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Fluorinated Calix[4]pyrrole and Dipyrrolylquinoxaline. Neutral Anion Receptors with Augmented Affinities and Enhanced Selectivities.

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Supporting Information

^{1}H and ^{19}F NMR titration experiments for **2**

Fluorescence titration experiments for **4**

Job plots for **4**

X-ray experimental and crystallographic data for the aggregated form of **2**: **2**(aggreg).

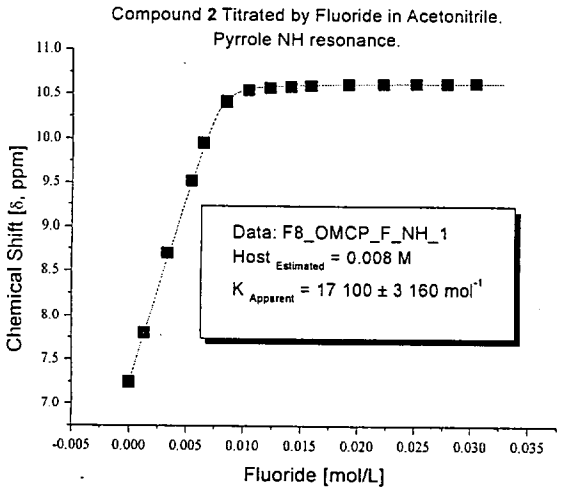
X-ray experimental and crystallographic data for DMSO complex of **2**: **2**(DMSO).

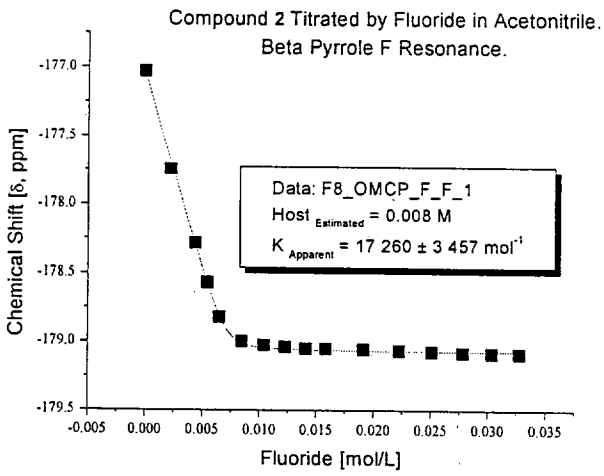
X-ray experimental and crystallographic data for fluoride complex of **2**: **2**(F).

^{1}H and ^{19}F NMR titrations.

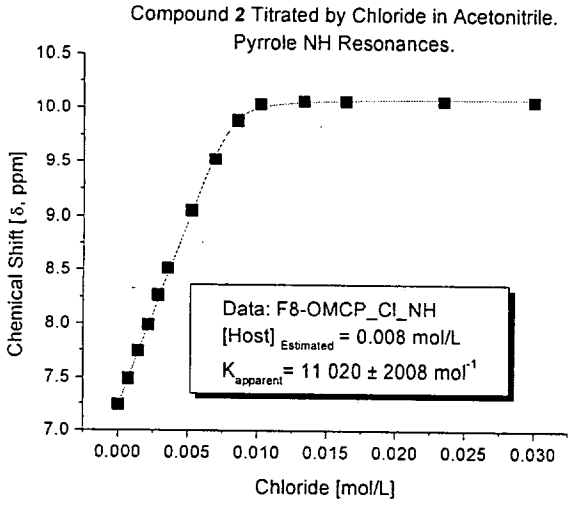
The receptor **2**, as a 0.014 M acetonitrile-d_3 (0.5% v/v D_2O) solution, was titrated by addition of concentrated acetonitrile-d_3 (0.5% v/v D_2O) solutions of the anions in question (in the form of their tetrabutylammonium salts). In order to account for dilution effects, these anion solutions also contained receptor **2** at its initial concentration. The data were fit to a 1:1 binding profile according to the method of Wilcox (Wilcox, C. S. in *Frontiers in Supramolecular Organic Chemistry and Photochemistry;* Schneider, H.-J., Dürr, H., Eds.; VCH: Weinheim, 1991) using changes in both the NH and β-F pyrrolic resonances in the ^{1}H and ^{19}F NMR spectra, respectively, that were assigned to the portion of the total receptor concentration that was considered to be monomeric. Estimated errors were <20%.

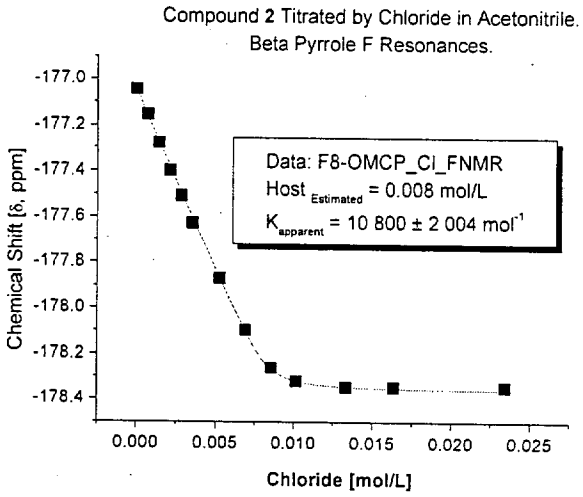
Anion binding isotherms for compound **2** and fluoride anion determined by ^{1}H and ^{19}F NMR.



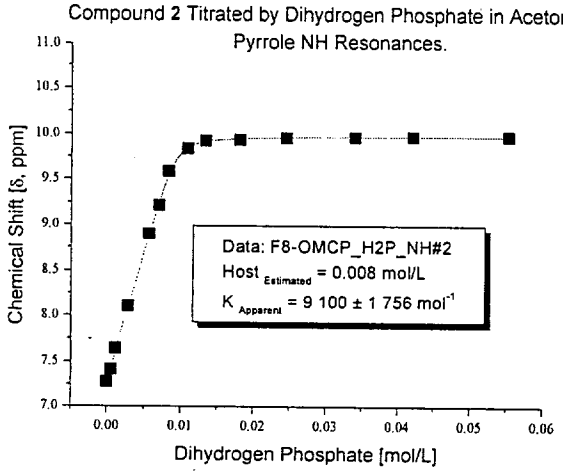


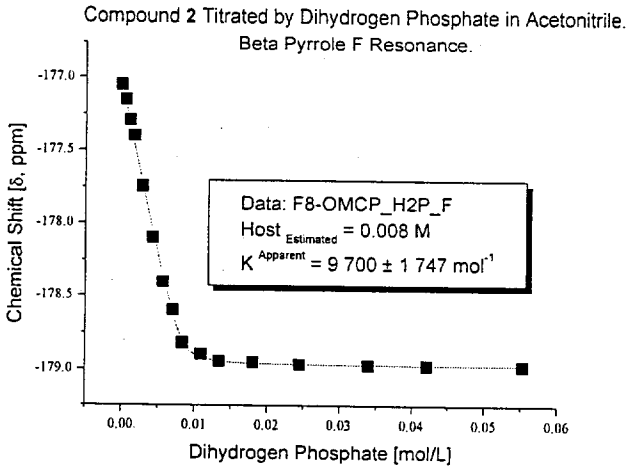
Anion binding isotherms for compound **2** and chloride anion determined by ^{1}H and ^{19}F NMR.



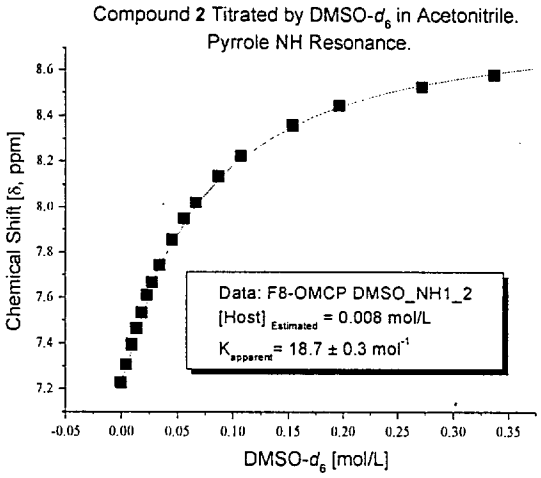


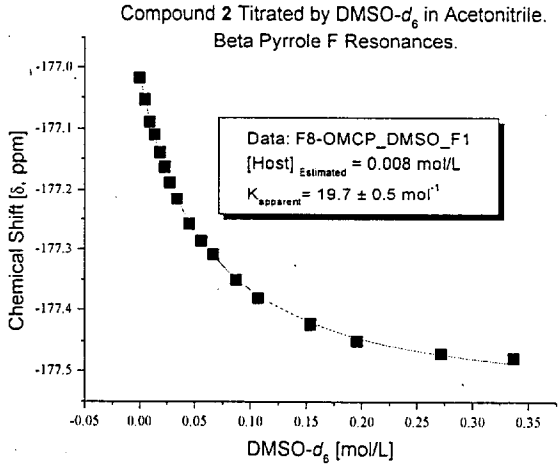
Anion binding isotherms for compound **2** and dihydrogen phosphate anion determined by ^{1}H and ^{19}F NMR.





Anion binding isotherms for compound **2** and DMSO-d_6 determined by ^{1}H and ^{19}F NMR.

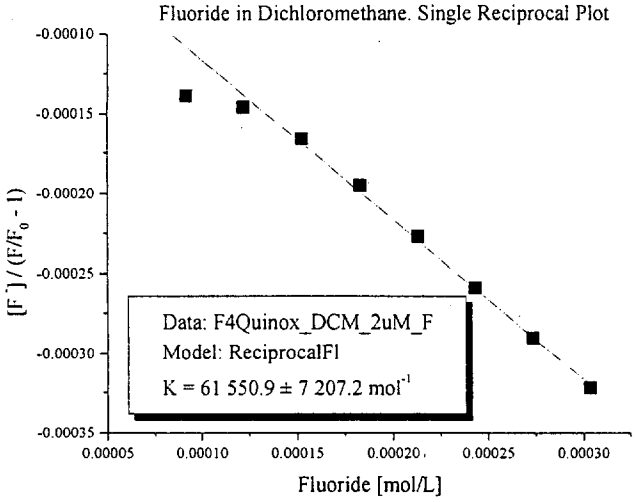




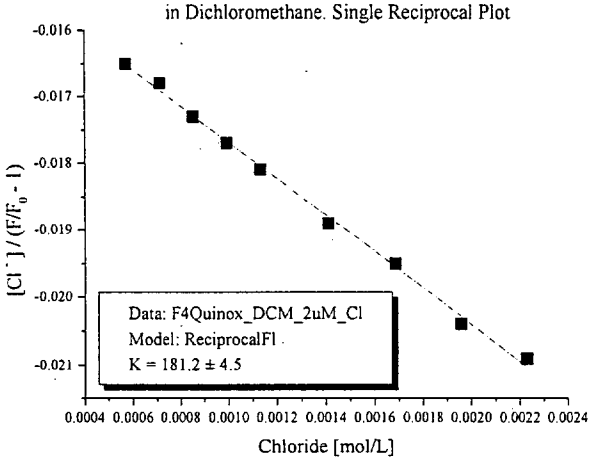
Fluorescence titration studies.

