ORGANIC LETTERS

Tribenzo[27]crown-9: A New Ring for Dibenzylammonium Rods

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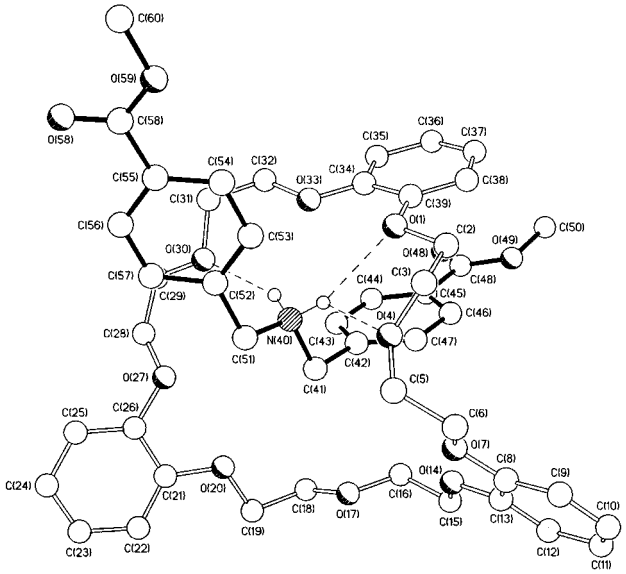
SUPPORTING INFORMATION
(13 PAGES)

EXPERIMENTAL PROCEDURES FOR **TB27C9** AND **3**·PF_6

KINETIC AND THERMODYNAMIC PARAMETERS FOR THE FORMATION OF [**TB27C9**·**3**][PF_6]

^{1}H NMR DILUTION EXPERIMENT WITH **TB27C9** AND **1**·PF_6

CRYSTAL DATA FOR [**TB27C9**·**2**][PF_6]



Experimental Section

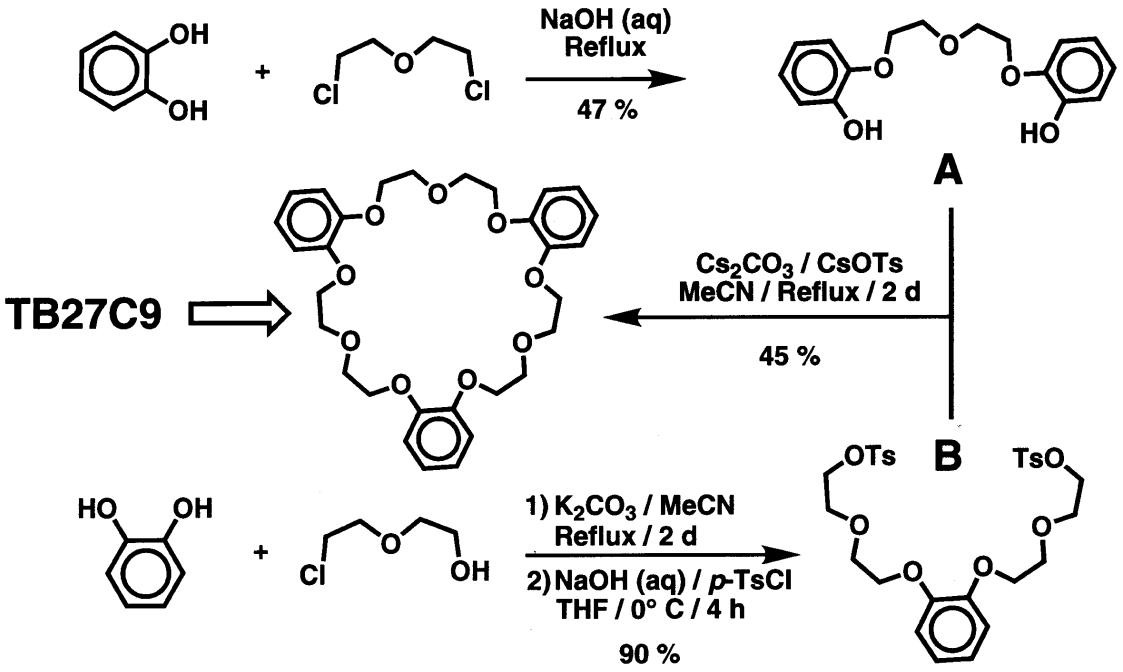
General

All reagents and solvents were used as received unless otherwise stated. Reactions were carried out under an atmosphere of anhydrous argon. $CDCl_3$ employed for the kinetic study of **TB27C9** and **3**·PF_6 was filtered through a pad of basic alumina (Activity I, 200 mesh) prior to use. Reactions were monitored by TLC on silica plates (Merck, 0.25 mm) and visualized with UV light (254 nm). Melting points given are uncorrected. NMR Tubes were soaked in a 5 % Na_2CO_3 bath for 12 h, rinsed with double distilled water and dried for 24 h in an oven prior to use. NMR Spectra were recorded on either a Bruker AC 360 MHz or AMX 400 spectrometer. Chemical shifts reported are referenced to the residual solvent peak. Samples for microanalysis were dried under high vacuum for 24 h prior to analysis (Quantitative Technologies, Inc., NJ).

