JA9720321

Supporting information for

Charge-localized p-Phenylenedihydrazine Radical Cations: ESR and Optical Studies of Intramolecular Electron Transfer Rates

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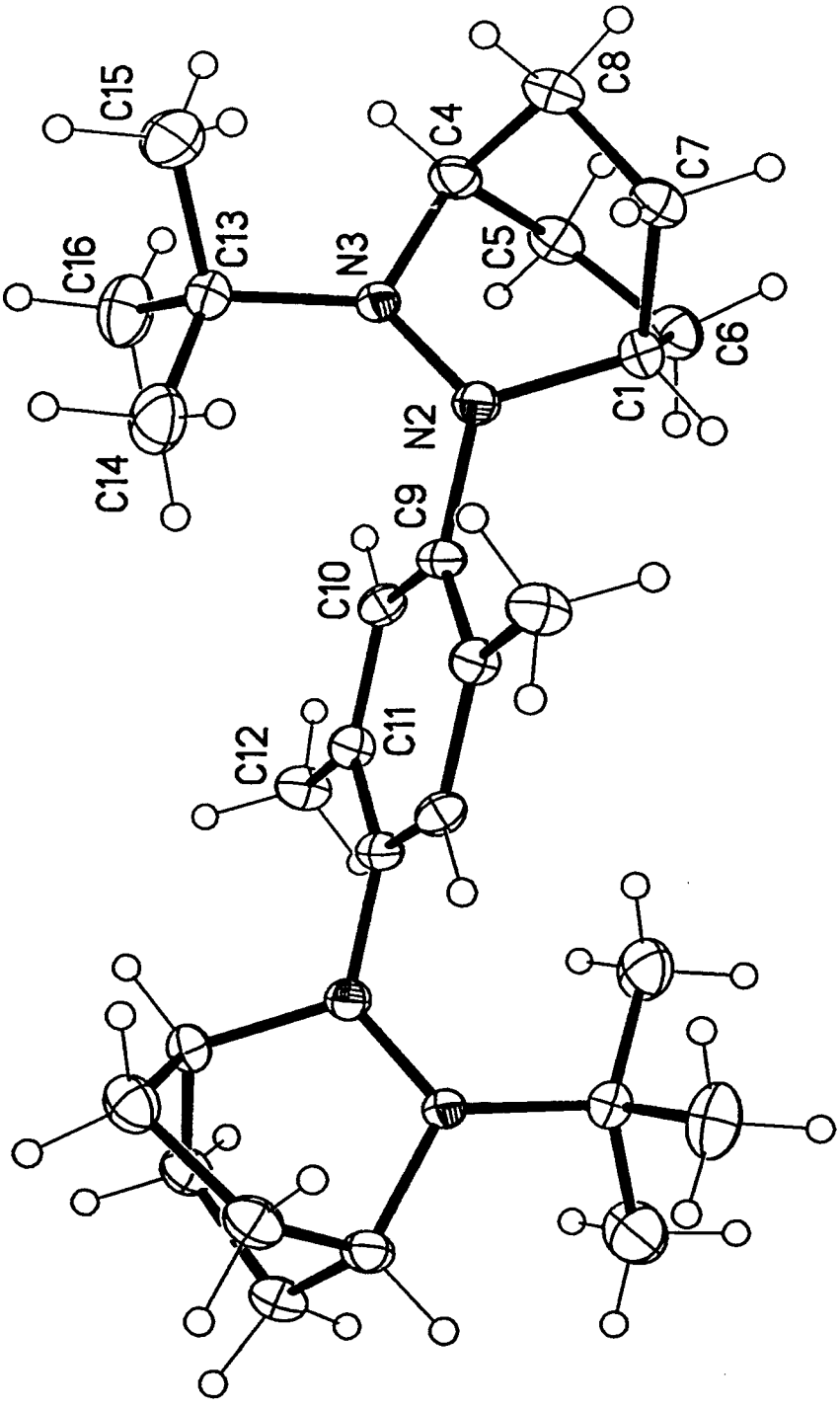
Table S1. Crystal data and structure refinement parameters

compound number	$3^{++}(BPh_4)_2^-$ [a]	$4^+BPh_4^-$	$4^{++}(BPh_4)_2^-$	$5^+B(C{\equiv}CH)_4^-$
empirical formula	$C_{80}H_{92}B_2N_6$	$C_{54}H_{70}BN_4$	$C_{78}H_{90}B_2N_4$	$C_{24}H_{28}BN_2$
temperature, K	133(2)	133(2)	133(2)	133(2)
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$
Z	2	4	2	4
a, Å	9.5607(2)	20.7130(3)	15.5579(6)	7.6781(4)
b, Å	13.7553(2)	9.6069(2)	11.2565(4)	13.1280(8)
c, Å	25.5637(2)	23.0974(4)	19.1583(7)	21.1967(12)
a, deg	90	90	90	90
b, deg	96.846(2)	100.102(2)	111.840(2)	92.418(2)
g, deg	90	90	90	90
Volume, $Å^3$	3337.92(9)	4524.85(14)	3114.3(2)	2134.7(2)
Density, (calcd), g/cm^3	1.153	1.154	1.179	1.106
F(000)	1248	1708	1192	764
Crystal size, mm	0.4×0.10×0.02	0.5×0.35×0.20	0.34×0.32×0.12	0.4×0.2×0.10
Reflections collected	14270	16640	11492	8260
Independent reflections [b]	7186 (0.0298)	7726 (0.0302)	5335(0.0234)	3652(0.0349)
Final R index [c]	0.0502	0.0643	0.0569	0.0518
wR index (all data)	0.1284	0.1524	0.1263	0.1206
Goodness-of-fit on F^2	1.025	1.178	1.250	1.154
Data/restraints/parameters	7185/0/397	7722/422/862	5334/255/534	3650/0/245
Largest dif. Map peaks, $eÅ^{-3}$	0.416 / -0.242	0.409 / -0.254	0.253/ -0.221	0.226/ -0.172