Fluorescence quenching experiments were carried out in the following manner: Solutions of sensor **4** in dichloromethane were titrated with increasing quantities of concentrated solutions of the anion in question (in the form of their tetrabutylammonium salts). To account for dilution effects, these concentrated anions solutions also contained sensor **4** at its initial concentration. The concentration of sensor **4** in all experiments was 2.0 μM. The emission scan parameters used were as follows: excitation at 410 nm, excitation and emission slits = 2 nm, spectrum increment = 1 nm, integration time = 1s. The binding isotherms (i.e., the dependence of F/Fo upon anion concentration) were linearized using Scott plot analyses as described by Connors[9] and detailed in a previous publication (Black, C. B.; Andrioletti, B.; Try, A. C.; Ruiperez, C.; Sessler, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 10438-10439).

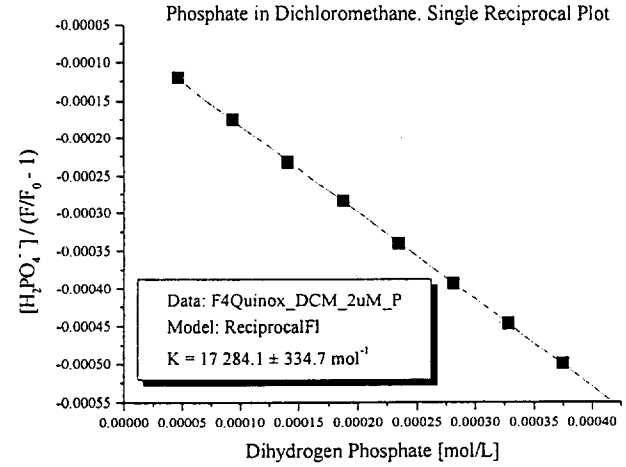
Bis(3,4-difluoropyrrole-2-yl)quinoxaline [2 μM] Titrated by Fluoride in Dichloromethane. Single Reciprocal Plot



Bis(3,4-difluoropyrrole-2-yl)quionoxaline [2.0 μM] Titrated by Chloride in Dichloromethane. Single Reciprocal Plot



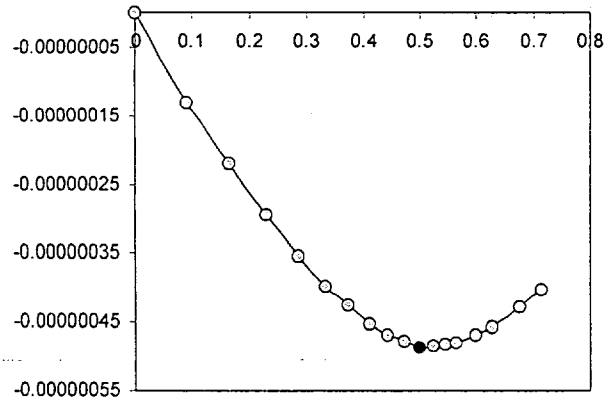
Bis(3,4-difluoropyrrole-2-yl)quinoxaline [2 μM] Titrated by Phosphate in Dichloromethane. Single Reciprocal Plot



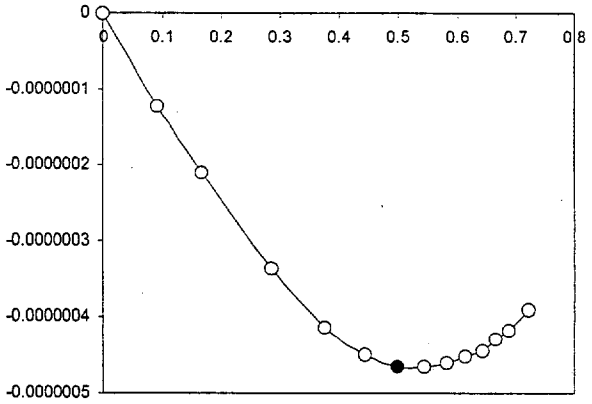
Studies of the sensor-anion complex stoichiometry (Job plots) for 4

Job plots were performed as fluorescence quenching experiments. All recorded Job plots for sensor **4** were found to exhibit maxima at 0.5 ± 0.05. This indicates that sensor **4** forms 1:1 complexes with the anions in question. Job plots were performed according to: Tsukube, H., Furuta, H., Odani, A., Takeda, Y., Kudo, Y., Inoue, Y., Liu, Y., Sakamoto, H., Kimura, K. *Determination of Stability Constants*, in *Comprehensive Supramolecular Chemistry*; Atwood, J.L., Davies, J.E.D., Macnicol, D.D., Vogtle, F., Eds.; Elsevier Science Ltd.: New York, 1996; Vol. 8, p 425-482.

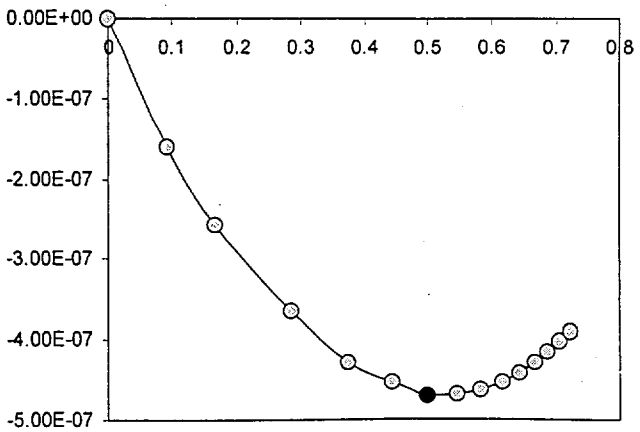
Job plot for **4** and fluoride anion.



Job plot for **4** and chloride anion.



Job plot for **4** and dihydrogenphosphate anion.



X-ray experimental and crystallographic data for the aggregated form of 2: 2(aggreg).

X-ray Experimental for 2(aggreg)

Table 1. Crystallographic Data for 2(aggreg).

Table 2. Fractional coordinates and equivalent isotropic thermal parameters ($Å^2$) for the non-hydrogen atoms of 2(aggreg).

Table 3. Anisotropic thermal parameters for the non-hydrogen atoms of 2(aggreg).

Table 4. Fractional coordinates and isotropic thermal parameters ($Å^2$) for the hydrogen atoms of 2(aggreg).

Figure 1. View of molecule 1 of 2(aggreg) showing the atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

Figure 2. View of molecule 2 of 2(aggreg) showing the atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale. The molecule lies on a crystallographic inversion center at ½, 0, ½. Atoms with labels appended with A are related by 1-x, -y, 1-z.

Figure 3. Unit cell packing diagram. The view is approximately down **a**. Molecules shown in ball and stick fashion lie around crystallographic inversion centers. Hydrogen bonding interactions are shown with dashed lines.

X-ray Experimental for 2(aggreg): Crystals grew as colorless lathes by slow evaporation from methanol and methylene chloride. The data crystal was cut from a long lathe and had approximate dimensions; 0.40 x 0.30 x 0.20 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 481 frames of data were collected using ω-scans with a scan range of 1.2° and a counting time of 114 seconds per frame. The data were collected at –150 °C using a Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.[1] The structure was solved by direct methods using SIR92[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms on nitrogen and oxygen were observed in a ΔF map. The N-H hydrogen atoms were refined with no restraints. The O-H hydrogen atoms did not refine well and were tied to the oxygen atom during refinement. There are two unique fluoro-calix pyrrole molecules per asymmetric unit. One molecule lies around a crystallographic inversion center. Two molecules of methanol are also found in the asymmetric unit. These molecules are H-bound to each other and to the calix pyrrole that lies around the inversion center. The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0355*P)^2 + (1.8122*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.1257, with R(F) equal to 0.0560 and a goodness of fit, S, = 1.121. Definitions used for calculating R(F),$R_w(F^2)$ and the goodness of fit, S, are given below.[2] The data were corrected for secondary extinction effects. The correction takes the form: $F_{corr} = kF_c/[1 + (1.3(2) \times 10^{-9})* F_c^2 \lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[5] All figures were generated using SHELXTL/PC.[6] Tables of positional and thermal parameters, bond lengths and angles, figures and lists of observed and calculated structure factors are located in tables 1 through 6.

References

1) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.

2) SIR92. (1993). A program for crystal structure solution. Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. J. Appl. Cryst. 26, 343-350.

3) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

4) $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.
$S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

5) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

6) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table 1. Crystal data and structure refinement for 2(aggreg).

Empirical formula	C44 H50 F12 N6 O2
Formula weight	922.90
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	a = 10.0565(2) Å alpha = 90°. b = 22.5491(3) Å beta = 99.0720(10)°. c = 19.2054(3) Å gamma = 90°.
Volume, Z	4300.63(12) Å^3, 6
Density (calculated)	1.425 Mg/m^3
Absorption coefficient	0.124 mm^-1
F(000)	1920
Crystal size	0.40 x 0.30 x 0.20 mm
Theta range for data collection	2.92 to 30.05°.
Limiting indices	-14<=h<=14, -31<=k<=31, -27<=l<=27
Reflections collected	24034
Independent reflections	12555 [R(int) = 0.0411]
Reflections observed	7778 [I>2(sigma(I))]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11253 / 0 / 602
Goodness-of-fit on F^2	1.121
Final R indices [I>2sigma(I)]	R1 = 0.0560, wR2 = 0.109
R indices (all data)	R1 = 0.108, wR2 = 0.126
Extinction coefficient	1.3(2) x 10^{-6}
Largest diff. peak and hole	0.28 and -0.32 e.Å^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 2(aggreg). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N1	7652(2)	3627(1)	5172(1)	25(1)
N2	4368(2)	3677(1)	4295(1)	25(1)
N3	3232(2)	3655(1)	5939(1)	25(1)
N4	6458(2)	3400(1)	6791(1)	23(1)
C1	8302(2)	3255(1)	5687(1)	24(1)
C2	8429(2)	2731(1)	5351(1)	28(1)
C3	7843(2)	2787(1)	4641(1)	29(1)
C4	7349(2)	3347(1)	4527(1)	25(1)
C5	6627(2)	3673(1)	3886(1)	28(1)
C6	5420(2)	3990(1)	4088(1)	25(1)
C7	5053(2)	4570(1)	4120(1)	27(1)
C8	3799(2)	4602(1)	4351(1)	26(1)
C9	3367(2)	4045(1)	4461(1)	25(1)
C10	2100(2)	3792(1)	4679(1)	27(1)
C11	2478(2)	3421(1)	5341(1)	24(1)
C12	2200(2)	2855(1)	5518(1)	26(1)
C13	2793(2)	2751(1)	6222(1)	27(1)
C14	3438(2)	3252(1)	6485(1)	25(1)
C15	4205(2)	3429(1)	7202(1)	29(1)
C16	5521(2)	3712(1)	7095(1)	25(1)
C17	6071(2)	4259(1)	7229(1)	26(1)
C18	7333(2)	4274(1)	6999(1)	25(1)
C19	7577(2)	3732(1)	6726(1)	22(1)
C20	8761(2)	3470(1)	6433(1)	24(1)
C21	7587(2)	4125(1)	3629(1)	41(1)
C22	6154(2)	3233(1)	3286(1)	41(1)
C23	1367(2)	3402(1)	4081(1)	36(1)
C24	1147(2)	4296(1)	4818(1)	36(1)
C25	4478(2)	2879(1)	7678(1)	41(1)
C26	3356(2)	3875(1)	7549(1)	43(1)
C27	9863(2)	3944(1)	6438(1)	32(1)
C28	9347(2)	2947(1)	6904(1)	32(1)
F2	8998(1)	2224(1)	5632(1)	40(1)
F3	7809(1)	2344(1)	4164(1)	44(1)
F7	5763(1)	5051(1)	3966(1)	38(1)
F8	3149(1)	5118(1)	4435(1)	36(1)
F12	1495(1)	2442(1)	5105(1)	36(1)
F13	2684(1)	2231(1)	6561(1)	38(1)
F17	5549(1)	4727(1)	7531(1)	38(1)
F18	8120(1)	4761(1)	7041(1)	34(1)
N1'	3573(2)	164(1)	3844(1)	27(1)
N2'	4457(2)	974(1)	5403(1)	26(1)
C1'	4426(2)	-183(1)	3517(1)	27(1)
C2'	5352(2)	202(1)	3326(1)	30(1)
C3'	5043(2)	774(1)	3530(1)	29(1)
C4'	3935(2)	753(1)	3853(1)	25(1)
C5'	3233(2)	1243(1)	4193(1)	27(1)
C6'	4102(2)	1398(1)	4888(1)	24(1)