Synthesis

Tribenzo[27]crown-9 (**TB27C9**): An oven dried 1 L three-necked round-bottomed flask was equipped with a stirrer bar, nitrogen inlet, addition funnel and condenser. The flask was purged with argon for 10 min and then charged with 200 mL of distilled MeCN. Cesium carbonate (9.77 g, 30.0 mmol) and cesium tosylate (0.365 g, 1.20 mmol) were added to the flask. The white suspension was stirred vigorously and heated under reflux. The addition funnel was charged with a solution of diol **A** (3.47 g, 12.0 mmol) and bistosylate **B** (7.10 g, 12.0 mmol) in 120 mL of freshly distilled MeCN. The solution was added dropwise over 5 h to the suspension. The suspension, which was pink in color, was heated under reflux for an additional 48 h. Upon cooling down to ambient temperature, the suspension was deep purple in color. TLC (SiO_2; EtOAc/hexanes; 1/1; v/v) revealed no starting material. The mixture was diluted with CH_2Cl_2 (150 mL), filtered, and the filtrate was concentrated under reduced pressure. The resulting dark tar was dissolved in CH_2Cl_2 (200 mL) and washed with 0.5 N KOH (H_2O/MeOH; 60/40; v/v). The organic layer was washed with brine (200 mL) and dried over Na_2SO_4 for 2 h. The mixture was

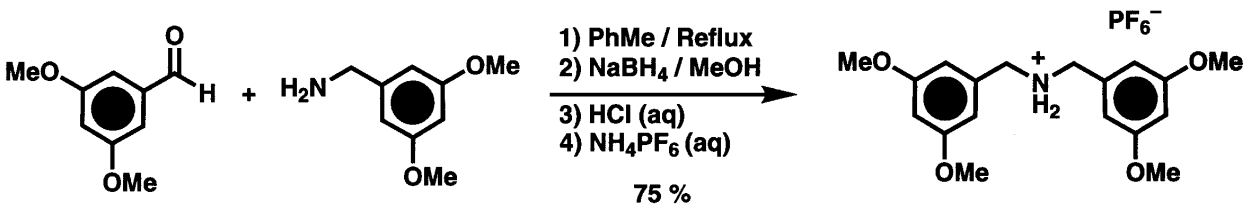
filtered, concentrated under reduced pressure, and dried to afford 5.80 g of a dark purple solid. Purification *via* filterpad of silica (180 g) by eluting with EtOAc/hexanes (1/1; v/v), followed by CH_2Cl_2/EtOH (100/1; v/v) and concentration of the desired fractions, afforded 3.40 g of a yellow solid. Recrystallization of the solid from EtOH, followed by drying under high vacuum for 12 h, afforded 2.82 g (45 %) of a white fibrous material which was shown to be the title compound.



M.p. 91-92 °C (lit.[6] m.p. 91-92 °C); ^{1}H NMR (400 MHz, CD_3CN): δ = 6.87-6.94 (m, 12H; ArH), 4.08-4.12 (m, 12H; ArOCH_2CH$_2$), 3.81-3.85 (m, 12H; ArOCH$_2$CH_2); ^{13}C NMR (100 MHz, CD_3CN): δ = 148.8, 122.3, 115.3, 70.7, 69.7; MS (FAB): *m/z* (%): 540 (100) $[M]^+$.

Bis(3,5-dimethoxybenzyl)ammonium Hexafluorophosphate (**3**·PF_6): A 250 mL round-bottomed flask was equipped with a heating block, stirrer bar, Dean-Stark trap, condenser and nitrogen inlet. To the flask was added 150 mL of toluene, 3.00 g (0.018 mol) of 3,5-dimethoxybenzylamine and 3.00 g (0.018 mol) of 3,5-dimethoxybenzaldehyde. The resulting solution was heated under reflux for 36 h while removing water (~ 1 mL) though azeotropic distillation. The solution was concentrated by rotary evaporation and dried for 3 h under high vacuum to afford 5.37 g of a yellow oil (94 %). This oil was presumed to be the desired