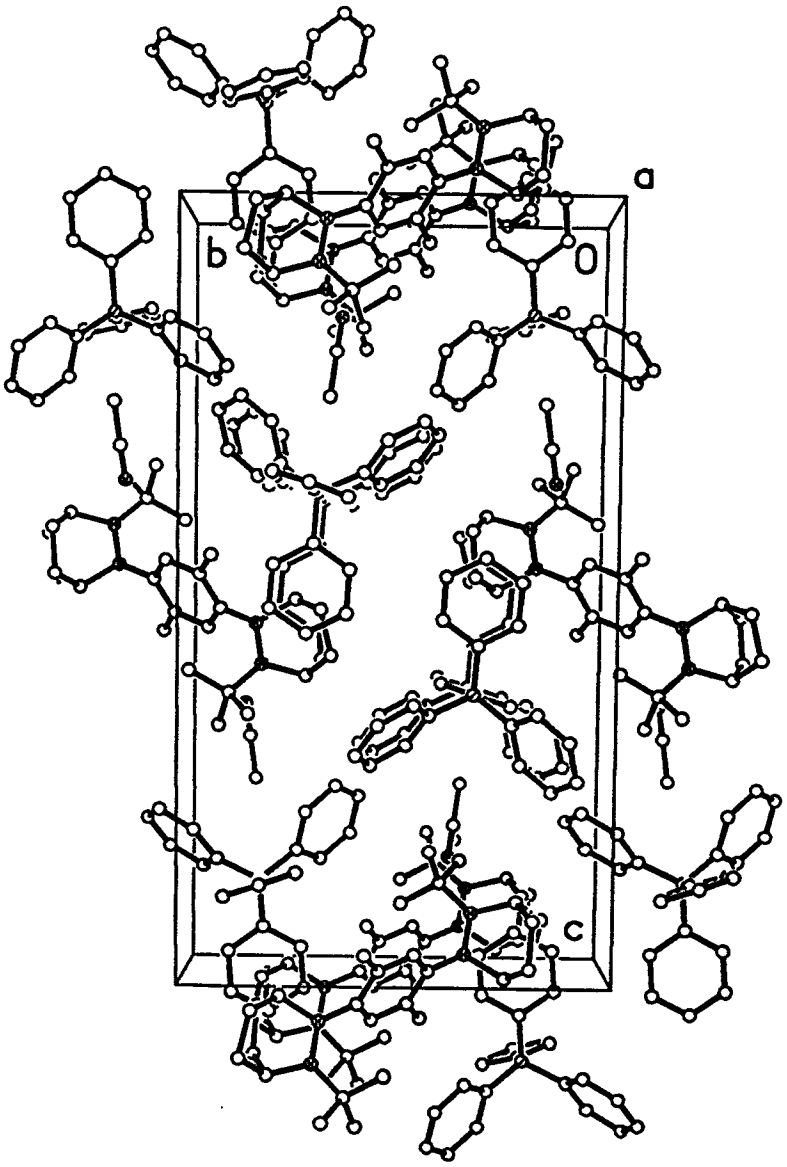
[a] For $3^{++}(BPh_4)_2^- 2(CH_3CN)$. [b] In parenthesis: R_{int}.

[c] R_1 [I > 2s(I)]. Full-matrix least-squares refinment on F^2.



Thermal Ellipsoid Drawing (50% Probability Level)

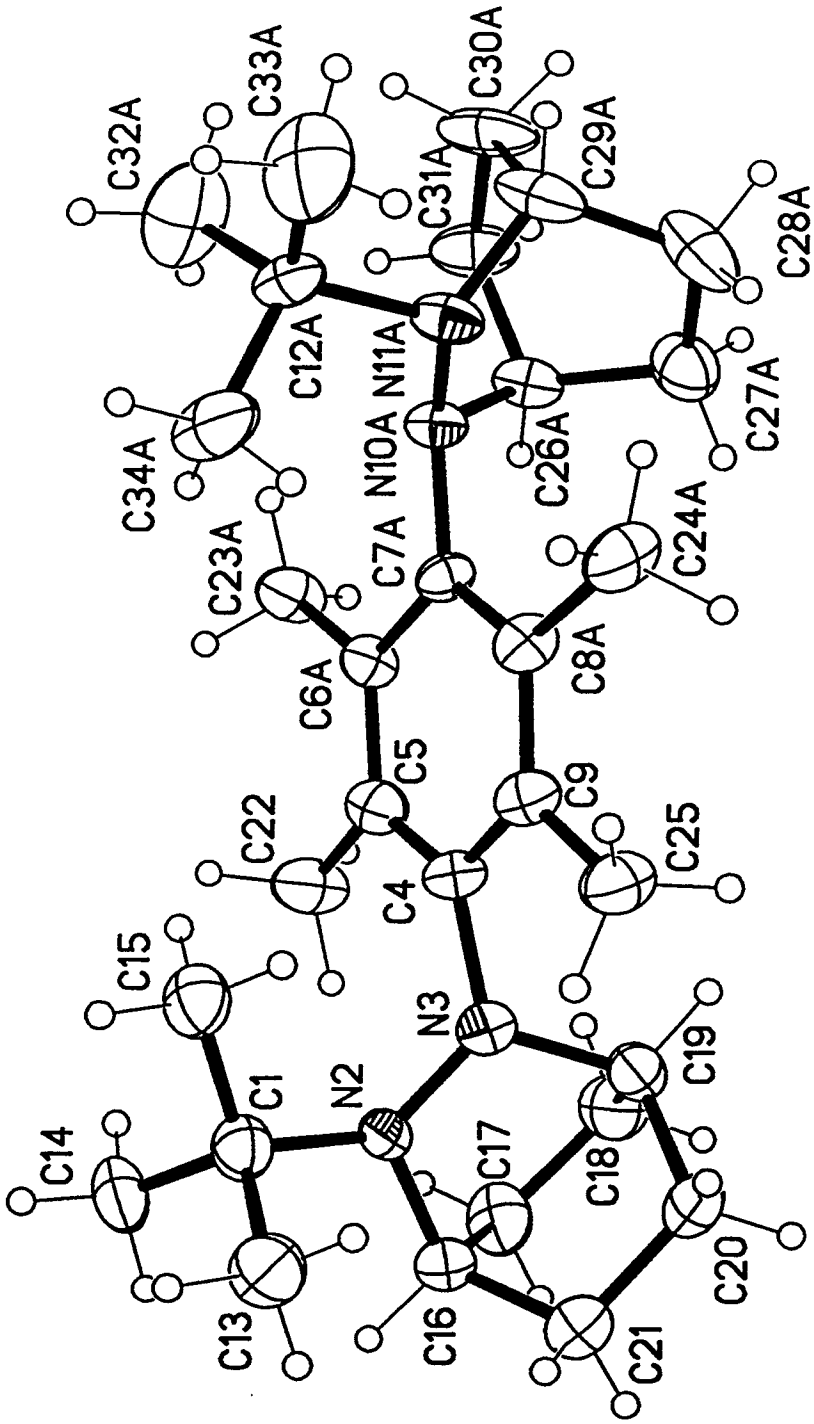
of the X-Ray Crystal Structure of $\mathbf{3}^{++}$



