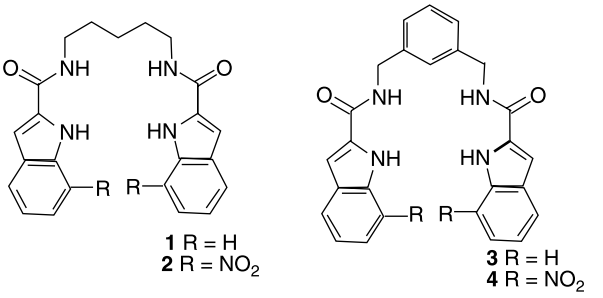
Four receptors containing either 2-amidoindole or 7-nitro-2-amidoindole groups have been synthesised and shown to complex oxoanions in DMSO-d_6/0.5% water solution. X-ray crystal structure elucidation reveals that receptor **1** complexes dihydrogen phosphate ion pairs in the solid state, which are part of a continuous chain. While this receptor binds dihydrogen phosphate in a 1:1 stoichiometry in solution, compound **4**, which contains 7-nitroindole groups, does form 1:2 receptor:dihydrogen phosphate complexes in DMSO-d_6/0.5% water.

Keywords: anion binding; indole; hydrogen bonding; crystallography

Introduction

Anion receptors based on organic frameworks are currently an area of intense interest (*1*). Recent work from the groups of Jeong (*2*) and others (*3*) has begun to focus attention on the use of indole as a hydrogen bond donor group in synthetic anion receptor systems (*4*). Indole (pK_a 21 in DMSO), like pyrrole (pK_a 23 in DMSO) (*5*), contains a single hydrogen bond donor group and yet its utility as a component of synthetic receptor systems, in comparison with pyrrole, is still largely unexplored. In biological systems, indole (as tryptophan) has been shown to form hydrogen bonds with anions such as chloride (*6*) and sulfate (*7*). We have used 2,3-dimethylindole in functionalised pyridine-2,6-dicarboxamides and isophthalamides to form fluoride-selective receptors (*8*) and, in collaboration with Albrecht and co-workers (*9*), have explored the use of 2,7-functionalised indoles as oxoanion receptors. This latter project, related to our work on amidopyrroles (*10*) and Albrecht's (*11*) work on quinoline-based receptors, led to the discovery that 1,3-diindolylureas are particularly effective dihydrogen phosphate receptors (*12*). In this paper, we report the synthesis of four 2-amidoindole-containing receptors **1**–**4** consisting of two 2-carboxyindole groups linked either via a flexible 1,5-diaminopentane linker or via a 1,3-phenylenediamine linking group. Two of the compounds contain nitro groups at the 7-position of the indole rings. The anion complexation properties of these receptors have been measured and the X-ray crystal structure of the dihydrogen phosphate complex of receptor **1** elucidated.



Experimental

General remarks

All reactions were performed using oven-dried glassware under slight positive pressure of nitrogen/argon (as specified). ^{1}H NMR (300 MHz) and ^{13}C{^{1}H} NMR (75 MHz) spectra were determined on a Bruker AV300 spectrometer. ^{1}H NMR (400 MHz) and ^{13}C{^{1}H} NMR (100 MHz) spectra were determined on a Bruker AV400 spectrometer. Chemical shifts for ^{1}H NMR are reported in parts per million (ppm), calibrated to the solvent peak set, with coupling constants reported in Hertz. The following abbreviations are used for spin multiplicity: s, singlet; d, doublet; t, triplet; m, multiplet. Chemical shifts for ^{13}C{^{1}H} NMR are reported in ppm, relative to the central line of a septet at $\delta = 39.52$ ppm for DMSO-d_6. Infrared (IR) spectra were recorded on a Matterson Satellite (ATR). FT-IR are reported in wave numbers (cm^{-1}). Elemental analysis was performed by Medac Ltd. Low-resolution

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mass spectra were recorded on a Micromass Platform single-quadrupole spectrometer. All solvents and starting materials were purchased from commercial chemical sources where available. NMR titrations were performed by adding aliquots of the putative anionic guest (as the TBA) salt (0.15 M) in a solution of the receptor (0.01 M) in DMSO-d_6 to a solution of the receptor (0.01 M).