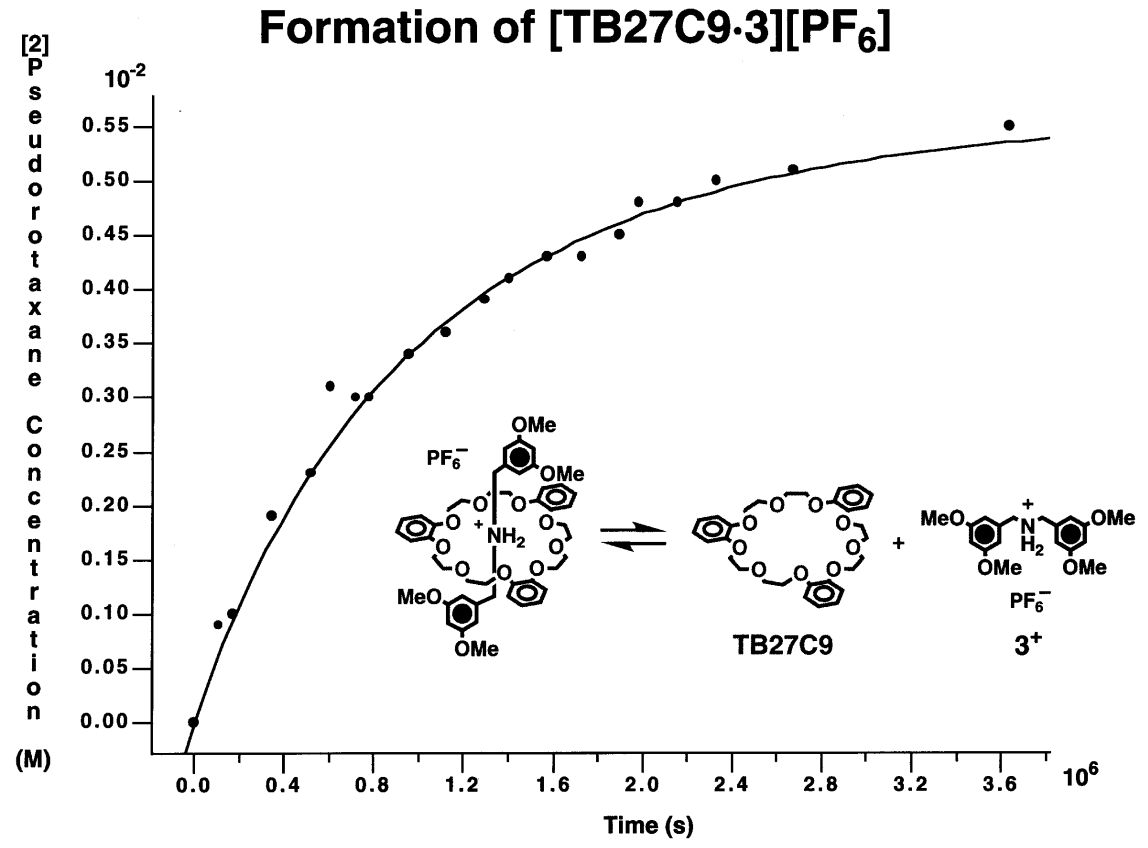
imine {^{1}H NMR, 400 MHz, $CDCl_3$ δ 8.28 (N=C*H*)}. To the yellow oil was added 70 mL of anhydrous MeOH at ambient temperature. The resulting solution was stirred vigorously under Ar while sodium borohydride (3.22 g, 0.085 mol) was added carefully in portions at ambient temperature. The resulting suspension was stirred at ambient temperature for 48 h. Aqueous HCl (6 N) was added until the suspension was slightly acidic and the methanol was removed *in vacuo*. CH_2Cl_2 (100 mL) was added to the mixture and the aqueous layer was extracted with an additional 100 mL of CH_2Cl_2. The organic extracts were combined and washed with 1 N NaOH (aq) and then dried over anhydrous sodium sulfate for 12 h. The mixture was filtered, concentrated under reduced pressure and dried under high vacuum to afford a white solid. A solution of the resulting amine was prepared by the addition of 150 mL of CH_2Cl_2. Upon vigorous stirring, 16 mL of 6N HCl was added dropwise to the solution. A white precipitate appeared within 5 mins. The mixture was filtered, and the white solid was stirred in boiling water until a solution was obtained. Ammonium hexafluorophosphate was added (5 g, 0.031 mol) as an aqueous solution. A white precipitate formed instantly, and the reaction mixture was stirred for another 2 h upon cooling to ambient temperature. The white solid was filtered, dried, and recrystallized from 1-propanol to afford 5.89 g (75 %) of white crystalline flakes which were shown to be the title compound.



M.p. > 235 °C (decomp.); ^{1}H NMR (400 MHz, CD_3CN): δ = 6.58 (d, *J* = 2 Hz, 4H; ArH), 6.54 (t, *J* = 2 Hz, 2H; ArH), 4.12 (s, 4H; $ArCH_2$), 3.78 (s, 12H; OCH_3); ^{13}C NMR (100 MHz, CD_3CN): δ = 162.2, 133.2, 108.7, 101.9, 56.1, 52.2; MS (FAB): *m/z* (%): 318 (25) $[M\text{-}PF_6]^+$; $C_{18}H_{24}F_6NO_4P$ (463.4): calcd C 46.66, H 5.22, N 3.02; found C 46.87, H 5.13, N 2.83.

Reference

(6) Kyba, E. P.; Helgeson, R. C.; Madan, K.; Gokel. G. W.; Tarnowski, T. L.; Moore, S. S.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 2564-2571.


Formation of [TB27C9·3][PF6]
[2] Pseudorotaxane Concentration (M)
10-2
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
10^6
Time (s)
OMe
PF6−
NH2
MeO
TB27C9
3+