C7'	4745(2)	1900(1)	5151(1)	27(1)
C8'	5481(2)	1775(1)	5819(1)	27(1)
C9'	5310(2)	1195(1)	5975(1)	26(1)
C10'	5826(2)	837(1)	6626(1)	31(1)
C11'	3074(2)	1787(1)	3700(1)	33(1)
C12'	1821(2)	1049(1)	4317(1)	33(1)
C13'	7351(2)	948(1)	6842(1)	45(1)
C14'	5080(3)	1037(1)	7229(1)	44(1)
F2'	6371(1)	77(1)	2969(1)	45(1)
F3'	5757(1)	1267(1)	3424(1)	40(1)
F7'	4730(1)	2437(1)	4833(1)	37(1)
F8'	6221(1)	2175(1)	6240(1)	38(1)
O1A	1906(2)	-352(1)	4904(1)	52(1)
C2A	2102(3)	-936(1)	5182(1)	51(1)
O1B	-694(2)	-310(1)	4160(1)	65(1)
C2B	-1107(3)	-810(2)	3732(2)	81(1)

Table 3. Anisotropic displacement parameters (Å^2 x 10^3) for 2(aggreg). The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N1	27(1)	23(1)	25(1)	-1(1)	6(1)	4(1)
N2	26(1)	21(1)	29(1)	4(1)	8(1)	1(1)
N3	23(1)	26(1)	27(1)	2(1)	5(1)	-4(1)
N4	24(1)	22(1)	24(1)	-3(1)	6(1)	-2(1)
C1	20(1)	27(1)	25(1)	1(1)	7(1)	1(1)
C2	30(1)	23(1)	32(1)	2(1)	8(1)	3(1)
C3	34(1)	26(1)	27(1)	-8(1)	8(1)	-1(1)
C4	23(1)	30(1)	24(1)	-2(1)	7(1)	-1(1)
C5	26(1)	37(1)	22(1)	0(1)	7(1)	1(1)
C6	26(1)	28(1)	21(1)	4(1)	5(1)	-1(1)
C7	31(1)	24(1)	25(1)	4(1)	4(1)	-4(1)
C8	32(1)	21(1)	25(1)	-1(1)	2(1)	6(1)
C9	27(1)	26(1)	21(1)	2(1)	4(1)	5(1)
C10	25(1)	33(1)	25(1)	3(1)	5(1)	2(1)
C11	20(1)	30(1)	24(1)	1(1)	5(1)	2(1)
C12	22(1)	26(1)	29(1)	-3(1)	6(1)	-1(1)
C13	26(1)	26(1)	31(1)	7(1)	9(1)	2(1)
C14	20(1)	31(1)	25(1)	4(1)	6(1)	1(1)
C15	23(1)	42(1)	24(1)	2(1)	6(1)	-2(1)
C16	21(1)	33(1)	21(1)	-1(1)	5(1)	2(1)
C17	27(1)	26(1)	25(1)	-4(1)	5(1)	5(1)
C18	25(1)	25(1)	24(1)	-2(1)	2(1)	-4(1)
C19	20(1)	27(1)	20(1)	0(1)	4(1)	-1(1)
C20	21(1)	28(1)	25(1)	0(1)	5(1)	1(1)
C21	33(1)	55(1)	36(1)	16(1)	11(1)	2(1)
C22	39(1)	56(1)	26(1)	-9(1)	3(1)	13(1)
C23	31(1)	46(1)	30(1)	2(1)	0(1)	-4(1)
C24	31(1)	42(1)	38(1)	8(1)	11(1)	13(1)
C25	31(1)	59(1)	32(1)	16(1)	2(1)	-12(1)
C26	24(1)	73(2)	33(1)	-14(1)	10(1)	-2(1)
C27	23(1)	41(1)	32(1)	-5(1)	8(1)	-4(1)
C28	29(1)	40(1)	28(1)	1(1)	5(1)	9(1)
F2	54(1)	26(1)	40(1)	4(1)	7(1)	12(1)
F3	64(1)	33(1)	35(1)	-12(1)	6(1)	7(1)
F7	43(1)	27(1)	42(1)	6(1)	6(1)	-11(1)
F8	44(1)	23(1)	41(1)	-1(1)	6(1)	9(1)
F12	39(1)	32(1)	36(1)	-6(1)	4(1)	-8(1)
F13	45(1)	29(1)	39(1)	11(1)	9(1)	-2(1)
F17	38(1)	35(1)	41(1)	-13(1)	10(1)	7(1)
F18	34(1)	27(1)	41(1)	-6(1)	5(1)	-8(1)
N1'	32(1)	24(1)	24(1)	0(1)	5(1)	-2(1)
N2'	35(1)	19(1)	25(1)	1(1)	3(1)	-4(1)
C1'	33(1)	25(1)	21(1)	-1(1)	1(1)	3(1)
C2'	33(1)	31(1)	27(1)	1(1)	9(1)	5(1)
C3'	34(1)	24(1)	30(1)	4(1)	7(1)	-3(1)
C4'	29(1)	22(1)	22(1)	1(1)	0(1)	-1(1)
C5'	30(1)	25(1)	25(1)	1(1)	4(1)	1(1)
C6'	29(1)	21(1)	24(1)	2(1)	6(1)	2(1)

C7'	31(1)	19(1)	31(1)	4(1)	8(1)	2(1)
C8'	29(1)	25(1)	27(1)	-6(1)	3(1)	-2(1)
C9'	29(1)	23(1)	25(1)	-2(1)	4(1)	0(1)
C10'	40(1)	25(1)	26(1)	-2(1)	-1(1)	0(1)
C11'	43(1)	28(1)	26(1)	3(1)	3(1)	7(1)
C12'	30(1)	33(1)	34(1)	-2(1)	3(1)	2(1)
C13'	45(1)	26(1)	55(1)	0(1)	-16(1)	-1(1)
C14'	76(2)	32(1)	26(1)	-4(1)	9(1)	6(1)
F2'	48(1)	39(1)	55(1)	1(1)	28(1)	7(1)
F3'	41(1)	29(1)	51(1)	4(1)	17(1)	-5(1)
F7'	46(1)	20(1)	44(1)	9(1)	3(1)	-3(1)
F8'	44(1)	25(1)	41(1)	-7(1)	-4(1)	-6(1)
O1A	58(1)	38(1)	62(1)	5(1)	20(1)	3(1)
C2A	57(2)	42(1)	53(1)	3(1)	6(1)	5(1)
O1B	61(1)	74(1)	59(1)	-8(1)	4(1)	10(1)
C2B	59(2)	105(3)	75(2)	-39(2)	-6(2)	14(2)

Table 4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 2(aggreg).

	x	y	z	U(eq)
H1N	7368(20)	3950(9)	5262(10)	26(5)
H2N	4405(20)	3301(10)	4383(11)	34(6)
H3N	3585(21)	3984(10)	5962(11)	34(6)
H4N	6344(17)	3068(8)	6639(9)	14(5)
H21A	7882(2)	4402(1)	4001(1)	61
H21B	8353(2)	3921(1)	3503(1)	61
H21C	7129(2)	4334(1)	3226(1)	61
H22A	5552(2)	2950(1)	3443(1)	61
H22B	5697(2)	3442(1)	2882(1)	61
H22C	6920(2)	3029(1)	3159(1)	61
H23A	1947(2)	3084(1)	3986(1)	54
H23B	565(2)	3241(1)	4220(1)	54
H23C	1131(2)	3638(1)	3664(1)	54
H24A	1588(2)	4544(1)	5191(1)	54
H24B	911(2)	4528(1)	4398(1)	54
H24C	346(2)	4131(1)	4954(1)	54
H25A	5003(2)	2599(1)	7461(1)	62
H25B	4963(2)	2994(1)	8129(1)	62
H25C	3637(2)	2702(1)	7740(1)	62
H26A	3183(2)	4220(1)	7256(1)	64
H26B	2517(2)	3696(1)	7611(1)	64
H26C	3843(2)	3988(1)	8000(1)	64
H27A	9512(2)	4273(1)	6149(1)	47
H27B	10152(2)	4078(1)	6912(1)	47
H27C	10614(2)	3776(1)	6255(1)	47
H28A	8674(2)	2646(1)	6909(1)	48
H28B	10101(2)	2785(1)	6718(1)	48
H28C	9638(2)	3087(1)	7375(1)	48
H1'N	2968(25)	9(11)	4076(12)	53(7)
H2'N	4219(21)	592(10)	5369(11)	39(6)
H11A	3946(2)	1914(1)	3617(1)	49
H11B	2533(2)	1681(1)	3260(1)	49
H11C	2645(2)	2102(1)	3916(1)	49
H12A	1896(2)	710(1)	4624(1)	49
H12B	1399(2)	1368(1)	4530(1)	49
H12C	1286(2)	947(1)	3874(1)	49
H13A	7814(2)	824(1)	6467(1)	67
H13B	7512(2)	1362(1)	6934(1)	67
H13C	7674(2)	724(1)	7259(1)	67
H14A	4133(3)	970(1)	7093(1)	67
H14B	5401(3)	813(1)	7647(1)	67
H14C	5239(3)	1451(1)	7322(1)	67
H1BA	187(2)	-363(1)	4353(1)	78
H2AA	1784(3)	-968(1)	5627(1)	61
H2AB	3044(3)	-1029(1)	5239(1)	61
H2AC	1631(3)	-1211(1)	4850(1)	61
H1AA	1490(2)	-168(1)	5233(1)	98
H2BA	-433(3)	-1114(2)	3804(2)	97
H2BB	-1262(3)	-693(2)	3245(2)	97
H2BC	-1939(3)	-958(2)	3849(2)	97

Figure 1. View of molecule 1 of 2(aggreg) showing the atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

