Supporting information for

Effects of Bridge Redox State Levels on the Electron Transfer and Optical Properties of Intervalence Compounds with Hydrazine Charge-Bearing Units

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UV/VIS spectra were obtained on a Hewlett-Packard HP 8452 diode array spectrophotometer (190-820 nm range) and Perkin Elmer Lambda 20 UV/VIS spectrometer (190-1100 nm). A Nicolet 740 IR spectrometer was used to obtain NIR spectra. NMR spectra were acquired on Bruker AM-500 or AC-300 instruments. ESR spectra were obtained on a Bruker ESR 300E spectrometer. Intensity data for crystallographic analysis were measured with a Siemens P4/CCD diffractometer using graphite monochromated MoKa radiation (λ = 0.71073 Å). The structures were solved using the SHELXS-86 program and refined using the SHELXS-93 program which refines on F^2 values.

Compound Preparation.

1,4-bis(2-tert-butyl-2,3-diazabicyclo[2.2.2]oct-3-yl)-anthracene-9,10-diyl (2). 9,10-dibromoanthracene (168 mg, 0.50 mmole) was placed into an oven dried 50 mL Schlenk flask under N_2. Ether (5 mL) was added and the mixture was cooled down to -78 °C with a Dry-Ice / acetone bath. t-BuLi (1.74 M in pentane, 1.15 mL, 2.0 mmole) was added slowly. The orange mixture was stirred for 1 hour and 2-t-Bu-2,3-diazabicyclo[2.2.2]oct-2-ene iodide (300 mg, 1.02 mmole) was added. The cooling bath was lowered so the bottom of the flask was just touching acetone and the mixture was stirred for 35 min. The cooling bath was gradually lowered and then removed in 20 minutes. The mixture started to turn very dark red. After the yellow

crystals of the diazenium salt disappeared (usually several days) the mixture was quenched with water (20 mL), extracted with warm toluene (4 x 30 mL), dried with $MgSO_4$ and evaporated to give 0.25 g of dark red solid. The solid was dissolved in refluxing toluene (20 mL) and CH_3CN (*ca* 50 mL) was added to precipitate a deep-red solid (137 mg, 54 %), m.p. 252 °C. MS : m/e 510.3729, I = 18.5 %, calcd. for $C_{34}H_{46}N_4$ 510.3722. ^1H NMR (500 MHz, C_6D_6, 75 °C) : δ 10.73 and 10.65 (br. s., 2H, ArH), 8.90 (br. s., 2H, ArH), 7.41 (br. s., 4H, ArH), 3.41 (s., 2H, NCH), 3.28 and 3.26 (s., 2H, NCH), 2.80 (br. s., 2H, CH_2), 2.58 (br. s., 2H, CH_2), 2.13 (br. s., 2H, CH_2), 1.93 - 1.65 (br. s., 2H, CH_2), 1.59 - 1.41 (br. s., 4H, CH_2), 1.19 and 1.16 (s., 18H, $C(CH_3)_3$), 1.30 - 0.94 (br. s., 4H, CH_2). ^{13}C NMR (125 MHz, C_6D_6, 75 °C) : δ 60.65 and 60.54 ($C(CH_3)_3$), 57.17 and 56.84 (NCH), 47.85 and 47.71 (NCH), ca. 29.15 (shoulder on the t-Bu signal, CH_2), 29.03 and 28.91 ($C(CH_3)_3$), 27.35 (CH_2), 24.22 (CH_2), 22.80 (CH_2). At elevated temperatures employed due to very low solubility the NMR signals of aromatic and bicyclic carbon and hydrogen atoms were broadened. Due to the broadening and low solubility the signals of the aromatic carbon atoms were not observed with sufficient signal-to-noise ratio to be reported.

2-tert-butyl-3-(anthracen-9-yl)-2,3-diazabicyclo[2.2.2]octane (3). 9-Bromoanthracene (257 mg, 1.0 mmole) was placed into an oven dried 50 mL Schlenk flask under N_2. Ether (7 mL) was added and the mixture was cooled down to -78 °C. t-BuLi (1.74 M in pentane, 1.15 mL, 2.0 mmole) was added dropwise and the mixture was stirred for 20 min. 2-t-Bu-2,3-diazabicyclo[2.2.2]oct-2-ene iodide (295 mg, 1.0 mmole) was added and the cooling bath was slowly lowered and removed. Yellow-orange suspension gradually turned red and in 3 hours everything dissolved. The mixture was quenched with water (3 mL) and then extracted with pentane (3 x 30 mL), dried with $MgSO_4$ and evaporated to give 0.34 g of the product. X-ray

crystallographic analysis of single crystals afforded by slow evaporation of a benzene solution confirmed the structure. Recrystallization from aqueous ethanol gave red needles, m.p. 176-177 °C (sublimation). MS : m/e 344.2263, I = 29 %, calcd. for $C_{24}H_{28}N_2$ 344.2252. ^{1}H NMR (500 MHz, C_6D_6) : δ 10.65 (d., J = 9.4 Hz, 1H, ArH), 8.78 (d., J = 8.9 Hz, 1H, ArH), 8.00 (s., 1H, ArH), 7.84 (dd., J = 11.81, 8.36 Hz, 2H, ArH), 7.38 (m., 2H, ArH), 7.29 (m., 2H, ArH), 3.33 (s., 2H, NCH), 2.77 (m., 1H, CH_2), 2.50 (m., 1H, CH_2), 2.02 (m., 1H, CH_2), 1.62 (m., 1H, CH_2), 1.42 (m., 2H, CH_2),1.19 - 1.05 (m., 1H, CH_2), 1.15 (s., 9H, $C(CH_3)_3$), 0.88 (m., 1H, CH_2). ^{13}C NMR + DEPT-135 (125 MHz, C_6D_6) : δ 145.33 (C_{ar}), 133.52 (C_{ar}), 133.37 (C_{ar}), 129.53 ($C_{ar}H$), 129.10 ($C_{ar}H$), 128.81 (C_{ar}), 127.51 ($C_{ar}H$), 127.31 (C_{ar}), 126.22 ($C_{ar}H$), 125.19 ($C_{ar}H$), 125.02 ($C_{ar}H$), 124.80 ($C_{ar}H$), 122.79 ($C_{ar}H$), 122.58 ($C_{ar}H$), 60.47 ($C(CH_3)_3$), 56.94 (NCH), 47.33 (NCH), 28.81 ($C(CH_3)_3$), 28.75 (CH_2), 26.96 (CH_2), 23.85 (CH_2), 22.82 (CH_2).