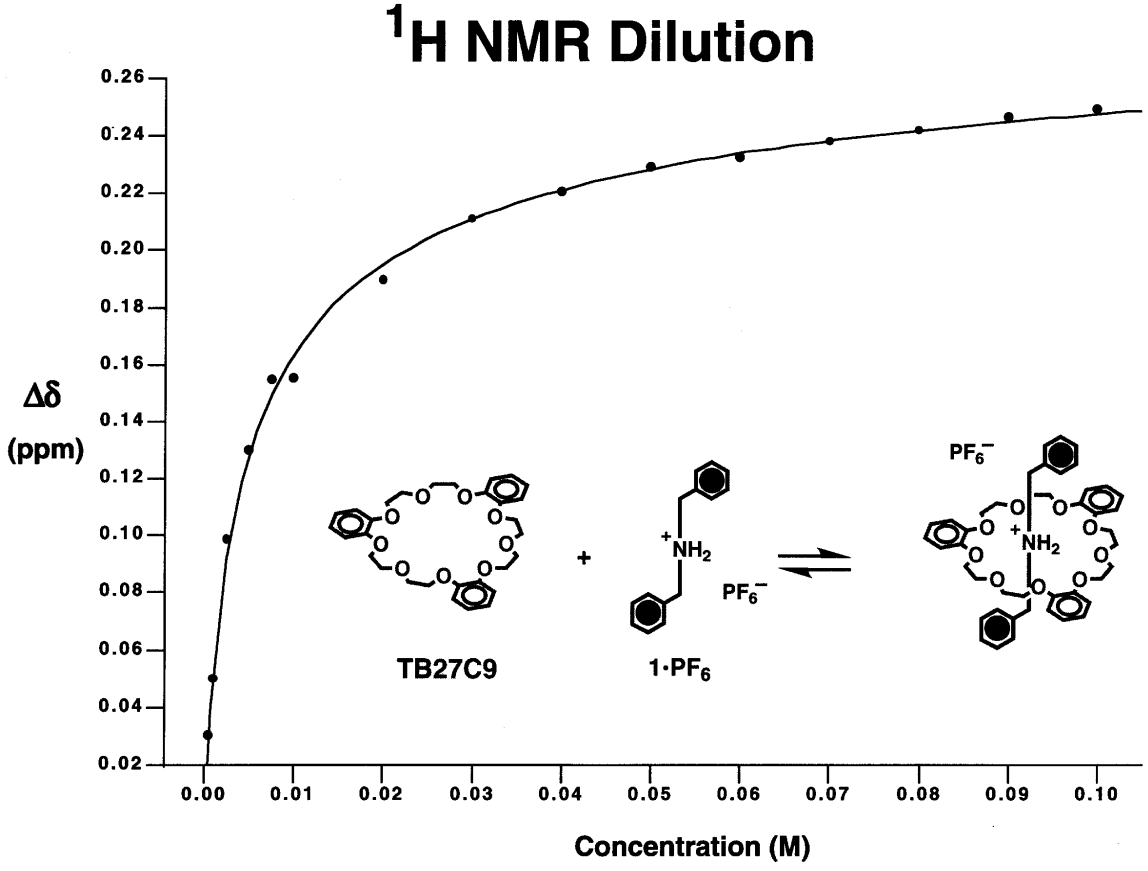

1H NMR Dilution
Δδ (ppm)
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.10
Concentration (M)
TB27C9
1·PF6
PF6−
NH2

Table 1. Crystal data and structure refinement for [**TB27C9·2**][PF_6]

Identification code	FS9908
Empirical formula	$[C_{48}H_{56}NO_{13}][PF_6]$. MeCN
Formula weight	1040.96
Temperature	293(2) K
Diffractometer Used	Siemens P4/PC
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 14.241(2) Å alpha = 90° b = 16.425(2) Å beta = 93.943(8)° c = 22.169(2) Å gamma = 90°
Volume, Z	5173.2(10) $Å^3$, 4
Density (calculated)	1.337 Mg/m^3
Absorption coefficient	1.214 mm^{-1}
F(000)	2184
Crystal colour/morphology	Clear blocks
Crystal size	0.23 x 0.20 x 0.13 mm
θ range for data collection	3.11 to 59.99°
Limiting indices	$0 \le h \le 15$, $0 \le k \le 18$, $-24 \le l \le 24$
Scan type	ω-scans
Reflections collected	8029
Independent reflections	7680 (R_{int} = 0.0461)
Observed reflections [F>4σ(F)]	3576
Absorption correction	None
Structure solution method	Direct
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6343 / 42 / 670
Goodness-of-fit on F^2	1.040
Final R indices [F>4σ(F)]	R1 = 0.0867, wR2 = 0.2146
R indices (all data)	R1 = 0.1798, wR2 = 0.2884
Extinction coefficient	0.00038(11)
Largest diff. peak and hole	0.576 and -0.297 $eÅ^{-3}$
Mean and maximum shift/error	0.000 and -0.002