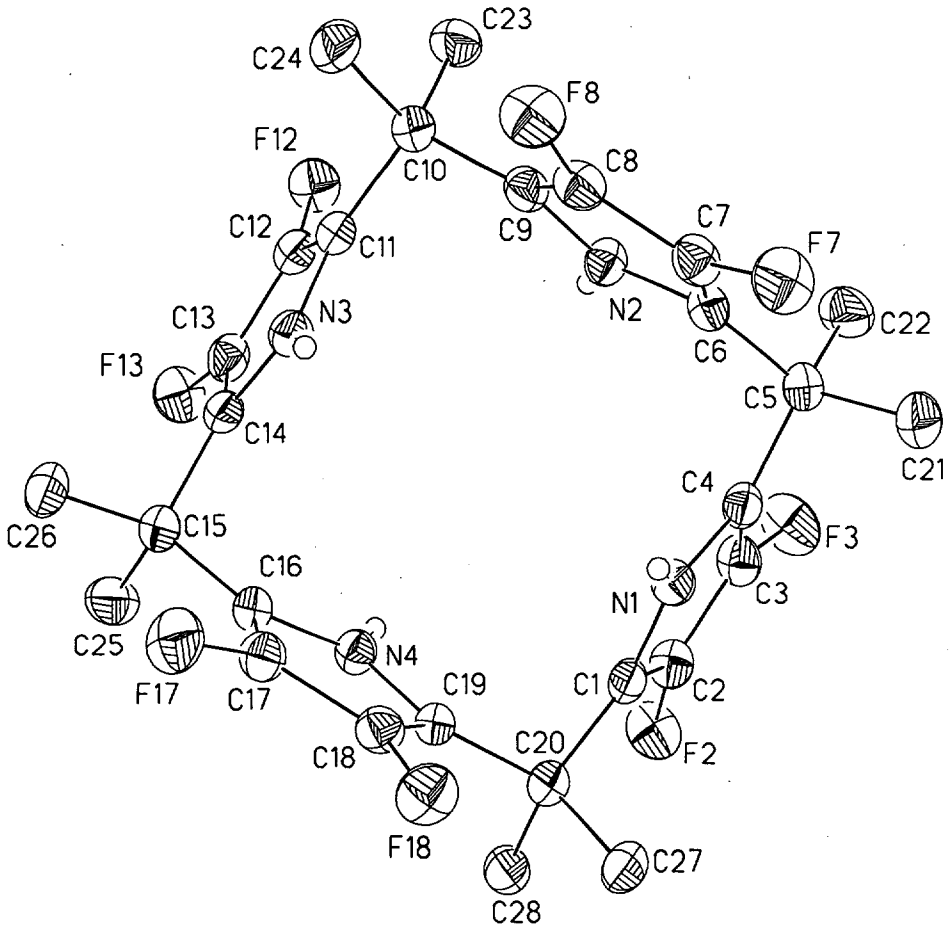


Figure 2. View of molecule 2 of 2(aggreg) showing the atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale. The molecule lies on a crystallographic inversion center at ½, 0, ½. Atoms with labels appended with A are related by 1-x, -y, 1-z.

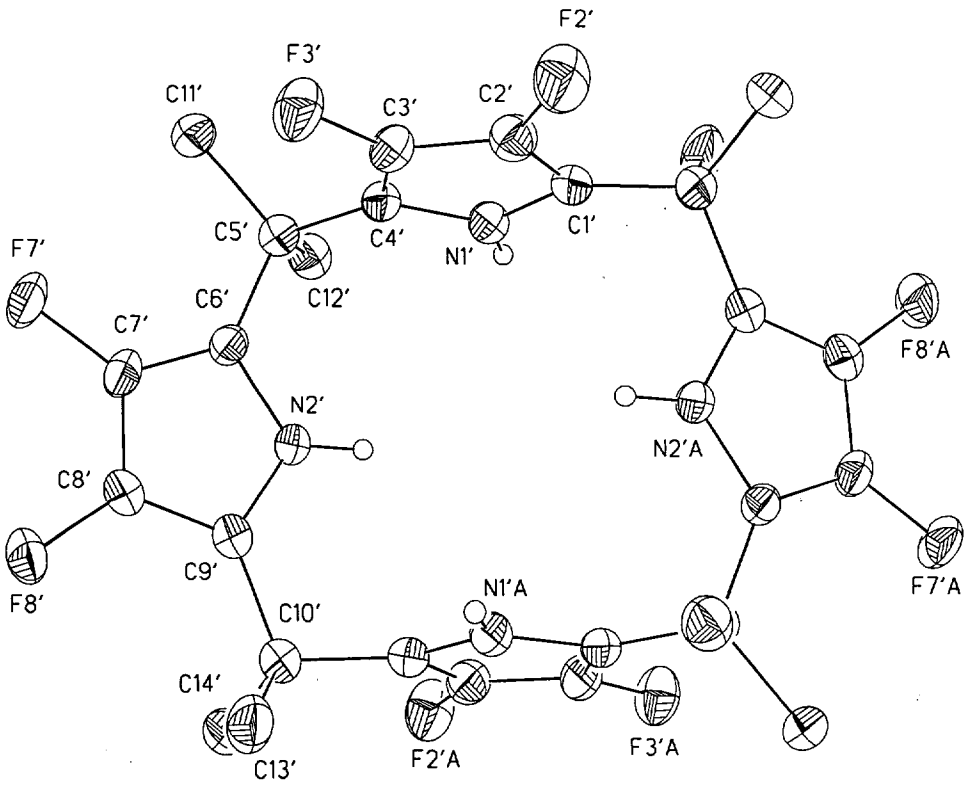
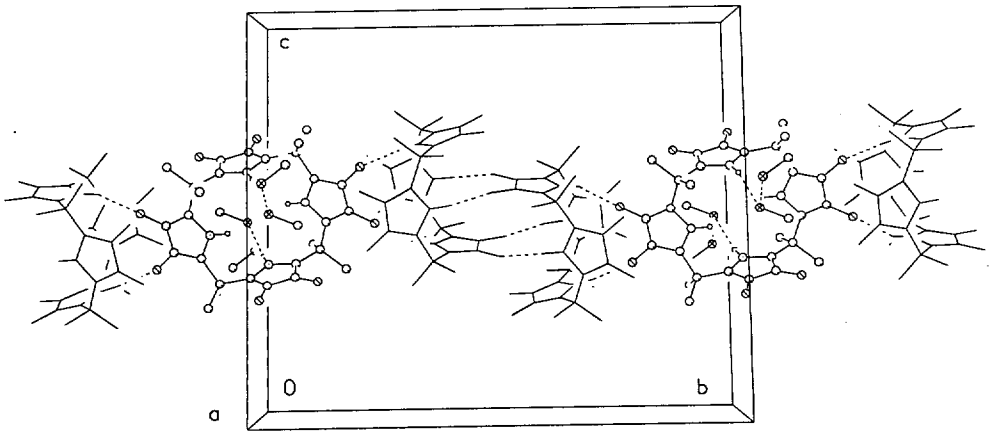


Figure 3. Unit cell packing diagram for **2**(aggreg). The view is approximately down **a**. Molecules shown in ball and stick fashion lie around crystallographic inversion centers. Hydrogen bonding interactions are shown with dashed lines.



X-ray experimental and crystallographic data for DMSO complex of 2: 2(DMSO).

X-ray Experimental for **2**(DMSO).

Table 1. Crystallographic Data for **2**(DMSO).

Table 2. Fractional coordinates and equivalent isotropic thermal parameters ($Å^2$) for the non-hydrogen atoms of **2**(DMSO).

Table 3. Anisotropic thermal parameters for the non-hydrogen atoms of **2** (DMSO).

Table 4. Fractional coordinates and isotropic thermal parameters ($Å^2$) for the hydrogen atoms of **2** (DMSO).

Figure 1. View of molecule 1 of **2**(DMSO) showing the atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

Figure 2. View of molecule 2 of **2**(DMSO) showing the atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

Figure 3. View of molecule 1 of **2**(DMSO) showing a partial atom labeling scheme and the H-bonding interactions with the DMSO molecules. Dashed lines indicate close N-H···O interactions. Two DMSO molecules are H-bound to the calixpyrrole. One is H-bound to three pyrroles while the second in H-bound to the remaining pyrrole. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

Figure 4. View of molecule 2 of **2**(DMSO) showing a partial atom labeling scheme and the H-bonding interactions with the DMSO molecules. Dashed lines indicate close N-H···O interactions. Two DMSO molecules are H-bound to the calixpyrrole. One is H-bound to three pyrroles while the second in H-bound to the remaining pyrrole. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

Figure 5. Unit cell packing diagram for **2**(DMSO). The view is approximately down the **b** axis. Molecules pack in layers parallel to **bc**. Layers are alternately composed of molecules 1 and molecules 2. Atoms from molecules 2 are shown in wireframe form.

Figure 6. View of the fit by least-squares of atoms from molecule 1 of **2**(DMSO) (dashed lines) to equivalent atoms of molecule 2 (solid lines). Atoms of molecule 2 used in the fit are labeled.

X-ray Experimental for 2(DMSO) {$C_{28}H_{28}N_4F_8$-2[$(CH_3)_2SO$]}: Crystals grew as colorless prisms by slow evaporation from DMSO and CH_2Cl_2. The data crystal was cut from a larger crystal and had approximate dimensions; 0.46 x 0.30 x 0.20 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 155 frames of data were collected using ω-scans with a scan range of 1.7° and a counting time of 102 seconds per frame. The data were collected at –150°C using a Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.[1] While the crystallographic metric symmetry is orthorhombic, the Laue symmetry is 2/m. The Rint for merging in Laue symmetry mmm is 58%. The structure was solved by direct methods using SIR92[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atom positions on N were observed in a ΔF map and refined with isotropic displacement parameters. Near the final stages of refinement, a large peak approximately 1.4 e/Å^3, persisted in the vicinity of one of the DMSO molecules. The position of this peak was consistent with an inversion of the DMSO molecule through the plane defined by the oxygen and carbon atoms. Such a situation results in a disorder of the sulfur atom of the group, S1A'. Site occupancy factors for the two sulfur positions refined to 95(1)% for the major component and 5(1)% for the minor component atom, S1AA while refining an isotropic displacement parameter common to the two atoms. For the final refinement, S1A' was refined anisotropically while the minor component, S1AA, was refined isotropically. The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0420*P)^2 + (5.2000*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.1156, with R(F) equal to 0.0469 and a goodness of fit, S, = 0.974. Definitions used for calculating R(F),$R_w(F^2)$ and the goodness of fit, S, are given below.[4] Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[5] All figures were generated using SHELXTL/PC.[6] Tables of positional and thermal parameters, bond lengths and angles, figures and lists of observed and calculated structure factors are located in tables 1 through 6. The hydrogen atoms on nitrogen were observed in a ΔF map and refined with isotropic

displacement parameters. There are two molecules of the fluoro calixpyrrole per asymmetric unit. Each molecule is H-bound to two molecules of DMSO via the oxygen atom. For each calixpyrrole, one DMSO molecule is H-bond to three pyrroles while the second DMSO molecule is H-bond to one pyrrole (Table 7).

References

1) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.

2) SIR92. (1993). A program for crystal structure solution. Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. J. Appl. Cryst. 26, 343- 350.

3) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

4) $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = \{\Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.
$S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

5) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

6) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table 1. Crystal data and structure refinement for 2(DMSO).