Synthesis

N,N′-*(Pentane-1,5-diyl)bis(1H-indole-2-carboxamide) (**1**)*

A solution of indole-2-carboxylic acid (0.63 g, 3.91 mM) and carbonyldiimidazole (CDI; 0.80 g, 5.00 mM) in chloroform (30 ml) was heated at reflux for 1.5 h. After this time, 1,5-diaminopentane (0.200 g, 1.96 mM) in chloroform (5 ml) was added dropwise and the solution was left at reflux overnight. The reaction mixture was then left to cool to room temperature and the precipitate that had formed was removed by filtration, washed with ether (10 ml) and dried affording the product as a white powder (0.56 g, 73%). ^{1}H NMR (300 MHz, DMSO-d_6): δ1.40–1.42 (2H, br m, CH_2), δ1.55–1.62 (4H, br m, CH_2), δ3.33 (4H, m, CH_2), δ7.02 (2H, t, $J = 7.4$ Hz, ArCH), δ7.09 (2H, s, ArCH), δ7.16 (2H, t, $J = 7.9$ Hz, ArCH), δ7.42 (2H, d, $J = 7.9$ Hz, ArCH), δ7.58 (2H, d, $J = 7.8$ Hz, ArCH), δ8.44 (2H, s, NH), δ11.51 (2H, s, NH). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ24.0 (CH_2), δ29.0 (CH_2), δ38.7 (CH_2), δ102.2 (CH), δ112.3 (CH), δ119.7 (CH), δ121.4 (CH), δ123.2 (CH), δ127.1 (C), δ131.9 (C), δ136.4 (C), δ161.0 (C). MS (ESI +) *m/z*: calcd, 388.2; found, 389.2 $(M + H)^+$. Anal calcd for $C_{23}H_{24}N_4O_2$: C = 71.11%, H = 6.23%, N = 14.42%; found: C = 70.89%, H = 6.11%, N = 14.69%. IR (ν, cm^{-1}): 3272, 2942, 2359, 2342, 1614, 1547; mp 270–272°C.

N,N′-*(Pentane-1,5-diyl)bis(7-nitro-1*H*-indole-2-carboxamide) (**2**)*

A solution of 7-nitro-1-indole carboxylic acid (0.63 g, 3.91 mM) and CDI (0.4 g) in chloroform (20 ml) was heated at reflux for 1.5 h. After this time, 1,5-diaminopentane (0.1 g, 0.98 mM) in chloroform (2 ml) was added dropwise and the solution was left at reflux overnight under nitrogen. The reaction mixture was then left to cool to room temperature and the solution washed three times with water and the organic phase dried over magnesium sulfate. The solvent was then removed under *in vacuo* and an orange solid was obtained. Column chromatography on silica gel 60 eluting with 9:1 CH_2Cl_2:MeOH afforded the product as a yellow powder. Yield: (0.22 g, 47%), mp 200–202°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ1.43 (2H, m, CH_2), δ1.63 (4H, m, CH_2), δ3.33 (4H, m, CH_2), δ7.27–7.35 (4H, m, ArCH), δ8.14–8.22 (4H, m, ArCH), δ8.95 (2H, s, NH), δ10.70–10.81 (2H, s, NH). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ14.7 (CH_2), δ24.0 (CH_2), δ28.7 (CH_2), δ106.0 (CH), δ119.8 (CH), δ120.9 (CH), δ128.6, δ130.5 (CH), δ130.9 (C), δ132.9 (C), δ134.8 (C), δ159.4 (C). MS (ESI-) *m/z*: calcd, 478.2; found, 377.2 $(M - H)^-$. Anal calcd for $C_{23}H_{22}N_6O_6$: C = 57.74%, H = 4.63%, N = 17.56%; found: C = 57.41%, H = 4.71%, N = 17.82%. IR (ν, cm^{-1}): 3462, 3370, 2930, 2859, 2359, 2342, 1631, 1559.