Packing Diagram for $3^{++}(BPh_4)_2^{-}$ $2(CH_3CN)$

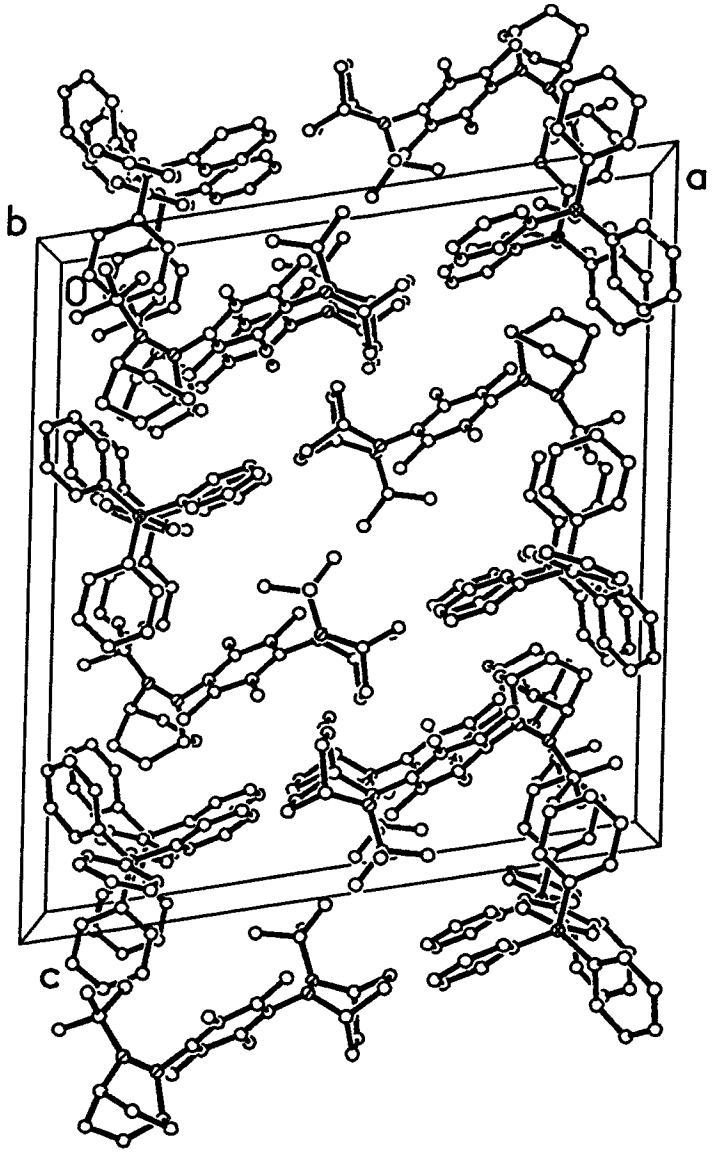
Table S2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for $3^{++}(BPh_4)_2^-\ 2(CH_3CN)$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	0.3736(2)	0.26057(12)	0.49324(7)	0.0195(4)
N(2)	0.35163(14)	0.16797(10)	0.46225(5)	0.0173(3)
N(3)	0.32060(13)	0.18278(10)	0.40933(5)	0.0158(3)
C(4)	0.3299(2)	0.28656(12)	0.39437(7)	0.0204(4)
C(5)	0.4812(2)	0.32020(13)	0.41444(7)	0.0226(4)
C(6)	0.5014(2)	0.31356(13)	0.47557(7)	0.0251(4)
C(7)	0.2396(2)	0.32217(13)	0.48051(7)	0.0227(4)
C(8)	0.2220(2)	0.34701(13)	0.42115(7)	0.0230(4)
C(9)	0.4263(2)	0.08184(12)	0.48145(7)	0.0171(3)
C(10)	0.5398(2)	0.04884(12)	0.45638(6)	0.0173(3)
C(11)	0.6164(2)	-0.03358(12)	0.47432(6)	0.0174(3)
C(12)	0.7453(2)	-0.06488(13)	0.44946(7)	0.0218(4)
C(13)	0.2397(2)	0.10841(13)	0.37238(7)	0.0219(4)
C(14)	0.2024(2)	0.0175(2)	0.40118(8)	0.0343(5)
C(15)	0.1033(2)	0.1571(2)	0.34685(9)	0.0405(5)
C(16)	0.3332(2)	0.0825(2)	0.32959(8)	0.0378(5)
B(17)	0.8426(2)	0.31888(14)	0.62741(7)	0.0157(4)
C(18)	0.6707(2)	0.31276(12)	0.63023(6)	0.0165(3)
C(19)	0.5820(2)	0.39286(13)	0.61539(7)	0.0223(4)
C(20)	0.4369(2)	0.39126(14)	0.61771(8)	0.0258(4)
C(21)	0.3735(2)	0.30765(14)	0.63447(7)	0.0258(4)
C(22)	0.4562(2)	0.22614(14)	0.64790(7)	0.0273(4)
C(23)	0.6013(2)	0.22887(13)	0.64502(7)	0.0228(4)
C(24)	0.8612(2)	0.30973(12)	0.56397(6)	0.0163(3)
C(25)	0.8660(2)	0.39208(12)	0.53112(7)	0.0182(3)
C(26)	0.8665(2)	0.38533(13)	0.47616(7)	0.0205(4)
C(27)	0.8616(2)	0.29449(13)	0.45172(7)	0.0206(4)
C(28)	0.8580(2)	0.21103(13)	0.48280(7)	0.0220(4)
C(29)	0.8571(2)	0.21915(13)	0.53745(7)	0.0202(4)
C(30)	0.9259(2)	0.23245(12)	0.66445(6)	0.0162(3)
C(31)	1.0402(2)	0.17776(12)	0.65022(7)	0.0177(3)
C(32)	1.1107(2)	0.10716(13)	0.68330(7)	0.0212(4)
C(33)	1.0692(2)	0.08803(13)	0.73263(7)	0.0236(4)
C(34)	0.9578(2)	0.14160(13)	0.74868(7)	0.0254(4)
C(35)	0.8898(2)	0.21217(13)	0.71559(7)	0.0211(4)
C(36)	0.9096(2)	0.42245(12)	0.65303(6)	0.0162(3)
C(37)	1.0393(2)	0.45879(12)	0.63993(7)	0.0181(4)
C(38)	1.1058(2)	0.54082(13)	0.66389(7)	0.0219(4)
C(39)	1.0441(2)	0.59122(13)	0.70253(7)	0.0248(4)
C(40)	0.9159(2)	0.55832(13)	0.71659(7)	0.0248(4)
C(41)	0.8511(2)	0.47594(12)	0.69209(7)	0.0209(4)
N(42)	0.2904(2)	0.86539(14)	0.64628(7)	0.0415(5)
C(43)	0.2857(2)	0.85373(13)	0.69015(7)	0.0240(4)
C(44)	0.2787(2)	0.8395(2)	0.74657(7)	0.0330(5)