Empirical formula	C32 H40 F8 N4 O2 S2
Formula weight	728.80
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 18.0507(3) Å alpha = 90°. b = 18.6046(4) Å beta = 90.02(1)°. c = 20.2428(4) Å gamma = 90°.
Volume, Z	6798.1(2) Å^3, 8
Density (calculated)	1.424 Mg/m^3
Absorption coefficient	0.237 mm^-1
F(000)	3040
Crystal size	0.46 x 0.30 x 0.20 mm
Theta range for data collection	3.0 to 27.5°.
Limiting indices	-23<=h<=23, -19<=k<=24, -26<=l<=26
Reflections collected	25623
Independent reflections	15329 [R(int) = 0.0292]
Reflections observed	10851 [I>2(sigma(I))]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13999 / 0 / 901
Goodness-of-fit on F^2	0.974
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.0974
R indices (all data)	R1 = 0.0817, wR2 = 0.1156
Largest diff. peak and hole	0.313 and -0.308 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 2(DMSO). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S1B	9625(1)	2463(1)	2825(1)	26(1)
S1A	10365(1)	2547(1)	5879(1)	26(1)
S1A'	5993(1)	2132(1)	5410(1)	30(1)
S1AA	6081(7)	1959(7)	4728(6)	34
S1B'	3962(1)	2675(1)	7892(1)	33(1)
O1A	10329(1)	2516(1)	5126(1)	26(1)
N1	8903(1)	2355(1)	4556(1)	22(1)
N2	10301(1)	1208(1)	4107(1)	22(1)
N3	11400(1)	2565(1)	3586(1)	22(1)
N4	10042(1)	3711(1)	4114(1)	21(1)
F2	7522(1)	2985(1)	3488(1)	35(1)
F3	7664(1)	1439(1)	3523(1)	37(1)
F7	9322(1)	-257(1)	3453(1)	42(1)
F8	10821(1)	-103(1)	2959(1)	43(1)
F12	12354(1)	1849(1)	4942(1)	41(1)
F13	12152(1)	3386(1)	4991(1)	41(1)
F17	10386(1)	5178(1)	3075(1)	46(1)
F18	8855(1)	5057(1)	3511(1)	38(1)
C1	8534(1)	2934(1)	4287(1)	22(1)
C2	8032(1)	2636(1)	3862(1)	25(1)
C3	8102(1)	1891(1)	3879(1)	25(1)
C4	8655(1)	1708(1)	4309(1)	22(1)
C5	8980(1)	990(1)	4512(1)	24(1)
C6	9651(1)	810(1)	4091(1)	22(1)
C7	9785(1)	279(1)	3642(1)	26(1)
C8	10502(1)	356(1)	3391(1)	28(1)
C9	10826(1)	942(1)	3677(1)	23(1)
C10	11612(1)	1224(1)	3616(1)	23(1)
C11	11675(1)	1964(1)	3903(1)	22(1)
C12	12001(1)	2228(1)	4465(1)	27(1)
C13	11915(1)	2972(1)	4483(1)	27(1)
C14	11540(1)	3192(1)	3931(1)	23(1)
C15	11353(1)	3927(1)	3664(1)	26(1)
C16	10531(1)	4095(1)	3730(1)	25(1)
C17	10130(1)	4647(1)	3472(1)	30(1)
C18	9398(1)	4594(1)	3694(1)	27(1)
C19	9338(1)	4009(1)	4098(1)	22(1)
C20	8692(1)	3707(1)	4487(1)	22(1)
C21	8388(1)	401(1)	4419(1)	32(1)
C22	9198(1)	998(1)	5249(1)	29(1)
C23	12133(1)	697(1)	3983(1)	33(1)
C24	11841(1)	1240(1)	2881(1)	29(1)
C25	11567(1)	3968(1)	2927(1)	34(1)
C26	11794(1)	4503(1)	4044(1)	40(1)
C27	7999(1)	4169(1)	4365(1)	31(1)
C28	8870(1)	3744(1)	5230(1)	29(1)
O1B	10393(1)	2471(1)	2524(1)	31(1)

O1A'	5302(1)	2136(1)	4989(1)	34(1)
N1'	4077(1)	2316(1)	5803(1)	21(1)
N2'	5016(1)	1148(1)	6728(1)	23(1)
N3'	6215(1)	2421(1)	7300(1)	25(1)
N4'	5156(1)	3655(1)	6402(1)	24(1)
F2'	2688(1)	3308(1)	6601(1)	34(1)
F3'	2607(1)	1781(1)	6825(1)	36(1)
F7'	4732(1)	-468(1)	5875(1)	39(1)
F8'	6054(1)	-447(1)	6694(1)	42(1)
F12'	7640(1)	1409(1)	6579(1)	37(1)
F13'	7764(1)	2946(1)	6379(1)	40(1)
F17'	6686(1)	4457(1)	5625(1)	43(1)
F18'	5385(1)	4335(1)	4799(1)	40(1)
C1'	3769(1)	2977(1)	5941(1)	21(1)
C2'	3179(1)	2836(1)	6342(1)	24(1)
C3'	3138(1)	2094(1)	6445(1)	25(1)
C4'	3697(1)	1763(1)	6106(1)	22(1)
C5'	3871(1)	983(1)	5976(1)	26(1)
C6'	4595(1)	749(1)	6292(1)	23(1)
C7'	4953(1)	106(1)	6237(1)	28(1)
C8'	5584(1)	117(1)	6639(1)	29(1)
C9'	5629(1)	764(1)	6949(1)	24(1)
C10'	6187(1)	1063(1)	7441(1)	26(1)
C11'	6519(1)	1756(1)	7182(1)	24(1)
C12'	7145(1)	1893(1)	6822(1)	26(1)
C13'	7209(1)	2635(1)	6728(1)	29(1)
C14'	6623(1)	2971(1)	7026(1)	25(1)
C15'	6370(1)	3746(1)	7042(1)	26(1)
C16'	5884(1)	3883(1)	6442(1)	24(1)
C17'	6034(1)	4168(1)	5836(1)	29(1)
C18'	5410(1)	4101(1)	5431(1)	27(1)
C19'	4857(1)	3782(1)	5783(1)	22(1)
C20'	4048(1)	3658(1)	5621(1)	23(1)
C21'	3923(1)	861(1)	5224(1)	35(1)
C22'	3248(1)	504(1)	6251(1)	38(1)
C23'	5803(1)	1195(1)	8109(1)	32(1)
C24'	6813(1)	513(1)	7548(1)	34(1)
C25'	7048(1)	4251(1)	7022(1)	36(1)
C26'	5935(1)	3908(1)	7676(1)	30(1)
C27'	3964(1)	3597(1)	4866(1)	29(1)
C28'	3592(1)	4304(1)	5867(1)	32(1)
C1A	11107(1)	1978(2)	6114(1)	44(1)
C2A	10775(1)	3392(1)	6083(1)	42(1)
C1B	9160(1)	1732(1)	2438(1)	36(1)
C2B	9139(1)	3180(1)	2436(1)	37(1)
C1A'	6380(1)	1258(1)	5301(1)	39(1)
C2A'	6663(2)	2616(2)	4947(2)	54(1)
O1B'	4638(1)	2563(1)	7462(1)	26(1)
C1B'	4308(2)	2936(1)	8681(1)	41(1)
C2B'	3648(2)	1798(2)	8125(1)	51(1)

Table 3. Anisotropic displacement parameters (Å^2 x 10^3) for 2(DMSO). The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S1B	29(1)	26(1)	22(1)	-2(1)	-4(1)	3(1)
S1A	25(1)	30(1)	23(1)	1(1)	-3(1)	-2(1)
S1A'	24(1)	35(1)	30(1)	-8(1)	4(1)	-5(1)
S1B'	27(1)	51(1)	23(1)	6(1)	1(1)	6(1)
O1A	27(1)	29(1)	23(1)	0(1)	-4(1)	-1(1)
N1	20(1)	22(1)	24(1)	2(1)	-5(1)	-2(1)
N2	23(1)	19(1)	24(1)	-3(1)	0(1)	-2(1)
N3	22(1)	22(1)	22(1)	-1(1)	-3(1)	-1(1)
N4	22(1)	20(1)	22(1)	1(1)	3(1)	1(1)
F2	29(1)	38(1)	38(1)	5(1)	-14(1)	7(1)
F3	33(1)	36(1)	42(1)	-6(1)	-15(1)	-6(1)
F7	43(1)	31(1)	51(1)	-14(1)	4(1)	-16(1)
F8	46(1)	32(1)	51(1)	-19(1)	13(1)	-1(1)
F12	42(1)	55(1)	26(1)	-1(1)	-12(1)	18(1)
F13	35(1)	52(1)	35(1)	-22(1)	-10(1)	-1(1)
F17	45(1)	29(1)	64(1)	20(1)	17(1)	-1(1)
F18	36(1)	28(1)	51(1)	13(1)	4(1)	9(1)
C1	18(1)	25(1)	23(1)	3(1)	3(1)	2(1)
C2	19(1)	31(1)	24(1)	3(1)	-2(1)	2(1)
C3	21(1)	28(1)	26(1)	-4(1)	-3(1)	-5(1)
C4	20(1)	22(1)	24(1)	0(1)	1(1)	-3(1)
C5	23(1)	21(1)	28(1)	1(1)	-2(1)	-3(1)
C6	24(1)	19(1)	23(1)	3(1)	-2(1)	-2(1)
C7	28(1)	20(1)	32(1)	-2(1)	-4(1)	-5(1)
C8	34(1)	20(1)	29(1)	-3(1)	2(1)	4(1)
C9	26(1)	20(1)	25(1)	2(1)	-1(1)	2(1)
C10	22(1)	23(1)	24(1)	1(1)	1(1)	3(1)
C11	18(1)	26(1)	21(1)	2(1)	1(1)	1(1)
C12	20(1)	41(1)	21(1)	0(1)	-3(1)	7(1)
C13	20(1)	35(1)	26(1)	-12(1)	-2(1)	-1(1)
C14	18(1)	25(1)	26(1)	-7(1)	2(1)	-5(1)
C15	24(1)	20(1)	32(1)	-5(1)	5(1)	-4(1)
C16	25(1)	21(1)	28(1)	-3(1)	4(1)	-3(1)
C17	34(1)	20(1)	37(1)	5(1)	9(1)	-3(1)
C18	29(1)	19(1)	34(1)	1(1)	0(1)	5(1)
C19	23(1)	19(1)	23(1)	-2(1)	0(1)	1(1)
C20	22(1)	21(1)	24(1)	0(1)	3(1)	3(1)
C21	29(1)	26(1)	42(1)	3(1)	3(1)	-9(1)
C22	32(1)	26(1)	28(1)	5(1)	2(1)	0(1)
C23	28(1)	33(1)	37(1)	5(1)	-1(1)	7(1)
C24	33(1)	28(1)	26(1)	-1(1)	5(1)	0(1)
C25	38(1)	28(1)	37(1)	2(1)	14(1)	2(1)
C26	31(1)	29(1)	59(2)	-14(1)	6(1)	-11(1)
C27	26(1)	31(1)	38(1)	2(1)	3(1)	6(1)
C28	34(1)	27(1)	26(1)	-2(1)	5(1)	3(1)
O1B	27(1)	39(1)	27(1)	-1(1)	-5(1)	2(1)
O1A'	25(1)	42(1)	35(1)	-3(1)	2(1)	2(1)
N1'	19(1)	22(1)	23(1)	0(1)	2(1)	-2(1)