Table 2. Atomic coordinates [x 10^4], equivalent isotropic displacement parameters [$Å^2$ x 10^3] and site occupancy factors for [**TB27C9·2**][PF_6]. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)	sof
O(1)	4154(3)	3035(3)	2761(2)	57(1)	1
C(2)	5070(5)	2844(5)	3037(4)	65(2)	1
C(3)	5588(5)	3610(5)	3196(4)	68(2)	1
O(4)	5093(3)	4082(3)	3601(2)	60(1)	1
C(5)	5684(6)	4559(5)	4003(4)	64(2)	1
C(6)	6133(5)	4090(5)	4527(3)	66(2)	1
O(7)	5402(3)	3819(3)	4888(2)	60(1)	1
C(8)	5671(5)	3354(4)	5388(3)	54(2)	1
C(9)	6580(5)	3127(5)	5558(4)	65(2)	1
C(10)	6777(6)	2664(5)	6071(4)	68(2)	1
C(11)	6077(6)	2436(5)	6421(4)	71(2)	1
C(12)	5146(6)	2665(5)	6257(3)	64(2)	1
C(13)	4930(5)	3128(4)	5738(3)	52(2)	1
O(14)	4051(3)	3347(3)	5536(2)	60(1)	1
C(15)	3309(5)	3102(5)	5903(4)	63(2)	1
C(16)	2384(5)	3310(5)	5579(3)	62(2)	1
O(17)	2271(3)	4163(3)	5505(2)	64(1)	1
C(18)	1313(5)	4391(6)	5447(4)	76(3)	1
C(19)	1204(6)	5274(6)	5390(3)	73(2)	1
O(20)	1292(4)	5508(3)	4770(2)	65(1)	1
C(21)	1022(5)	6291(5)	4611(3)	57(2)	1
C(22)	849(7)	6890(6)	5024(4)	81(3)	1
C(23)	549(8)	7638(7)	4812(5)	101(3)	1
C(24)	436(7)	7808(6)	4211(6)	96(3)	1
C(25)	631(6)	7198(6)	3799(5)	80(3)	1
C(26)	902(5)	6440(5)	3997(3)	58(2)	1
O(27)	1101(4)	5826(4)	3606(2)	74(2)	1
C(28)	439(8)	5666(8)	3165(5)	121(4)	1
C(29)	618(7)	5248(7)	2636(4)	102(4)	1
O(30)	1347(4)	4750(4)	2586(2)	79(2)	1
C(31)	1408(7)	4393(6)	2010(4)	82(3)	1
C(32)	1533(6)	3513(5)	2049(4)	75(2)	1
O(33)	2432(3)	3347(3)	2342(2)	58(1)	1
C(34)	2667(5)	2543(5)	2400(3)	56(2)	1
C(35)	2060(7)	1902(5)	2255(4)	78(3)	1
C(36)	2356(9)	1095(6)	2318(4)	88(3)	1
C(37)	3245(10)	947(6)	2516(4)	93(3)	1
C(38)	3883(7)	1571(5)	2678(4)	76(2)	1
C(39)	3593(6)	2366(4)	2618(3)	58(2)	1
N(40)	3062(4)	4493(3)	3332(2)	46(1)	1
C(41)	2855(5)	4276(4)	3964(3)	54(2)	1
C(42)	2555(5)	3398(5)	3969(3)	50(2)	1
C(43)	1627(6)	3179(5)	3826(4)	68(2)	1
C(44)	1365(7)	2376(6)	3790(4)	78(2)	1
C(45)	1999(6)	1772(5)	3908(4)	67(2)	1
C(46)	2947(7)	1972(5)	4076(4)	72(2)	1
C(47)	3210(6)	2790(5)	4110(3)	62(2)	1
C(48)	1722(9)	904(7)	3843(5)	96(3)	1
O(48)	915(7)	710(5)	3717(6)	165(4)	1
O(49)	2434(7)	388(4)	3915(4)	116(3)	1
C(50)	2215(12)	-482(6)	3797(7)	164(7)	1
C(51)	3371(6)	5341(4)	3251(3)	56(2)	1
C(52)	3494(5)	5538(4)	2601(3)	50(2)	1

C(53)	4055(6)	5070(5)	2252(4)	69(2)	1
C(54)	4189(6)	5268(5)	1652(4)	69(2)	1
C(55)	3745(6)	5938(4)	1398(3)	63(2)	1
C(56)	3171(6)	6393(5)	1730(4)	75(2)	1
C(57)	3052(6)	6191(4)	2322(4)	63(2)	1
C(58)	3898(10)	6190(7)	772(5)	109(4)	1
O(58)	3521(10)	6773(8)	557(5)	207(5)	1
O(59)	4530(6)	5821(4)	507(3)	113(3)	1
C(60)	4743(11)	6075(8)	-105(5)	138(5)	1
P(10)	8585(2)	3362(1)	2935(1)	66(1)	1
F(11)	7713(5)	3145(5)	2507(3)	153(3)	1
F(12)	9149(5)	3594(6)	2390(3)	160(3)	1
F(13)	8893(6)	2460(4)	2910(5)	179(4)	1
F(14)	7995(4)	3144(4)	3491(3)	115(2)	1
F(15)	8276(7)	4245(4)	2990(4)	166(3)	1
F(16)	9450(4)	3550(4)	3392(3)	121(2)	1
N(70)	2425(18)	909(17)	5530(9)	142(8)	0.60
C(71)	2049(26)	390(19)	5460(11)	132(9)	0.60
C(72)	1494(22)	-382(18)	5483(13)	172(11)	0.60
N(70')	617(34)	-193(30)	5514(21)	205(17)	0.40
C(71')	1015(35)	307(30)	5256(20)	152(14)	0.40
C(72')	1645(26)	922(26)	5418(16)	118(11)	0.40

Table 3. Bond Lengths [Å] and angles [°] for [**TB27C9·2**][PF_6].