Thermal Ellipsoid Drawing (50% Probability Level)

of the X-Ray Crystal Structure of 4^+

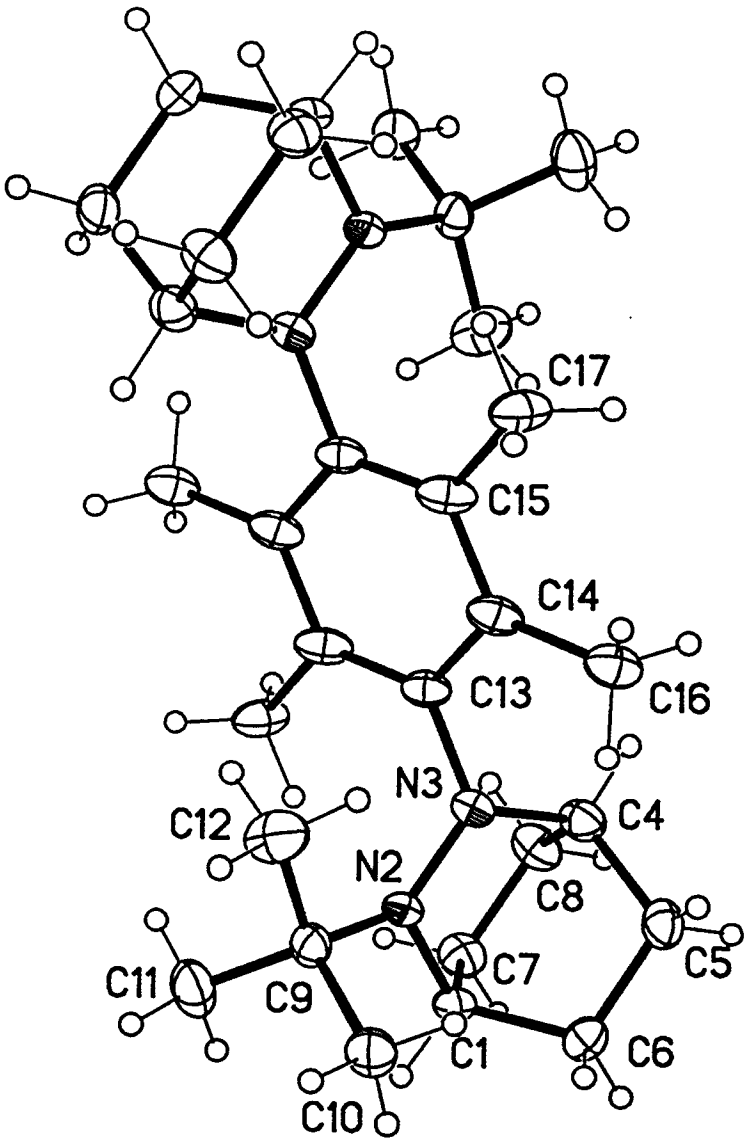


Packing Diagram for $4^{+}BPh_4^{-}$

Table S3. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for $4^+BPh_4^-$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