N,N′-*(1,3-Phenylenebis(methylene))bis(1*H*-indole-2-carboxamide) (**3**)*

A chloroform solution of CDI (0.6 g, 3.7 mM) and indole-2-carboxylic acid (0.476 g, 2.937 mM) was placed under nitrogen at reflux for 1.25 h. A solution of 1,3-bis(aminomethyl)benzene (0.2 g, 1.469 mM) in DMF (5 ml) was added dropwise to the reaction mixture which was then left under nitrogen at reflux overnight. The solution was then left to cool to room temperature and ether (20 ml) was added. The white precipitate that had formed was removed by suction filtration (crop 1) and the filtrate was taken to dryness, by evaporation under reduced pressure and cold-finger evaporation. The yellow solid produced was suspended in CH_2Cl_2, removed by suction filtration (crop 2) and then washed with ether (10 ml) to afford the product as a white powder. Yield: (0.44 g, 70%), mp 257–258°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ4.52 (4H, d, $J = 5.9$ Hz, CH_2), δ7.04 (2H, t, $J = 7.0$ Hz, ArCH), δ7.16–7.30 (8H, m ArCH), δ7.32–7.35 (2H, m, ArCH), δ7.43–7.62 (2H, m, ArCH), δ7.42 (2H, d, $J = 6.4$ Hz ArCH), δ7.59 (2H, d, $J = 6.0$ Hz, ArCH), δ9.06 (2H, s, NH), δ11.60 (2H, s, NH). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6): δ42.2 (CH_2), δ102.7 (CH), δ112.3 (CH), δ119.8 (CH), δ121.5 (CH), δ123.3 (CH), δ125.9 (CH), δ126.3 (CH), δ127.1 (C), δ128.4 (CH), δ131.7 (C), δ136.5 (C), δ139.8 (C), δ161.2 (C). MS (ESI −) *m/z*: calcd, 422.2; found, 421.2 $(M - H)^-$. Anal calcd for $C_{26}H_{22}N_4O_2$: C = 73.92%, H = 5.25%, N = 13.25%; found: C = 73.62%, H = 5.32%, N = 13.46%. IR (ν, cm^{-1}) 3294, 1615, 1591, 1542.

N,N′-*(1,3-Phenylenebis(methylene))bis(7-nitro-1H-indole-2-carboxamide) (**4**)*

A chloroform (60 ml) solution of 7-nitroindole-2-carboxylic acid (0.606 g, 2.939 mM) and CDI (0.600 g, 3.700 mM) was stirred at reflux under nitrogen for 2 h until a clear orange solution had been produced. A DMF (5 ml) solution of bis(aminomethyl)benzene was prepared and added dropwise to the solution. This solution was then left at reflux under nitrogen overnight and a yellow precipitate was obtained, which was removed by filtration. Ether (20 ml) was then added to the filtrate and the yellow precipitate that was obtained was again removed by

Table 1. Stability constants of compounds **1**–**4** with anionic guests added as tetrabutylammonium salts in DMSO-d_6/0.5% water solution at 298 K.

Anion	Compound **1**	Compound **2**	Compound **3**	Compound **4**
F^-	83	–[a]	<10	–[a]
CH_3COO^-	46	149	38	97
$PhCOO^-$	25	24	18	11
$H_2PO_4^-$	260	99	176	$K_1 = 108$ $K_2 = 216$
Cl^-	<10	<10	<10	<10

1:1 stoichiometries were observed except where noted. Errors in fitting estimated <15% except for chloride (see ESI).[a] NH proton resonance disappeared during the titration and hence a stability constant could not be obtained.

suction filtration. The yellow precipitate was dried and then washed with dilute HCl (100 ml) and the insoluble precipitate removed by suction filtration and then washed with ether and dried *in vacuo* affording the product as a yellow powder. Yield: (0.55 g, 72%), mp 268–269°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ4.54 (4H, d, $J = 6.0$ Hz, CH_2), δ7.26–7.40 (8H, m, ArCH), δ8.11 (2H, d, $J = 7.5$ Hz, ArCH), δ8.17 (2H, d, $J = 8.0$ Hz, ArCH), δ9.55 (2H, t, $J = 6.0$ Hz, NH), δ11.27 (2H, s, NH). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ42.8 (CH_2), δ106.9 (CH), δ120.3 (CH), δ121.5 (CH), δ126.6 (CH), δ126.6 (CH), δ128.9 (CH), δ129.1, δ130.9 (CH), δ131.3 (C), δ133.4 (C), δ134.9 (C), δ139.8 (C), δ159.9 (C). MS (ESI −) *m/z*: calcd, 512.1; found, 511.2 $(M - H)^-$. Anal calcd for $C_{26}H_{20}N_6O_6$: C = 60.94%, H = 3.93%, N = 16.40%; found: C = 61.05%, H = 3.97%, N = 16.32%. IR (ν, cm^{-1}) 3464, 3449, 3302, 2360, 2341, 1643, 1557, 1517.