O(1)-C(39)	1.383(9)	O(1)-C(2)	1.437(8)
C(2)-C(3)	1.489(11)	C(3)-O(4)	1.412(9)
O(4)-C(5)	1.420(8)	C(5)-C(6)	1.499(10)
C(6)-O(7)	1.427(8)	O(7)-C(8)	1.380(9)
C(8)-C(9)	1.375(10)	C(8)-C(13)	1.401(10)
C(9)-C(10)	1.381(11)	C(10)-C(11)	1.358(11)
C(11)-C(12)	1.401(11)	C(12)-C(13)	1.396(10)
C(13)-O(14)	1.350(8)	O(14)-C(15)	1.434(8)
C(15)-C(16)	1.497(10)	C(16)-O(17)	1.418(9)
O(17)-C(18)	1.412(8)	C(18)-C(19)	1.464(12)
C(19)-O(20)	1.442(9)	O(20)-C(21)	1.380(9)
C(21)-C(22)	1.377(11)	C(21)-C(26)	1.382(10)
C(22)-C(23)	1.372(13)	C(23)-C(24)	1.361(14)
C(24)-C(25)	1.396(13)	C(25)-C(26)	1.366(11)
C(26)-O(27)	1.372(9)	O(27)-C(28)	1.337(10)
C(28)-C(29)	1.397(8)	C(29)-O(30)	1.332(9)
O(30)-C(31)	1.413(9)	C(31)-C(32)	1.458(12)
C(32)-O(33)	1.422(9)	O(33)-C(34)	1.367(9)
C(34)-C(35)	1.386(10)	C(34)-C(39)	1.403(10)
C(35)-C(36)	1.394(13)	C(36)-C(37)	1.333(14)
C(37)-C(38)	1.399(13)	C(38)-C(39)	1.374(11)
N(40)-C(51)	1.475(9)	N(40)-C(41)	1.496(9)
C(41)-C(42)	1.504(10)	C(42)-C(43)	1.386(10)
C(42)-C(47)	1.387(10)	C(43)-C(44)	1.372(12)
C(44)-C(45)	1.354(12)	C(45)-C(46)	1.414(12)
C(45)-C(48)	1.484(13)	C(46)-C(47)	1.396(11)
C(48)-O(48)	1.208(13)	C(48)-O(49)	1.322(13)
O(49)-C(50)	1.482(12)	C(51)-C(52)	1.500(10)
C(52)-C(57)	1.369(10)	C(52)-C(53)	1.382(10)
C(53)-C(54)	1.395(11)	C(54)-C(55)	1.371(10)
C(55)-C(56)	1.360(11)	C(55)-C(58)	1.477(12)
C(56)-C(57)	1.375(11)	C(58)-O(58)	1.183(12)
C(58)-O(59)	1.264(12)	O(59)-C(60)	1.470(11)

C(39)-O(1)-C(2)	114.6(6)	O(1)-C(2)-C(3)	109.7(6)
O(4)-C(3)-C(2)	110.7(6)	C(3)-O(4)-C(5)	113.7(6)
O(4)-C(5)-C(6)	114.0(6)	O(7)-C(6)-C(5)	107.8(6)
C(8)-O(7)-C(6)	116.8(5)	C(9)-C(8)-O(7)	125.0(7)
C(9)-C(8)-C(13)	120.5(7)	O(7)-C(8)-C(13)	114.4(6)
C(8)-C(9)-C(10)	120.6(8)	C(11)-C(10)-C(9)	120.4(8)
C(10)-C(11)-C(12)	119.8(8)	C(13)-C(12)-C(11)	120.7(8)
O(14)-C(13)-C(12)	124.5(7)	O(14)-C(13)-C(8)	117.6(6)
C(12)-C(13)-C(8)	117.9(7)	C(13)-O(14)-C(15)	116.1(6)
O(14)-C(15)-C(16)	108.8(6)	O(17)-C(16)-C(15)	111.8(7)
C(18)-O(17)-C(16)	112.0(6)	O(17)-C(18)-C(19)	111.5(7)
O(20)-C(19)-C(18)	109.3(7)	C(21)-O(20)-C(19)	116.8(6)
C(22)-C(21)-O(20)	123.7(7)	C(22)-C(21)-C(26)	120.8(8)
O(20)-C(21)-C(26)	115.5(7)	C(23)-C(22)-C(21)	118.6(9)
C(24)-C(23)-C(22)	122.1(10)	C(23)-C(24)-C(25)	118.6(10)
C(26)-C(25)-C(24)	120.5(9)	C(25)-C(26)-O(27)	122.2(8)
C(25)-C(26)-C(21)	119.5(8)	O(27)-C(26)-C(21)	118.3(7)
C(28)-O(27)-C(26)	116.2(6)	O(27)-C(28)-C(29)	123.4(8)
O(30)-C(29)-C(28)	124.1(8)	C(29)-O(30)-C(31)	115.3(6)
O(30)-C(31)-C(32)	111.9(8)	O(33)-C(32)-C(31)	108.6(7)
C(34)-O(33)-C(32)	115.8(6)	O(33)-C(34)-C(35)	124.6(7)
O(33)-C(34)-C(39)	116.8(6)	C(35)-C(34)-C(39)	118.6(8)
C(34)-C(35)-C(36)	121.3(9)	C(37)-C(36)-C(35)	118.7(9)
C(36)-C(37)-C(38)	122.4(9)	C(39)-C(38)-C(37)	119.0(9)
C(38)-C(39)-O(1)	124.6(7)	C(38)-C(39)-C(34)	119.9(8)