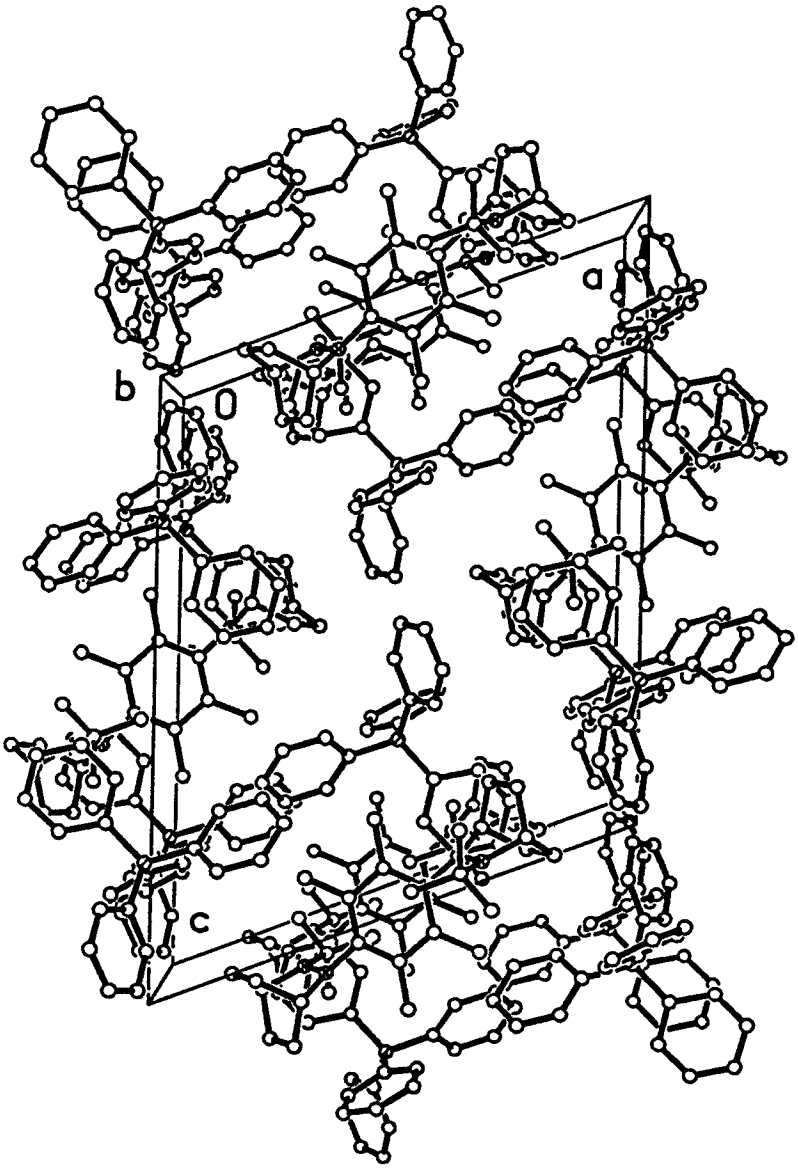
	x	y	z	U(eq)
C(1)	1328(1)	3371(3)	6096(1)	34(1)
N(2)	1725(1)	2833(2)	6676(1)	27(1)
N(3)	2235(1)	3515(2)	6995(1)	33(1)
C(4)	2763(1)	4183(2)	6757(1)	32(1)
C(5)	3168(1)	3440(2)	6441(1)	36(1)
C(9)	2880(1)	5562(2)	6921(1)	33(1)
C(13)	695(1)	4007(3)	6233(1)	44(1)
C(14)	1182(1)	2118(3)	5687(1)	40(1)
C(15)	1682(1)	4486(3)	5807(1)	40(1)
C(16)	1417(1)	1842(2)	7037(1)	36(1)
C(17)	1938(1)	791(2)	7308(1)	43(1)
C(18)	2509(1)	1596(3)	7682(1)	45(1)
C(19)	2352(1)	3146(2)	7636(1)	35(1)
C(20)	1733(1)	3468(3)	7876(1)	40(1)
C(21)	1171(1)	2612(3)	7537(1)	42(1)
C(22)	3045(1)	1928(3)	6270(1)	45(1)
C(25)	2407(1)	6336(3)	7237(1)	38(1)
C(6A)	3762(2)	3959(5)	6306(3)	26(2)
C(7A)	3921(2)	5324(5)	6508(3)	24(1)
C(8A)	3495(2)	6051(5)	6815(3)	26(2)
N(10A)	4537(2)	5841(4)	6366(2)	28(1)
N(11A)	4595(2)	7335(5)	6281(2)	31(1)
C(12A)	4377(2)	7717(4)	5635(2)	33(1)
C(23A)	4212(3)	3181(9)	5963(4)	38(2)
C(24A)	3609(5)	7530(6)	7039(4)	41(2)
C(26A)	5139(2)	5266(5)	6748(2)	33(1)
C(27A)	5253(3)	6013(5)	7338(2)	45(2)
C(28A)	5333(4)	7579(5)	7225(2)	56(2)
C(29A)	5259(2)	7806(5)	6559(2)	45(1)
C(30A)	5828(2)	7031(4)	6358(3)	53(2)
C(31A)	5730(3)	5456(5)	6443(3)	46(2)
C(32A)	4766(3)	7106(8)	5201(3)	72(3)
C(33A)	4408(4)	9286(6)	5603(4)	75(3)
C(34A)	3672(3)	7265(8)	5462(4)	69(3)
C(6B)	3630(4)	4311(7)	6232(5)	26(3)
C(7B)	3770(4)	5725(7)	6370(5)	23(2)
C(8B)	3356(4)	6379(7)	6712(5)	17(3)
N(10B)	4241(3)	6734(7)	6220(3)	29(2)
N(11B)	4821(3)	6199(8)	6034(2)	30(2)
C(12B)	5390(3)	6241(5)	6553(3)	42(2)
C(23B)	4027(7)	3619(15)	5818(6)	31(4)
C(24B)	3439(8)	7878(8)	6916(7)	20(3)
C(26B)	3926(3)	7809(6)	5789(3)	26(2)
C(27B)	4412(4)	8994(9)	5769(6)	38(3)
C(28B)	4981(5)	8408(7)	5492(6)	48(3)
C(29B)	4929(4)	6815(7)	5470(3)	47(2)