Results and discussion

Compounds **1**–**4** were synthesised by coupling either commercially available indole-2-carboxylic acid or 7-nitroindole-2-carboxylic acid with either 1,5-diaminopentane or 1,3-phenylenediamine using CDI as an amide-coupling reagent in yields ranging from 42 to 73%.

Stability constants were determined by ^{1}H NMR titration techniques(*13*) in DMSO-d_6/0.5% water solution (Table 1). Stoichiometries were determined by Job plot analysis. The results show that the compounds have a moderate affinity for anions under these solvent conditions with selectivity for oxoanions and specifically dihydrogen phosphate (excepting compound **2**). On moving from compound **1** to compound **2**, one might expect stability constants to increase due to the electron-withdrawing nature of the nitro substituents. However, only in the case of acetate is enhanced binding observed. It is possible that steric interactions between the nitro groups occur if the receptor wraps around a single anionic guest, therefore destabilising the complex. In the case of compound **4** and dihydrogen phosphate, a 1:2 receptor:anion complex is formed with $K_2 > K_1$. Dihydrogen phosphate is known to oligomerise (*14*) and it is possible that in this case the receptor is binding a dihydrogen phosphate anion pair. It may be the case that steric interactions between the nitro groups disfavour the formation of a 1:1 complex with dihydrogen phosphate and hence promoting the formation of a 1:2 complex.

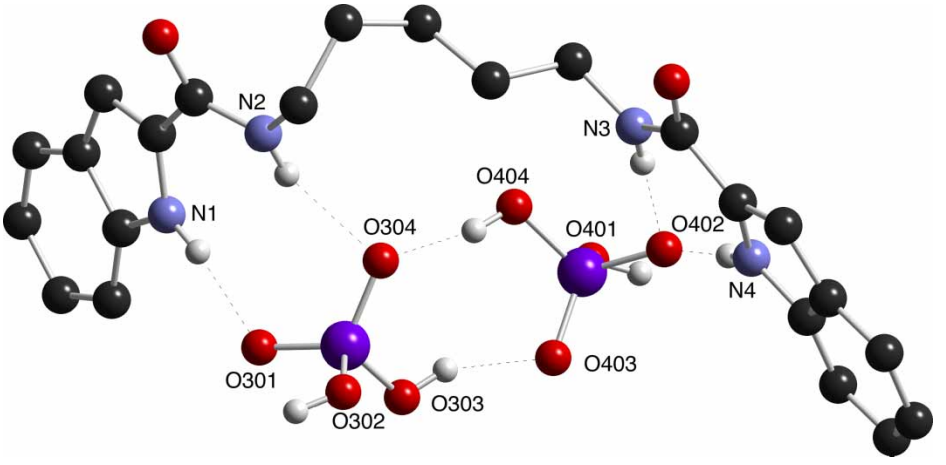

Figure 1. Receptor **1** binding a dihydrogen phosphate dimer in the solid state. Tetrabutylammonium counter cations have been omitted for clarity.

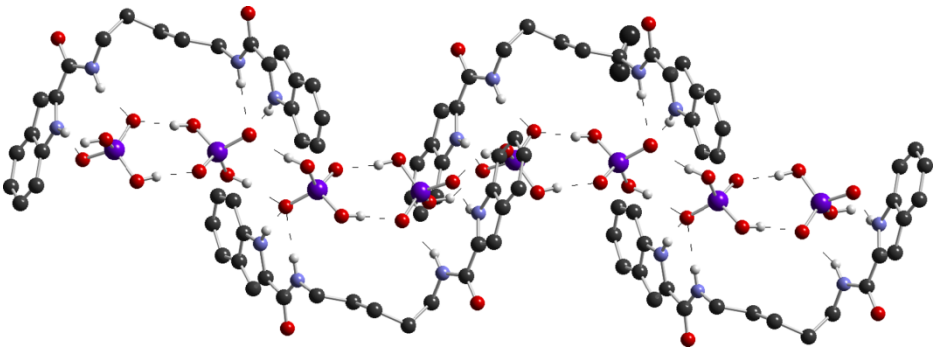

Figure 2. The dihydrogen phosphate chain in the crystal structure of the complex with receptor **1** showing the receptors complexing dihydrogen phosphate anion pairs. Tetrabutylammonium counter cations and non-acidic hydrogens have been omitted for clarity.