N2'	24(1)	20(1)	26(1)	1(1)	-6(1)	-2(1)
N3'	21(1)	26(1)	27(1)	1(1)	1(1)	-4(1)
N4'	26(1)	26(1)	21(1)	3(1)	0(1)	-8(1)
F2'	32(1)	39(1)	32(1)	-1(1)	10(1)	9(1)
F3'	26(1)	47(1)	35(1)	15(1)	5(1)	-8(1)
F7'	40(1)	24(1)	51(1)	-11(1)	-15(1)	-1(1)
F8'	34(1)	28(1)	65(1)	-9(1)	-15(1)	8(1)
F12'	27(1)	41(1)	44(1)	-6(1)	3(1)	4(1)
F13'	30(1)	47(1)	42(1)	5(1)	9(1)	-12(1)
F17'	31(1)	59(1)	39(1)	16(1)	2(1)	-18(1)
F18'	39(1)	57(1)	25(1)	16(1)	-1(1)	-12(1)
C1'	21(1)	23(1)	20(1)	-1(1)	-2(1)	-1(1)
C2'	23(1)	30(1)	21(1)	-1(1)	-1(1)	3(1)
C3'	21(1)	33(1)	21(1)	8(1)	0(1)	-6(1)
C4'	21(1)	25(1)	21(1)	3(1)	-5(1)	-6(1)
C5'	24(1)	23(1)	31(1)	3(1)	-9(1)	-4(1)
C6'	23(1)	21(1)	24(1)	4(1)	-3(1)	-7(1)
C7'	30(1)	20(1)	33(1)	-3(1)	-5(1)	-5(1)
C8'	26(1)	23(1)	37(1)	1(1)	-4(1)	2(1)
C9'	22(1)	23(1)	28(1)	5(1)	-3(1)	-1(1)
C10'	25(1)	26(1)	26(1)	3(1)	-5(1)	-1(1)
C11'	21(1)	26(1)	24(1)	-1(1)	-6(1)	-3(1)
C12'	22(1)	31(1)	27(1)	-4(1)	-4(1)	0(1)
C13'	23(1)	38(1)	25(1)	4(1)	-1(1)	-11(1)
C14'	23(1)	27(1)	24(1)	2(1)	-5(1)	-7(1)
C15'	28(1)	24(1)	28(1)	1(1)	-3(1)	-9(1)
C16'	26(1)	23(1)	24(1)	2(1)	-1(1)	-7(1)
C17'	24(1)	31(1)	31(1)	4(1)	2(1)	-9(1)
C18'	30(1)	28(1)	22(1)	4(1)	-1(1)	-4(1)
C19'	26(1)	19(1)	20(1)	-1(1)	0(1)	-3(1)
C20'	25(1)	20(1)	22(1)	0(1)	0(1)	0(1)
C21'	46(1)	25(1)	34(1)	-4(1)	-15(1)	1(1)
C22'	26(1)	29(1)	58(2)	10(1)	-10(1)	-10(1)
C23'	38(1)	31(1)	26(1)	6(1)	-3(1)	-6(1)
C24'	33(1)	31(1)	39(1)	2(1)	-12(1)	1(1)
C25'	35(1)	32(1)	40(1)	6(1)	-10(1)	-14(1)
C26'	36(1)	28(1)	26(1)	-3(1)	-5(1)	-6(1)
C27'	32(1)	32(1)	24(1)	4(1)	-4(1)	-5(1)
C28'	35(1)	20(1)	42(1)	-2(1)	4(1)	2(1)
C1A	40(1)	58(2)	35(1)	10(1)	-4(1)	15(1)
C2A	50(2)	43(2)	35(1)	-4(1)	-9(1)	-15(1)
C1B	40(1)	32(1)	36(1)	-4(1)	-2(1)	-4(1)
C2B	40(1)	31(1)	39(1)	3(1)	-4(1)	10(1)
C1A'	35(1)	38(2)	44(1)	-2(1)	-3(1)	2(1)
C2A'	42(2)	45(2)	74(2)	-3(2)	19(1)	-13(1)
O1B'	23(1)	33(1)	22(1)	1(1)	1(1)	-3(1)
C1B'	66(2)	31(1)	26(1)	0(1)	4(1)	-2(1)
C2B'	49(2)	74(2)	29(1)	2(1)	1(1)	-32(1)

Table 4. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for 2(DMSO).

	x	y	z	U(eq)
H1A	9282(15)	2390(14)	4792(13)	41(8)
H2A	10378(12)	1605(13)	4349(11)	25(6)
H3A	11147(14)	2545(13)	3264(13)	35(7)
H4A	10180(11)	3340(13)	4371(11)	23(6)
H21A	8237(1)	386(1)	3964(1)	48
H21B	8596(1)	-56(1)	4541(1)	48
H21C	7967(1)	502(1)	4693(1)	48
H22A	9564(1)	1365(1)	5319(1)	43
H22B	8772(1)	1096(1)	5518(1)	43
H22C	9401(1)	539(1)	5367(1)	43
H23A	11998(1)	678(1)	4441(1)	49
H23B	12088(1)	227(1)	3791(1)	49
H23C	12635(1)	860(1)	3942(1)	49
H24A	11523(1)	1565(1)	2646(1)	43
H24B	12345(1)	1400(1)	2845(1)	43
H24C	11797(1)	768(1)	2694(1)	43
H25A	11294(1)	3609(1)	2689(1)	51
H25B	11446(1)	4435(1)	2758(1)	51
H25C	12088(1)	3883(1)	2875(1)	51
H26A	11664(1)	4477(1)	4503(1)	59
H26B	12315(1)	4419(1)	3993(1)	59
H26C	11673(1)	4972(1)	3876(1)	59
H27A	7873(1)	4157(1)	3904(1)	47
H27B	7594(1)	3982(1)	4620(1)	47
H27C	8097(1)	4656(1)	4497(1)	47
H28A	9302(1)	3460(1)	5321(1)	43
H28B	8961(1)	4234(1)	5355(1)	43
H28C	8458(1)	3560(1)	5478(1)	43
H1'A	4454(13)	2247(13)	5534(12)	30(6)
H2'A	4888(14)	1582(16)	6878(13)	50(8)
H3'A	5796(14)	2486(13)	7481(12)	31(7)
H4'A	4947(13)	3380(14)	6692(12)	37(7)
H21D	4302(1)	1164(1)	5042(1)	52
H21E	4044(1)	367(1)	5143(1)	52
H21F	3456(1)	973(1)	5021(1)	52
H22D	3208(1)	580(1)	6718(1)	57
H22E	2784(1)	617(1)	6044(1)	57
H22F	3372(1)	11(1)	6166(1)	57
H23D	5413(1)	1540(1)	8049(1)	47
H23E	5598(1)	752(1)	8268(1)	47
H23F	6155(1)	1376(1)	8423(1)	47
H24D	7061(1)	427(1)	7136(1)	51
H24E	7161(1)	696(1)	7864(1)	51
H24F	6605(1)	72(1)	7709(1)	51
H25D	7335(1)	4156(1)	6633(1)	54
H25E	6879(1)	4740(1)	7016(1)	54
H25F	7349(1)	4173(1)	7407(1)	54
H26D	5511(1)	3598(1)	7701(1)	45

H26E	6244(1)	3833(1)	8055(1)	45
H26F	5774(1)	4400(1)	7664(1)	45
H27D	4243(1)	3191(1)	4711(1)	44
H27E	3451(1)	3534(1)	4752(1)	44
H27F	4149(1)	4027(1)	4662(1)	44
H28D	3642(1)	4341(1)	6338(1)	48
H28E	3777(1)	4735(1)	5665(1)	48
H28F	3080(1)	4242(1)	5755(1)	48
H1AA	10973(1)	1486(2)	6033(1)	66
H1AB	11209(1)	2042(2)	6576(1)	66
H1AC	11541(1)	2097(2)	5862(1)	66
H2AA	10434(1)	3773(1)	5982(1)	63
H2AB	11221(1)	3456(1)	5832(1)	63
H2AC	10890(1)	3402(1)	6546(1)	63
H1BA	9361(1)	1286(1)	2596(1)	54
H1BB	9226(1)	1761(1)	1968(1)	54
H1BC	8641(1)	1754(1)	2540(1)	54
H2BA	9327(1)	3632(1)	2594(1)	55
H2BB	8621(1)	3144(1)	2538(1)	55
H2BC	9207(1)	3152(1)	1966(1)	55
H1CA	6079(1)	910(1)	5526(1)	59
H1CB	6873(1)	1249(1)	5480(1)	59
H1CC	6397(1)	1146(1)	4839(1)	59
H2CA	6541(2)	3118(2)	4951(2)	81
H2CB	6667(2)	2444(2)	4500(2)	81
H2CC	7143(2)	2547(2)	5140(2)	81
H1DA	4509(2)	3412(1)	8655(1)	61
H1DB	4689(2)	2607(1)	8816(1)	61
H1DC	3912(2)	2928(1)	8998(1)	61
H2DA	3435(2)	1564(2)	7748(1)	76
H2DB	3282(2)	1841(2)	8467(1)	76
H2DC	4059(2)	1521(2)	8285(1)	76

Figure 1. View of molecule 1 of **2**(DMSO) showing the atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

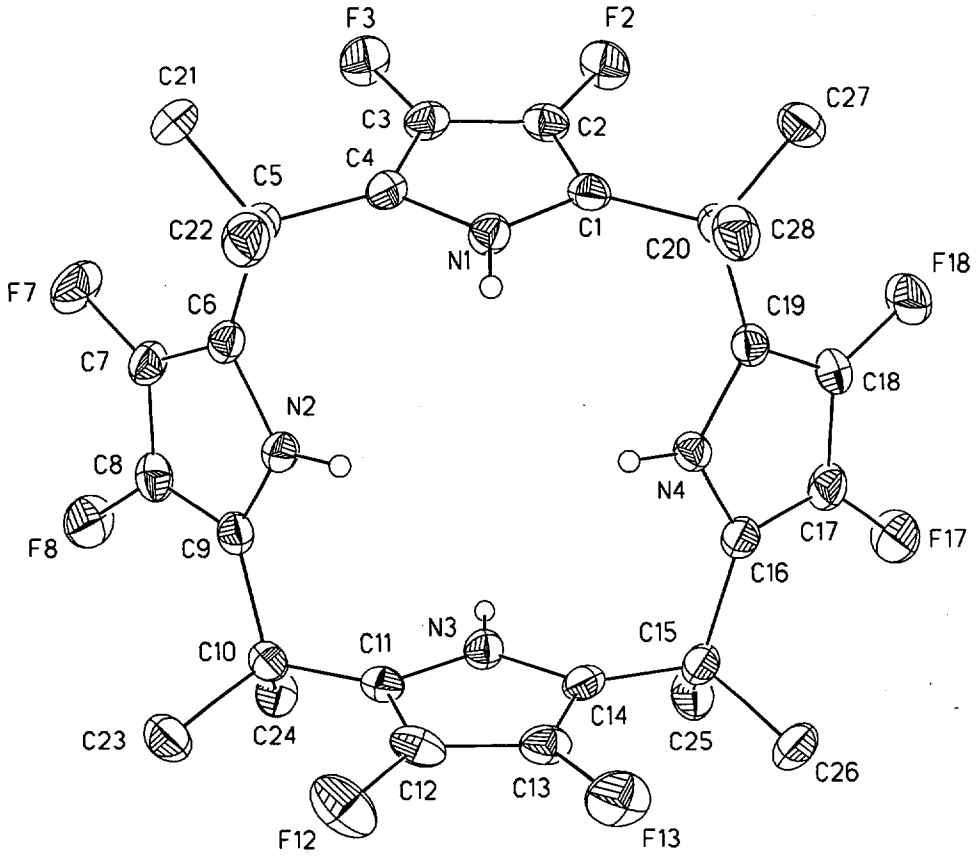


Figure 2. View of molecule 2 of **2**(DMSO) showing the atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