C(30B)	4318(3)	6457(12)	5016(4)	46(2)
C(31B)	3706(4)	7152(12)	5186(4)	34(2)
C(32B)	5995(4)	5747(11)	6306(5)	53(3)
C(33B)	5522(6)	7667(10)	6852(5)	50(3)
C(34B)	5216(7)	5171(11)	6998(5)	54(4)
C(6C)	3686(4)	4235(7)	6281(6)	31(3)
C(7C)	3781(3)	5651(7)	6440(5)	28(2)
C(8C)	3412(4)	6372(7)	6803(5)	22(2)
N(10C)	4331(3)	6121(8)	6173(2)	30(2)
N(11C)	4711(3)	7237(6)	6482(2)	29(2)
C(12C)	5277(2)	6665(5)	6932(2)	38(2)
C(23C)	4087(6)	3309(14)	5945(6)	24(3)
C(24C)	3593(7)	7802(9)	7058(7)	27(3)
C(26C)	4166(2)	6436(7)	5527(2)	36(2)
C(27C)	3755(4)	7756(7)	5421(5)	42(2)
C(28C)	4170(3)	8917(8)	5767(4)	42(2)
C(29C)	4837(3)	8353(6)	6072(3)	33(2)
C(30C)	5204(4)	7833(8)	5593(3)	42(2)
C(31C)	4802(4)	6601(10)	5287(5)	42(2)
C(32C)	5748(3)	7845(7)	7143(4)	42(2)
C(33C)	5627(4)	5524(7)	6654(4)	51(3)
C(34C)	4997(4)	6088(10)	7450(3)	56(3)
B(40)	1642(1)	7479(3)	4154(1)	26(1)
C(41)	2353(1)	8088(2)	4044(1)	29(1)
C(42)	2523(1)	9482(3)	4167(1)	40(1)
C(43)	3102(1)	10077(3)	4064(1)	50(1)
C(44)	3545(1)	9285(3)	3826(1)	52(1)
C(45)	3397(1)	7913(3)	3687(1)	47(1)
C(46)	2809(1)	7332(3)	3789(1)	35(1)
C(47)	1607(1)	5767(2)	4132(1)	28(1)
C(48)	2128(1)	4933(3)	4411(1)	33(1)
C(49)	2071(1)	3482(3)	4454(1)	43(1)
C(50)	1483(1)	2829(3)	4228(1)	44(1)
C(51)	964(1)	3613(3)	3952(1)	40(1)
C(52)	1032(1)	5049(2)	3904(1)	32(1)
C(53)	1091(1)	8179(2)	3637(1)	26(1)
C(54)	1035(1)	7743(2)	3050(1)	31(1)
C(55)	598(1)	8347(3)	2591(1)	37(1)
C(56)	203(1)	9442(3)	2703(1)	37(1)
C(57)	247(1)	9914(3)	3274(1)	34(1)
C(58)	683(1)	9293(2)	3729(1)	29(1)
C(59)	1495(1)	7862(2)	4817(1)	26(1)
C(60)	871(1)	7646(3)	4958(1)	33(1)
C(61)	733(1)	7863(3)	5517(1)	38(1)
C(62)	1220(1)	8283(3)	5969(1)	39(1)
C(63)	1843(1)	8487(3)	5848(1)	41(1)
C(64)	1972(1)	8291(2)	5283(1)	33(1)



Thermal Ellipsoid Drawing (50% Probability Level)