O(1)-C(39)-C(34)	115.4(6)	C(51)-N(40)-C(41)	114.7(5)
N(40)-C(41)-C(42)	108.0(5)	C(43)-C(42)-C(47)	118.8(7)
C(43)-C(42)-C(41)	121.0(7)	C(47)-C(42)-C(41)	120.3(6)
C(44)-C(43)-C(42)	120.9(8)	C(45)-C(44)-C(43)	121.3(9)
C(44)-C(45)-C(46)	119.5(8)	C(44)-C(45)-C(48)	121.1(9)
C(46)-C(45)-C(48)	119.4(9)	C(47)-C(46)-C(45)	119.1(8)
C(42)-C(47)-C(46)	120.4(8)	O(48)-C(48)-O(49)	124.7(11)
O(48)-C(48)-C(45)	121.2(12)	O(49)-C(48)-C(45)	114.1(10)
C(48)-O(49)-C(50)	116.5(10)	N(40)-C(51)-C(52)	112.0(5)
C(57)-C(52)-C(53)	116.7(7)	C(57)-C(52)-C(51)	121.5(7)
C(53)-C(52)-C(51)	121.8(7)	C(52)-C(53)-C(54)	121.7(7)
C(55)-C(54)-C(53)	119.4(8)	C(56)-C(55)-C(54)	119.6(7)
C(56)-C(55)-C(58)	119.2(8)	C(54)-C(55)-C(58)	121.2(8)
C(55)-C(56)-C(57)	120.2(7)	C(52)-C(57)-C(56)	122.4(7)
O(58)-C(58)-O(59)	121.3(11)	O(58)-C(58)-C(55)	120.8(12)
O(59)-C(58)-C(55)	117.3(8)	C(58)-O(59)-C(60)	119.4(9)

Table 4. Anisotropic displacement parameters [Å^2 x 10^3] for [**TB27C9·2**][PF_6]. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$(ha^*)^2U_{11}$ + ... + 2hka*b*U_{12}].

	U11	U22	U33	U23	U13	U12
O(1)	53(3)	57(3)	61(3)	-6(2)	-2(2)	5(2)
C(2)	58(5)	62(5)	74(5)	-5(4)	0(4)	17(4)
C(3)	40(4)	100(7)	63(5)	-4(5)	7(4)	15(4)
O(4)	44(3)	75(3)	59(3)	-11(3)	0(2)	-5(3)
C(5)	62(5)	63(5)	68(5)	2(4)	7(4)	-20(4)
C(6)	47(4)	89(6)	62(5)	-2(4)	6(4)	-21(4)
O(7)	42(3)	75(3)	64(3)	2(3)	3(2)	-7(2)
C(8)	50(4)	57(4)	55(4)	-13(4)	2(3)	1(4)
C(9)	47(4)	69(5)	77(5)	-14(4)	-8(4)	1(4)
C(10)	51(5)	78(6)	72(5)	-18(5)	-17(4)	12(4)
C(11)	77(6)	80(6)	54(5)	-6(4)	-7(4)	16(5)
C(12)	57(5)	85(6)	50(4)	4(4)	0(4)	10(4)
C(13)	46(4)	52(4)	58(4)	-10(3)	1(3)	6(3)
O(14)	42(3)	86(4)	53(3)	10(3)	8(2)	1(3)
C(15)	50(4)	76(5)	64(5)	13(4)	12(4)	0(4)
C(16)	52(4)	78(6)	58(4)	12(4)	13(4)	-3(4)
O(17)	37(3)	81(4)	76(3)	16(3)	7(2)	-1(3)
C(18)	43(4)	108(7)	79(6)	32(5)	12(4)	10(4)
C(19)	54(5)	109(7)	57(5)	13(5)	15(4)	22(5)
O(20)	64(3)	82(4)	48(3)	3(3)	8(2)	6(3)
C(21)	48(4)	63(5)	60(5)	4(4)	4(3)	2(4)
C(22)	84(6)	81(6)	77(6)	-16(5)	-7(5)	10(5)
C(23)	116(9)	83(7)	100(8)	-23(6)	-11(7)	8(6)
C(24)	91(7)	60(6)	135(10)	13(6)	4(7)	-6(5)
C(25)	64(5)	78(6)	99(7)	13(5)	7(5)	2(5)
C(26)	37(4)	69(5)	67(5)	-11(4)	7(3)	-4(4)
O(27)	71(4)	97(4)	54(3)	-6(3)	-8(3)	26(3)
C(28)	85(6)	145(8)	132(8)	-46(7)	1(6)	30(6)
C(29)	77(6)	143(10)	81(6)	-44(7)	-25(5)	33(7)
O(30)	77(4)	88(4)	68(4)	-21(3)	-21(3)	39(3)
C(31)	96(7)	96(7)	51(5)	-21(5)	-14(4)	27(6)
C(32)	60(5)	80(6)	82(6)	-22(5)	-17(4)	1(4)
O(33)	54(3)	51(3)	66(3)	-10(2)	-6(2)	1(2)
C(34)	55(5)	63(5)	49(4)	-17(4)	10(3)	-9(4)
C(35)	75(6)	73(6)	88(6)	-22(5)	6(5)	-20(5)
C(36)	115(9)	64(6)	85(7)	-19(5)	13(6)	-23(6)
C(37)	150(11)	51(5)	78(6)	-7(5)	21(7)	-1(7)
C(38)	95(7)	58(5)	75(5)	-6(4)	-1(5)	7(5)
C(39)	77(5)	48(4)	48(4)	-5(3)	8(4)	2(4)
N(40)	53(4)	44(3)	41(3)	-4(3)	10(3)	-1(3)
C(41)	57(4)	55(4)	52(4)	-11(3)	6(3)	0(4)
C(42)	41(4)	69(5)	41(3)	2(3)	8(3)	-3(4)
C(43)	58(5)	74(6)	70(5)	9(4)	1(4)	6(4)
C(44)	73(6)	83(6)	76(6)	10(5)	-3(5)	0(5)
C(45)	81(6)	59(5)	60(5)	3(4)	-1(4)	-17(4)
C(46)	84(6)	71(6)	62(5)	7(4)	8(4)	13(5)
C(47)	54(5)	76(6)	55(4)	-1(4)	9(4)	-2(4)
C(48)	109(9)	90(8)	87(7)	11(6)	-14(6)	-22(7)
O(48)	137(8)	104(7)	247(12)	5(7)	-35(8)	-43(6)
O(49)	151(7)	71(5)	122(6)	3(4)	-15(5)	-2(5)
C(50)	241(18)	53(7)	191(15)	1(8)	-42(13)	-24(9)
C(51)	65(5)	44(4)	58(4)	-7(3)	2(4)	-7(4)
C(52)	58(4)	39(4)	54(4)	-5(3)	7(3)	-5(3)