Crystals of the tetrabutylammonium dihydrogen phosphate complex of receptor **1** were grown by slow evaporation of an acetonitrile solution in the presence of excess tetrabutylammonium dihydrogen phosphate.[1] The structure shown in Figure 1 shows that each receptor complexes a dihydrogen phosphate ion pair in the solid state. Each ion pair is part of a continuous chain of dihydrogen phosphate anions (Figures 2 and 3) analogous to that observed in the solid-state structure of tetrabutylammonium dihydrogen phosphate (*15*). In this case, each amidoindole unit in the receptor binds to different dihydrogen phosphate anions in the ion pair with two different hydrogen bonding motifs (Figure 4). Hydrogen bond lengths and angles are shown in Table 2.

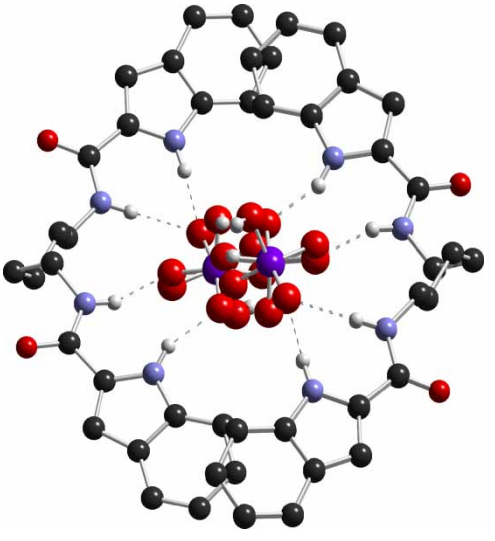

Figure 3. A view down the *c*-axis in the tetrabutylammonium dihydrogen phosphate complex of receptor **1**. Tetrabutylammonium counter cations and non-acidic hydrogens have been omitted for clarity.

Crystals of the fluoride complex of receptor **2** were obtained by slow evaporation of a solution of the receptor in acetonitrile in the presence of excess tetrabutylammonium fluoride.[2] This process produced an oil that was recrystallised from dichloromethane affording X-ray diffraction quality single crystals. The structure shows that each equivalent of receptor **2** is bound to two fluoride anions via indole and amide NH···F^- hydrogen bonds. The complexes form two crystallographically distinct hydrogen bonded cyclic structures, as shown in Figure 5, bridged through water molecules. For details of the hydrogen bond lengths and angles, see the electronic supplementary information.

Conclusions

While the receptors described here generally show a moderate-to-low affinity for anions, the formation of a 1:2 receptor:dihydrogen phosphate complex in solution by receptor **4** and in the solid state by receptor **1** is further evidence (*14*) to suggest that binding anionic dimers may be a potentially useful strategy for complexing oxoanions containing both hydrogen bond donors and acceptors. We are continuing to explore this and other aspects of anion complexation by indole-containing anion receptors. The results of these studies will be reported in due course.

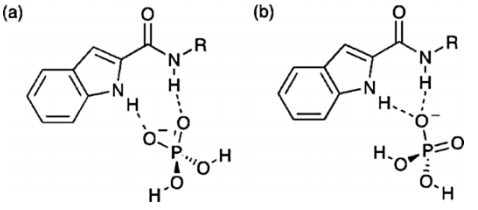

Figure 4. Two different dihydrogen phosphate-binding motifs are observed in the solid-state structure of the dihydrogen phosphate complex of receptor **1**.

Table 2. Hydrogen bonds (Å and °) in the tetrabutylammonium dihydrogen phosphate complex of receptor **1**.

D—H···*A*	*d*(*D*—H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*D*HA)
N1—H1···O301[a]	0.88	1.84	2.659(8)	154.4
N2—H2···O304[a]	0.88	2.08	2.901(8)	154.7
N3—H3···O402[a]	0.88	2.07	2.948(8)	179.1
N4—H4···O402[a]	0.88	1.85	2.719(8)	171.0
O302—H302···O301[a]	0.84	1.85	2.596(7)	147.2
O303—H303···O403	0.84	1.75	2.510(8)	148.9
O401—H401···O402[b]	0.84	1.81	2.641(7)	171.4
O404—H404···O304	0.84	1.75	2.578(7)	168.3

Atom labels are shown in Figure 1. Symmetry transformations used to generate equivalent atoms: [a] $-x+1, -y+1, -z$; [b] $-x+1, -y+1, -z+1$.