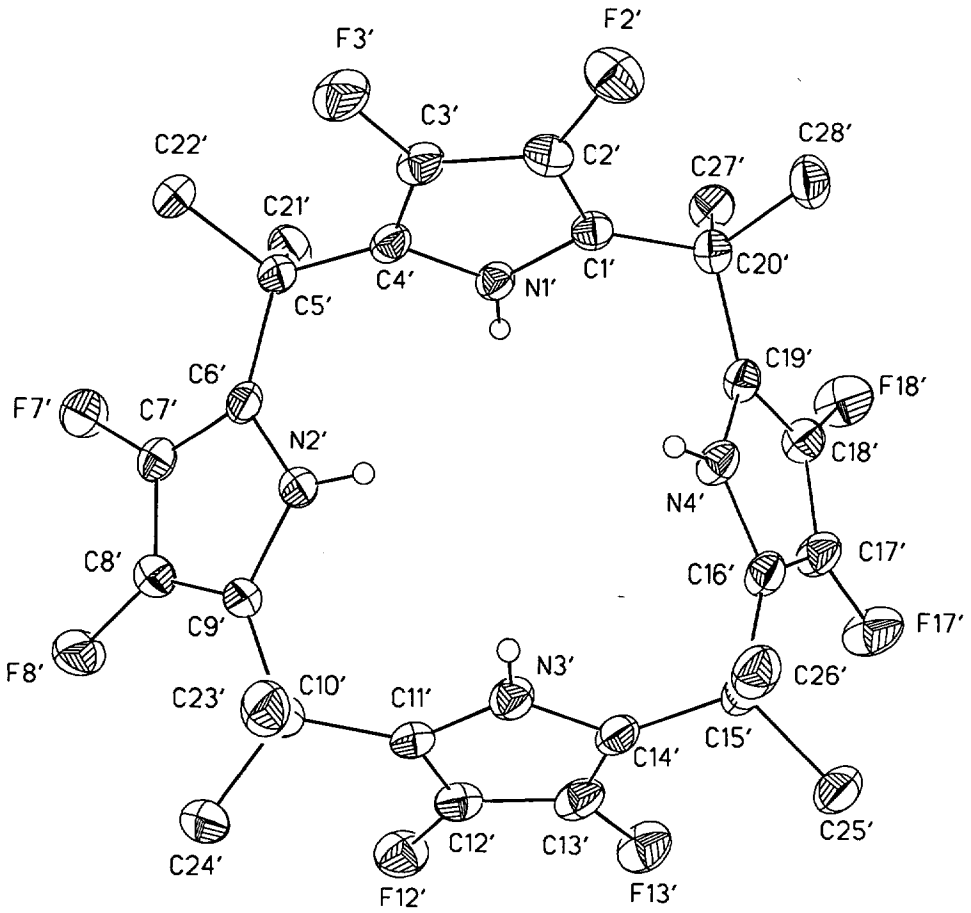


Figure 3. View of molecule 1 of **2**(DMSO) showing a partial atom labeling scheme and the H-bonding interactions with the DMSO molecules. Dashed lines indicate close N-H···O interactions. Two DMSO molecules are H-bound to the calixpyrrole. One is H-bound to three pyrroles while the second in H-bound to the remaining pyrrole. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

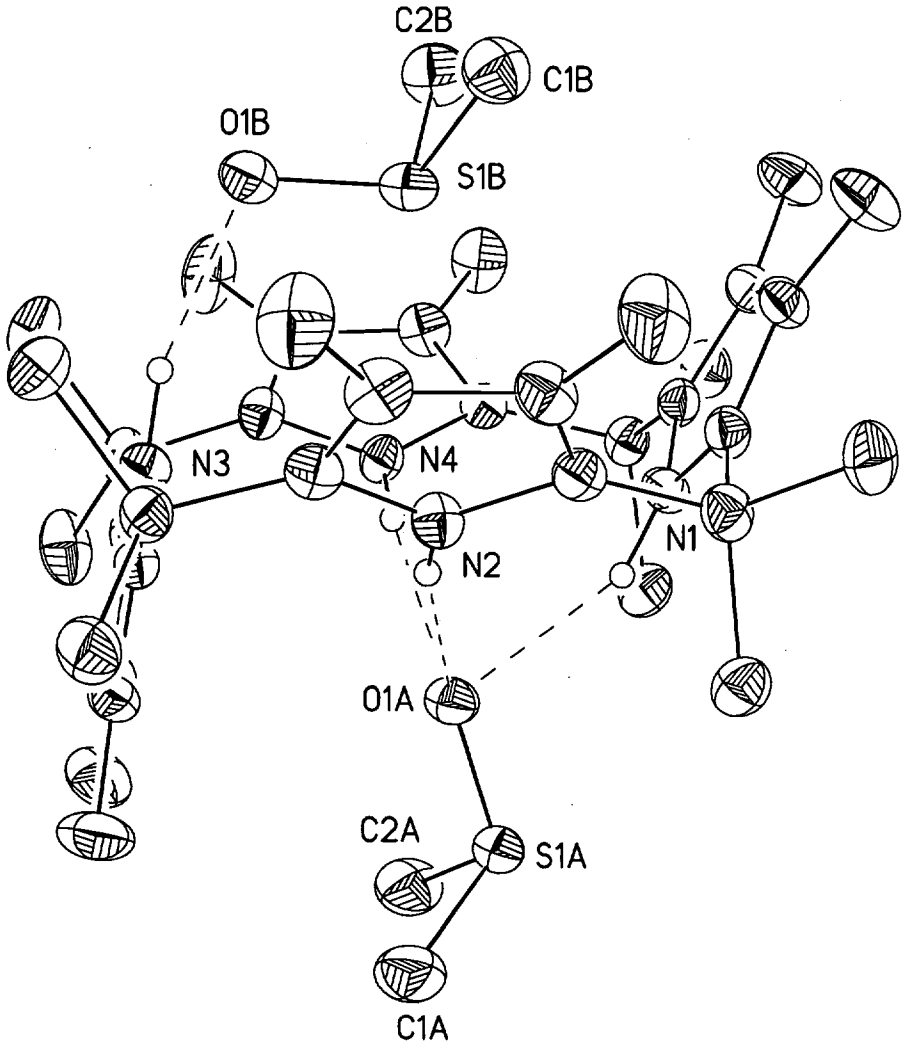


Figure 4. View of molecule 2 of **2**(DMSO) showing a partial atom labeling scheme and the H-bonding interactions with the DMSO molecules. Dashed lines indicate close N-H···O interactions. Two DMSO molecules are H-bound to the calixpyrrole. One is H-bound to three pyrroles while the second in H-bound to the remaining pyrrole. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

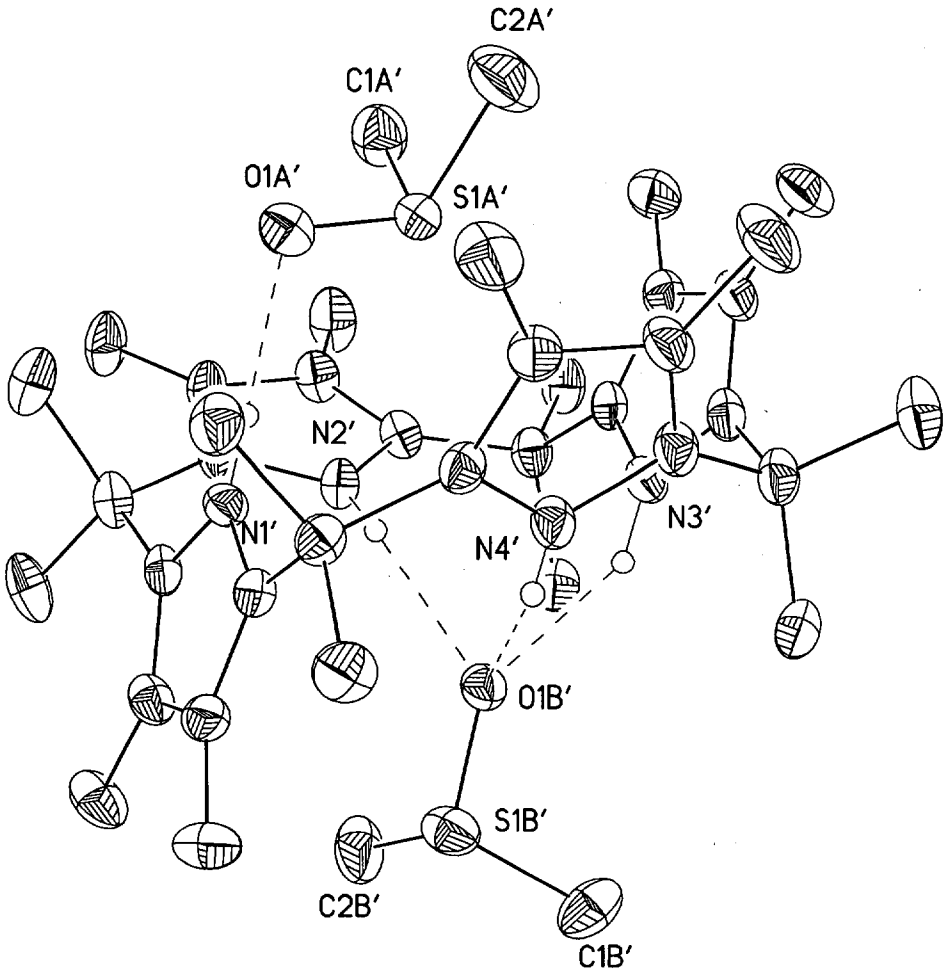


Figure 5. Unit cell packing diagram for **2**(DMSO). The view is approximately down the **b** axis. Molecules pack in layers parallel to **bc**. Layers are alternately composed of molecules 1 and molecules 2. Atoms from molecules 2 are shown in wireframe form.