Table 5. Hydrogen coordinates (x 10^4), isotropic displacement parameters ($Å^2$ x 10^3) and site occupancy factors for [**TB27C9·2**][PF_6].

	x	y	z	U(eq)	sof
H(2A)	5419(5)	2526(5)	2759(4)	78	1
H(2B)	5006(5)	2522(5)	3398(4)	78	1
H(3A)	6208(5)	3479(5)	3380(4)	81	1
H(3B)	5670(5)	3921(5)	2831(4)	81	1
H(5A)	5315(6)	4999(5)	4158(4)	77	1
H(5B)	6175(6)	4800(5)	3780(4)	77	1
H(6A)	6476(5)	3628(5)	4382(3)	79	1
H(6B)	6571(5)	4435(5)	4764(3)	79	1
H(9A)	7067(5)	3287(5)	5325(4)	78	1
H(10A)	7394(6)	2506(5)	6177(4)	81	1
H(11A)	6214(6)	2130(5)	6769(4)	85	1
H(12A)	4667(6)	2506(5)	6496(3)	77	1
H(15A)	3372(5)	3381(5)	6289(4)	75	1
H(15B)	3345(5)	2520(5)	5977(4)	75	1
H(16A)	2342(5)	3051(5)	5185(3)	75	1
H(16B)	1878(5)	3099(5)	5805(3)	75	1
H(18A)	1005(5)	4204(6)	5799(4)	91	1
H(18B)	1008(5)	4129(6)	5094(4)	91	1
H(19A)	591(6)	5436(6)	5516(3)	88	1
H(19B)	1682(6)	5546(6)	5650(3)	88	1
H(22A)	933(7)	6790(6)	5437(4)	97	1
H(23A)	418(8)	8041(7)	5089(5)	121	1
H(24A)	234(7)	8319(6)	4077(6)	115	1
H(25A)	575(6)	7308(6)	3386(5)	96	1
H(28A)	168(8)	6186(8)	3040(5)	145	1
H(28B)	-52(8)	5366(8)	3350(5)	145	1
H(29A)	58(7)	4931(7)	2527(4)	122	1
H(29B)	659(7)	5658(7)	2324(4)	122	1
H(31A)	1935(7)	4630(6)	1817(4)	98	1
H(31B)	839(7)	4514(6)	1760(4)	98	1
H(32A)	1044(6)	3275(5)	2276(4)	90	1
H(32B)	1489(6)	3277(5)	1647(4)	90	1
H(35A)	1444(7)	2012(5)	2112(4)	94	1
H(36A)	1942(9)	669(6)	2224(4)	105	1
H(37A)	3449(10)	410(6)	2547(4)	111	1
H(38A)	4494(7)	1448(5)	2824(4)	92	1
H(40A)	3510(28)	4128(26)	3256(26)	34(16)	1
H(40B)	2532(35)	4374(54)	3104(35)	101(33)	1
H(41A)	2358(5)	4621(4)	4099(3)	65	1
H(41B)	3413(5)	4354(4)	4235(3)	65	1
H(43A)	1174(6)	3583(5)	3754(4)	81	1
H(44A)	741(7)	2243(6)	3683(4)	93	1
H(46A)	3389(7)	1564(5)	4162(4)	87	1
H(47A)	3829(6)	2929(5)	4229(3)	74	1
H(50A)	2779(12)	-800(6)	3862(7)	247	1
H(50B)	1965(12)	-547(6)	3387(7)	247	1
H(50C)	1759(12)	-664(6)	4067(7)	247	1
H(51A)	3964(6)	5427(4)	3486(3)	67	1
H(51B)	2910(6)	5708(4)	3405(3)	67	1
H(53A)	4350(6)	4611(5)	2422(4)	82	1
H(54A)	4575(6)	4949(5)	1427(4)	83	1
H(56A)	2858(6)	6841(5)	1556(4)	90	1
H(57A)	2657(6)	6510(4)	2541(4)	76	1
H(60A)	5235(11)	5739(8)	-244(5)	207	1
H(60B)	4944(11)	6633(8)	-96(5)	207	1

H(60C)	4189(11)	6021(8)	-374(5)	207	1
H(72A)	929(22)	-334(18)	5223(13)	258	0.60
H(72B)	1332(22)	-481(18)	5890(13)	258	0.60
H(72C)	1864(22)	-827(18)	5349(13)	258	0.60
H(72D)	1423(26)	1426(26)	5240(16)	177	0.40
H(72E)	2249(26)	792(26)	5276(16)	177	0.40
H(72F)	1700(26)	976(26)	5850(16)	177	0.40