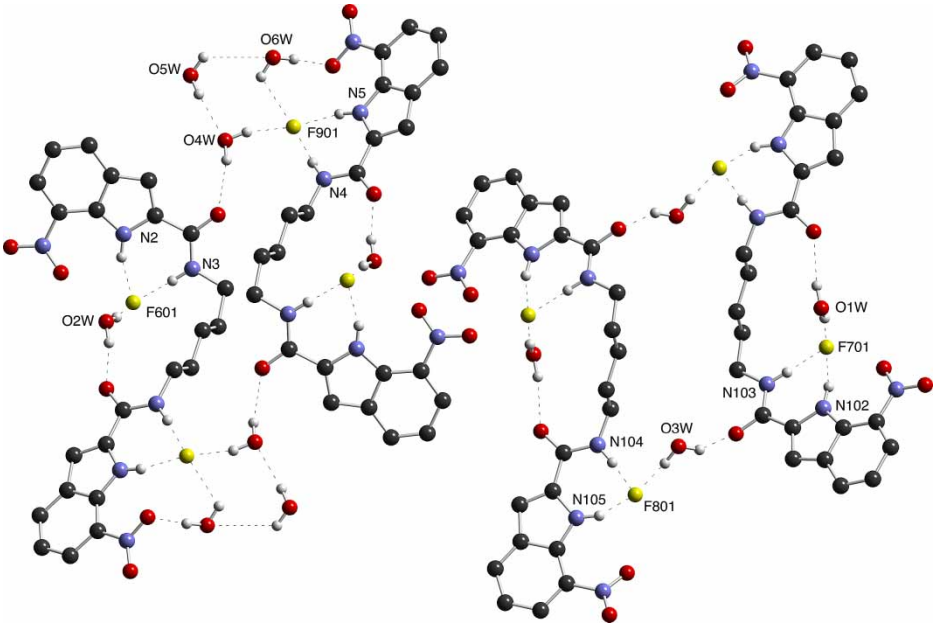

Figure 5. The X-ray crystal structure of the fluoride complex of receptor **2**. Tetrabutylammonium counter cations and non-acidic hydrogen atoms have been omitted for clarity.

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Notes

1. Crystal data for compound **1**· tetrabutylammonium dihydrogen phosphate CCDC 686083: $C_{55}H_{100}N_6O_{10}P_2$, Mr = 1067.35, $T = 120(2)$ K, triclinic space group $P\bar{1}$, $a = 14.4568(8)$, $b = 14.5325(8)$, $c = 16.3506(8)$ Å, $\alpha = 108.932(2)°$, $\beta = 104.053(2)°$, $\gamma = 98.051(2)°$, $V = 3061.1(3)$ Å^3, $\rho_{calc} = 1.158$ Mg/m^3, $\mu = 0.128$ mm^{-1}, $Z = 2$, reflections collected: 34256, independent reflections: 10399 [$R_{int} = 0.0662$], final R indices [$I > 2\sigma I$]: $R_1 = 0.1248$, $wR_2 = 0.3162$, R indices (all data): $R_1 = 0.1518$, $wR_2 = 0.3381$.
2. Crystal data for compound **2**· tetrabutylammonium fluoride CCDC 690147: $C_{55}H_{99.50}F_2N_8O_{8.75}$, Mr = 1050.93, $T = 120(2)$ K, triclinic space group $P\bar{1}$, $a = 18.2539(8)$, $b = 19.4067(5)$, $c = 20.2800(9)$ Å, $\alpha = 67.988(2)°$, $\beta = 83.891(2)°$, $\gamma = 63.829(2)°$, $V = 5962.7(4)$ Å^3, $\rho_{calc} = 1.171$ Mg/m^3, $\mu = 0.083$ mm^{-1}, $Z = 4$ reflections collected: 81556, independent reflections: 20977 [$R_{int} = 0.1296$], final R indices [$I > 2\sigma I$]: $R_1 = 0.1139$, $wR_2 = 0.2830$, R indices (all data): $R_1 = 0.2326$, $wR_2 = 0.3566$.

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