of the X-Ray Crystal Structure of $\mathbf{4}^{++}$

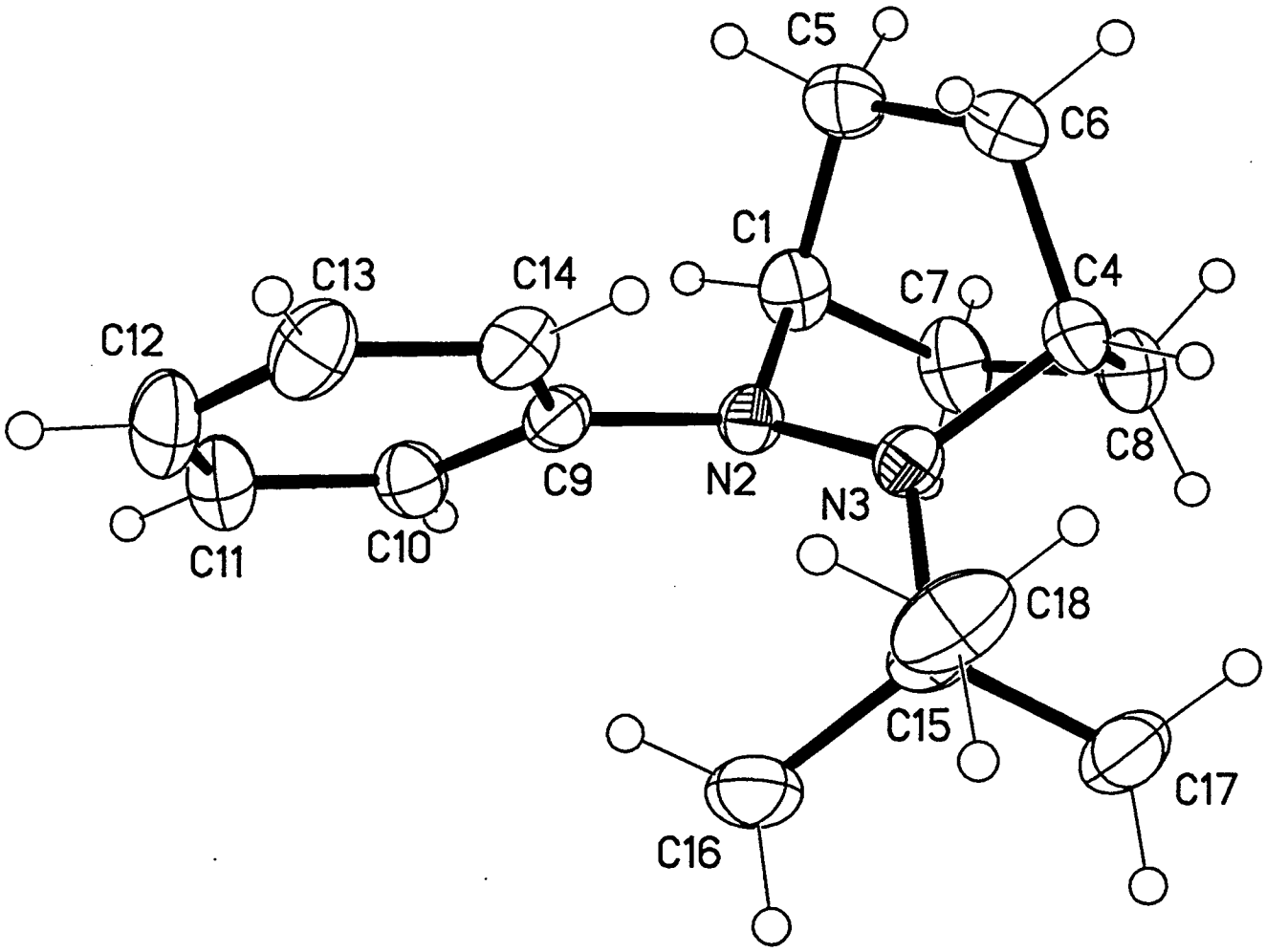


Packing Diagram for $4^{++}(BPh_4)_2^-$

Table S4. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for $4^{++}(BPh_4)_2^-$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

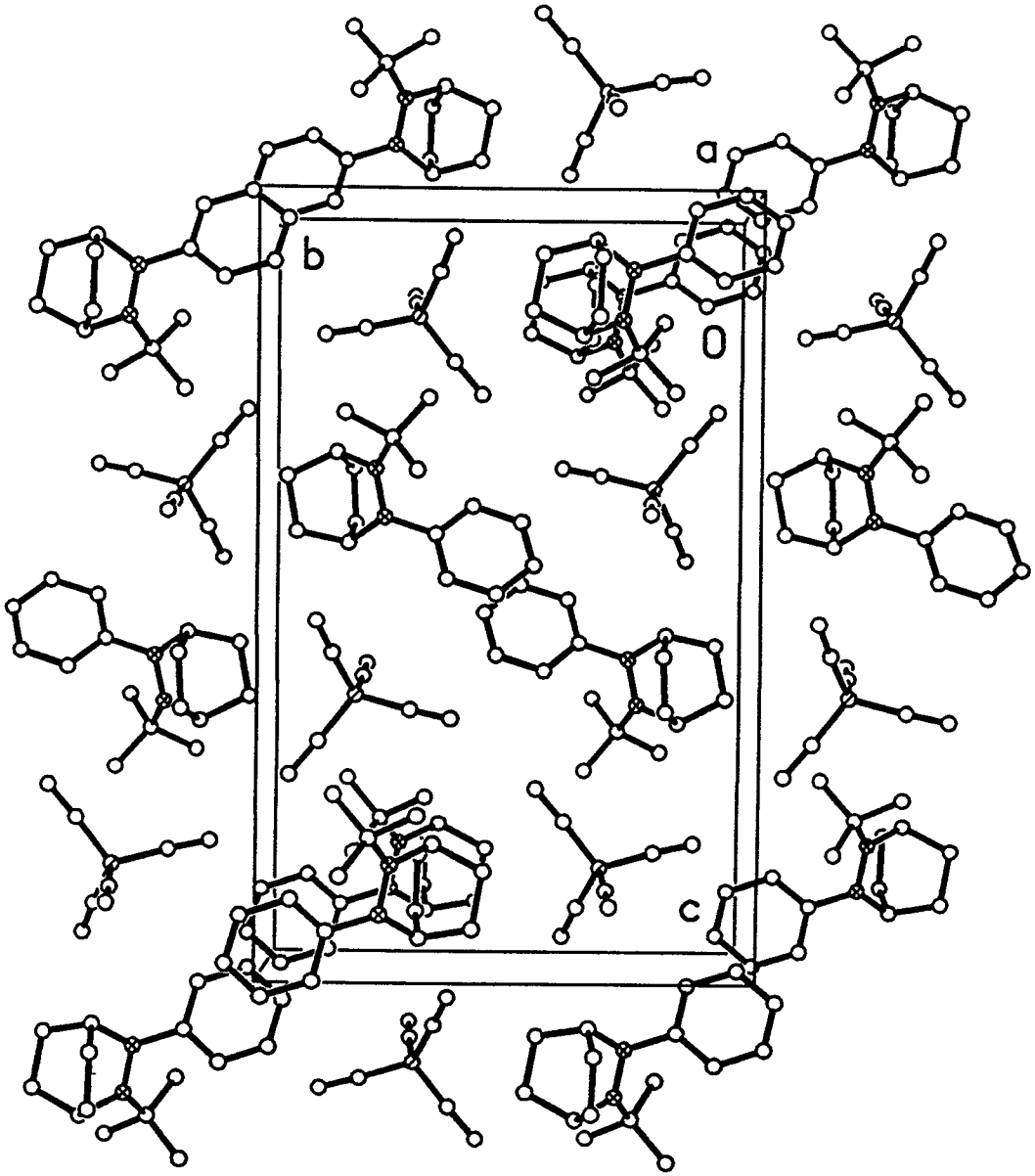
	x	y	z	U(eq)
C(1)	7307(2)	6746(2)	5534(1)	22(1)
N(2)	8192(2)	6783(2)	5409(1)	19(1)
N(3)	8659(1)	5740(2)	5586(1)	20(1)
C(4)	8176(3)	4818(5)	5856(2)	26(1)
C(5)	8044(2)	5287(2)	6560(2)	27(1)
C(6)	7503(2)	6462(2)	6363(2)	26(1)
C(7)	6701(2)	5765(3)	5037(2)	28(1)
C(8)	7230(2)	4585(3)	5230(2)	29(1)
C(9)	8640(2)	7982(2)	5404(2)	23(1)
C(10)	8687(2)	8653(3)	6108(2)	29(1)
C(11)	8017(3)	8625(3)	4693(2)	35(1)
C(12)	9616(2)	7889(3)	5408(2)	38(1)
C(13)	9330(2)	5369(3)	5274(2)	21(1)
C(14)	10185(2)	4976(3)	5796(2)	25(1)
C(15)	10884(2)	4649(3)	5510(2)	25(1)
C(16)	10388(3)	5013(3)	6626(2)	27(1)
C(17)	11817(2)	4289(3)	6073(2)	30(1)
C(1A)	7525(9)	7609(11)	5276(8)	21(3)
N(2A)	7960(9)	6459(11)	5202(9)	18(3)
N(3A)	8894(8)	6569(10)	5378(7)	19(2)
C(4A)	9241(12)	7761(13)	5613(9)	23(3)
C(5A)	8776(11)	8621(13)	4949(9)	25(3)
C(6A)	7719(13)	8521(20)	4742(12)	22(3)
C(7A)	7954(10)	8042(14)	6090(8)	24(3)
C(8A)	9021(11)	8154(17)	6301(9)	26(3)
C(9A)	7521(10)	5266(12)	5278(8)	17(3)
C(10A)	6560(11)	5507(18)	5276(11)	22(4)
C(11A)	8139(20)	4742(28)	6032(12)	18(6)
C(12A)	7431(11)	4441(12)	4623(8)	19(3)
C(13A)	9444(10)	5771(14)	5117(9)	14(3)
C(14A)	10252(14)	5331(18)	5699(12)	17(3)
C(15A)	10754(14)	4316(17)	5610(12)	20(4)
C(16A)	10385(20)	5498(20)	6533(11)	37(6)
C(17A)	11626(11)	3874(16)	6260(11)	18(4)
B(1')	4942(2)	3646(2)	2669(1)	21(1)
C(1')	4152(2)	3455(2)	1810(1)	20(1)
C(2')	3202(2)	3563(2)	1679(1)	25(1)
C(3')	2510(2)	3507(2)	967(1)	27(1)
C(4')	2735(2)	3319(2)	342(1)	27(1)
C(5')	3658(2)	3155(2)	447(1)	27(1)
C(6')	4347(2)	3222(2)	1167(1)	23(1)
C(7')	5980(2)	3244(2)	2711(1)	23(1)
C(8')	6441(2)	3811(2)	2292(1)	24(1)
C(9')	7331(2)	3495(2)	2347(1)	30(1)
C(10')	7799(2)	2586(3)	2821(1)	35(1)
C(11')	7367(2)	1985(2)	3232(1)	34(1)