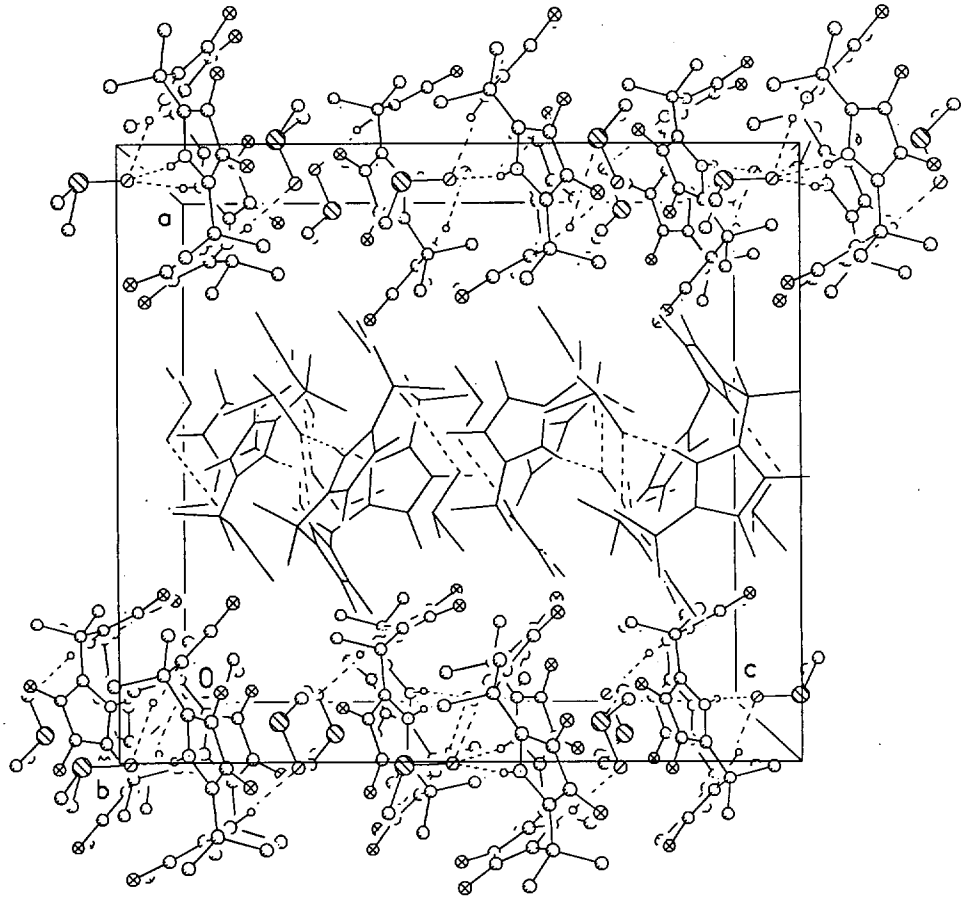
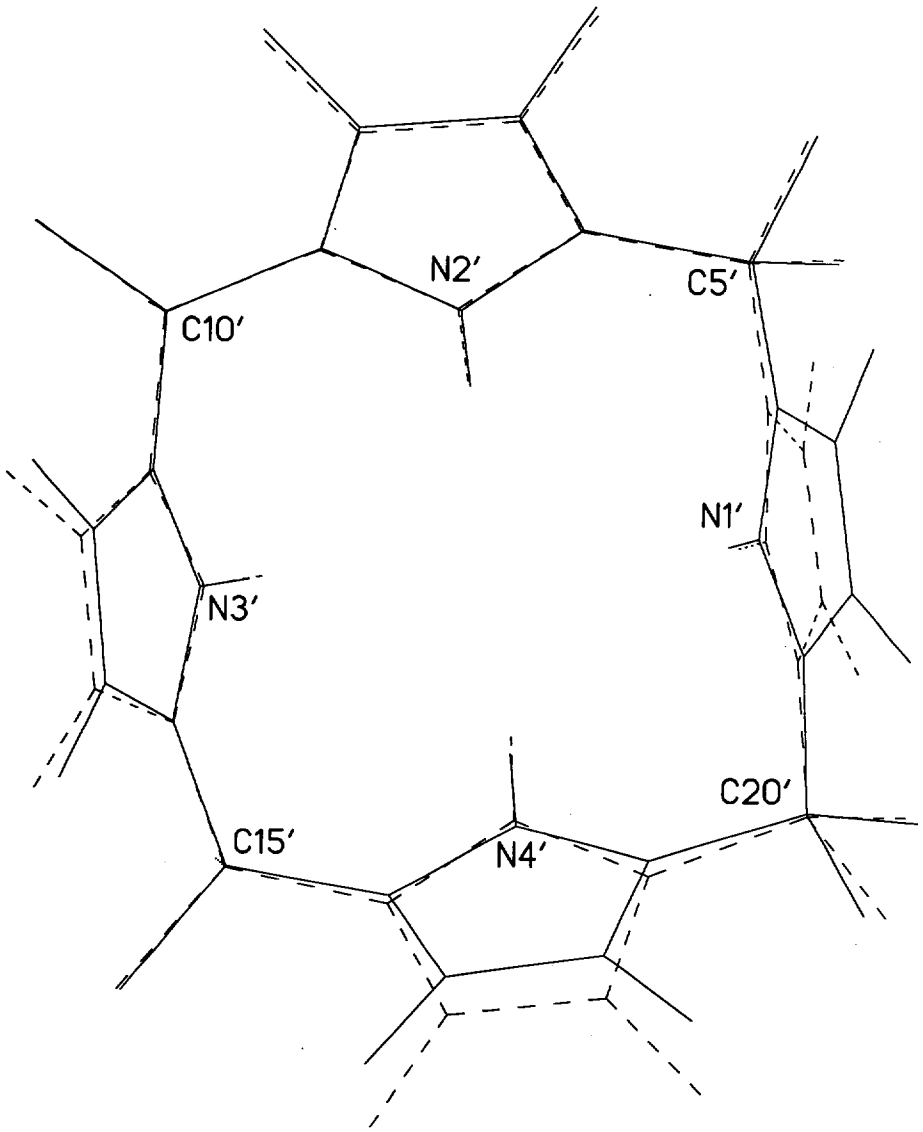


Figure 6. View of the fit by least-squares of atoms from molecule 1 of **2**(DMSO) (dashed lines) to equivalent atoms of molecule 2 (solid lines). Atoms of molecule 2 used in the fit are labeled.



X-ray experimental and crystallographic data for fluoride complex of 2: 2(F)

X-ray Experimental for **2**(F).

Table 1. Crystallographic Data for **2**(F).

Table 2. Fractional coordinates and equivalent isotropic thermal parameters ($Å^2$) for the non-hydrogen atoms of **2**(F).

Table 3. Anisotropic thermal parameters for the non-hydrogen atoms of **2**(F).

Table 4. Fractional coordinates and isotropic thermal parameters ($Å^2$) for the hydrogen atoms of **2**(F).

Figure 1. View of **2**(F) showing the atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale. The fluoride ion, F1, is within hydrogen bonding distance to the pyrrole N-H groups. The geometry of these interactions are: N1-H1N···F1, N···F 2.719(2)Å, H···F 1.84(3)Å, N-H···F 164(2)°; N2-H2N···F1, N···F 2.736(2)Å, H···F 1.80(3)Å, N-H···F 170(2)°; N3-H3N···F1, N···F 2.738(2)Å, H···F 1.85(3)Å, N-H···F 162(2)°; N4-H4N···F1, N···F 2.727(2)Å, H···F 1.81(3)Å, N-H···F 175(2)°.

Figure 2. View of tetrakis (n-butylammonium) cation of **2**(F) showing the atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level. Hydrogen atoms shown are drawn to an arbitrary scale.

Figure 3. Unit cell packing diagram for **2**(F). The view is approximately down the **a** axis. The cation is shown in wireframe format.

X-ray Experimental for 2(F): Crystals grew as colorless plates by slow evaporation from dichloromethane. The data crystal was a thin plate that had approximate dimensions; .39 x .34 x .06 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 329 frames of data were collected using ω-scans with a scan range of 2.0° and a counting time of 234 seconds per frame. The data were collected at –150°C using a Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.[1] The structure was solved by direct methods using SIR92[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms on nitrogen were observed in a ΔF map and refined with isotropic displacement parameters. A molecule of hexane was found to be disordered about a crystallographic inversion center. The contributions to the data by this molecule were removed using SQUEEZE as found in PLATON98.[4] The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0461*P)^2 + (1.2166*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.1373, with R(F) equal to 0.0582 and a goodness of fit, S, = 1.092. Definitions used for calculating R(F),$R_w(F^2)$ and the goodness of fit, S, are given below.[5] Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[6] All figures were generated using SHELXTL/PC.[7] Tables of positional and thermal parameters, bond lengths and angles, figures and lists of observed and calculated structure factors are located in tables 1 through 6.

References

1) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.

2) SIR92. (1993). A program for crystal structure solution. Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. J. Appl. Cryst. 26, 343-350.

3) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

4) Sluis, P. v. d. and Spek, A. L. (1990). PLATON98. Acta Cryst. A46, 194.

5) $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = \{\Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.
$S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

6) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

7) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Table 1. Crystal data and structure refinement for 2(F).

Empirical formula	C44 H64 F9 N5
Formula weight	834.00
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 12.6150(4) Å alpha = 94.680(2)°. b = 12.6810(4) Å beta = 93.683(2)°. c = 15.1240(3) Å gamma = 104.4180(13)°.
Volume, Z	2326.41(11) Å^3, 2
Density (calculated)	1.191 Mg/m^3
Absorption coefficient	0.095 mm^-1
F(000)	888
Crystal size	0.39 x 0.34 x 0.06 mm
Theta range for data collection	3.0 to 27.5°.
Limiting indices	-16<=h<=16, -16<=k<=14, -19<=l<=19
Reflections collected	19081
Independent reflections	10573 [R(int) = 0.0321]
Reflections observed	7202 [I>2(sigma(I))]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10573 / 0 / 539
Goodness-of-fit on F^2	1.092
Final R indices [I>2sigma(I)]	R1 = 0.0582, wR2 = 0.125
R indices (all data)	R1 = 0.0955, wR2 = 0.137
Largest diff. peak and hole	0.50 and -0.27 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 2(F). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
F1	7071(1)	2627(1)	760(1)	25(1)
F2	3991(1)	4219(1)	3040(1)	41(1)
F3	5445(1)	6181(1)	2542(1)	38(1)
F7	8812(1)	7412(1)	2084(1)	41(1)
F8	10693(1)	6533(1)	2400(1)	37(1)
F12	10922(1)	3467(1)	3457(1)	42(1)
F13	9446(1)	1477(1)	3888(1)	42(1)
F17	5919(1)	-225(1)	3786(1)	30(1)
F18	4038(1)	663(1)	3527(1)	31(1)
N1	5642(1)	3768(1)	1334(1)	24(1)
N2	8420(1)	4680(1)	1204(1)	22(1)
N3	8783(1)	2273(1)	1799(1)	23(1)
N4	6042(1)	1446(1)	2030(1)	24(1)
C1	4856(2)	3329(2)	1891(1)	24(1)
C2	4710(2)	4208(2)	2403(1)	27(1)
C3	5408(2)	5166(2)	2162(1)	26(1)
C4	5996(2)	4889(2)	1493(1)	22(1)
C5	6849(2)	5567(2)	964(1)	24(1)
C6	7997(2)	5581(2)	1331(1)	22(1)
C7	8824(2)	6370(2)	1802(1)	26(1)
C8	9731(2)	5942(2)	1955(1)	25(1)
C9	9484(2)	4884(2)	1584(1)	22(1)
C10	10137(2)	4032(2)	1517(1)	23(1)
C11	9697(2)	3118(2)	2086(1)	23(1)
C12	10037(2)	2892(2)	2907(1)	27(1)
C13	9325(2)	1923(2)	3114(1)	27(1)
C14	8539(2)	1532(2)	2426(1)	23(1)
C15	7579(2)	522(2)	2265(1)	25(1)
C16	6527(2)	787(2)	2517(1)	23(1)
C17	5814(2)	447(2)	3142(1)	23(1)
C18	4910(2)	885(2)	3022(1)	24(1)
C19	5048(2)	1515(2)	2327(1)	23(1)
C20	4319(2)	2110(2)	1839(1)	26(1)
C21	6666(2)	5088(2)	-21(1)	30(1)
C22	6721(2)	6744(2)	1003(2)	32(1)
C23	10072(2)	3563(2)	536(1)	29(1)
C24	11349(2)	4567(2)	1832(2)	31(1)
C25	7429(2)	81(2)	1270(1)	31(1)
C26	7815(2)	-380(2)	2804(2)	32(1)
C27	4111(2)	1620(2)	857(1)	31(1)
C28	3210(2)	1928(2)	2240(2)	33(1)
N30	3386(1)	7198(1)	4465(1)	24(1)
C31	2702(2)	6246(2)	4898(1)	28(1)
C32	2654(2)	6439(2)	5901(1)	36(1)
C33	2220(2)	5355(2)	6298(2)	46(1)
C34	1092(2)	4707(2)	5903(2)	57(1)
C35	4590(2)	7485(2)	4841(1)	30(1)