C(12')	6476(2)	2315(2)	3173(1)	28(1)
C(13')	4922(2)	5071(2)	2896(1)	20(1)
C(14')	4152(2)	5530(2)	3025(1)	28(1)
C(15')	4067(2)	6710(2)	3194(1)	31(1)
C(16')	4765(2)	7509(2)	3251(1)	32(1)
C(17')	5541(2)	7099(2)	3139(1)	29(1)
C(18')	5614(2)	5911(2)	2968(1)	24(1)
C(19')	4687(2)	2829(2)	3275(1)	21(1)
C(20')	5048(2)	3089(2)	4048(1)	26(1)
C(21')	4926(2)	2338(2)	4582(1)	34(1)
C(22')	4422(2)	1303(2)	4357(2)	37(1)
C(23')	4043(2)	1023(2)	3600(2)	36(1)
C(24')	4185(2)	1779(2)	3077(1)	29(1)



Thermal Ellipsoid Drawing (50% Probability Level)

of the X-Ray Crystal Structure of **5**$^{+}$



Packing Diagram for $5^{+}B(C{\equiv}CH)_4^{-}$

Table S5. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$Å^2 \times 10^3$] for $5^+B(C{\equiv}CH)_4^-$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	4157(3)	1704(2)	5605(1)	30(1)
N(2)	3102(2)	2468(1)	5932(1)	23(1)
N(3)	2971(2)	2274(1)	6554(1)	23(1)
C(4)	4144(3)	1452(2)	6781(1)	27(1)
C(5)	6034(3)	1796(2)	5875(1)	39(1)
C(6)	5988(3)	1751(2)	6601(1)	34(1)
C(7)	3411(3)	654(2)	5746(1)	37(1)
C(8)	3632(3)	443(2)	6460(1)	32(1)
C(9)	3107(3)	3510(2)	5716(1)	24(1)
C(10)	2297(3)	3742(2)	5136(1)	29(1)
C(11)	2274(3)	4749(2)	4938(1)	36(1)
C(12)	3049(3)	5502(2)	5312(1)	40(1)
C(13)	3904(3)	5255(2)	5879(1)	36(1)
C(14)	3940(3)	4255(2)	6085(1)	30(1)
C(15)	1462(3)	2648(2)	6930(1)	29(1)
C(16)	86(3)	3175(2)	6503(1)	39(1)
C(17)	617(3)	1715(2)	7229(1)	39(1)
C(18)	2163(3)	3362(2)	7451(1)	44(1)
B(1)	7961(3)	8078(2)	6377(1)	27(1)
C(19)	5952(3)	7981(2)	6146(1)	27(1)
C(20)	4432(3)	7937(2)	5996(1)	30(1)
C(21)	8081(3)	8830(2)	6974(1)	29(1)
C(22)	8137(3)	9417(2)	7403(1)	35(1)
C(23)	8719(3)	6965(2)	6553(1)	31(1)
C(24)	9318(4)	6142(2)	6656(1)	42(1)
C(25)	9103(3)	8525(2)	5824(1)	29(1)
C(26)	9992(3)	8817(2)	5412(1)	37(1)