2-tert-butyl-3-anthracenyl-2,3-diazabicyclo[2.2.2]octane radical cation nitrate ($3^+NO_3^-$). **3** (17.0 mg, 0.0493 mmole) and $AgNO_3$ (8.5 mg, 0.050 mmole) were vigorously stirred overnight in 2 mL CH_2Cl_2 under nitrogen. The color of the solution slowly changed from bright red to dark brown. The solution was filtered through celite and the product was precipitated by vapor diffusion with ether. Large but very thin brownish hexagonal plates (16 mg, 80 %) were obtained.

2-tert-butyl-3-anthracenyl-2,3-diazabicyclo[2.2.2]octane radical cation tetraphenylborate ($3^+BPh_4^-$). $3^+NO_3^-$ (8.7 mg, 0.021 mmole) was mixed with $NaBPh_4$ (9.0 mg, 0.026 mmole) and stirred with 2 mL of CH_3CN for 5 minutes to give red solution and white solid on the bottom ($NaNO_3$). The solution was filtered into a small test tube, diluted with 2 mL of CH_2Cl_2 and the test tube was placed into a jar with ether. Large red-brown blocks formed overnight (7 mg, 49 %), structure was confirmed by X-ray crystallography.

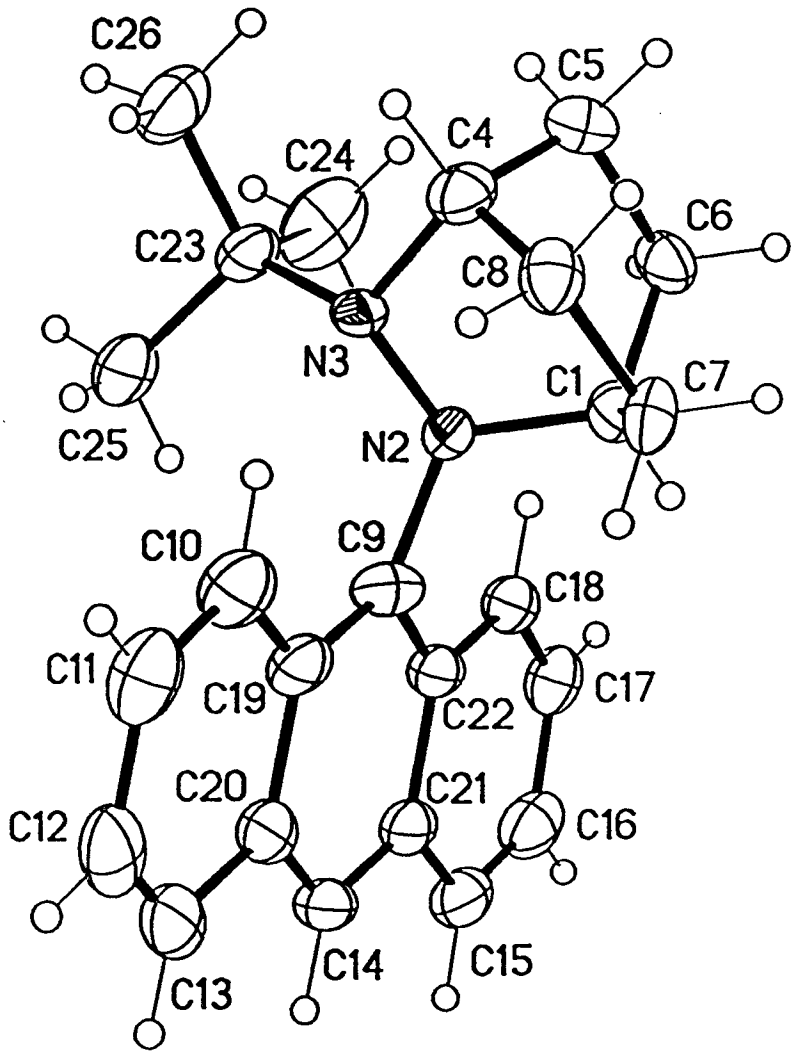
Preparation of the bis-hydrazine radical cation solutions for optical and ESR studies. In a typical experiment, $AgNO_3$ (160 mL of 0.08312M solution in CH_3CN, 0.0133 mmole) was added to **2** (7.05 mg, 0.0138 mmole) in 3 mL of CH_3CN and the mixture was vigorously stirred under nitrogen for 3 hours. The solution turned purple. The mixture was centrifuged and diluted to 10 mL with CH_3CN. The resulting solution was used for optical spectroscopy and after brief degassing with N_2 for ESR measurements.

Table S1. Crystal data and structure refinement parameters.

compound number	**3**	$3^{+}BPh_4^{-}$
empirical formula	$C_{24}H_{28}N_2$	$C_{48}H_{48}BN_2$
temperature, K	133(2)	133(2)
space group	$P2_1/c$	$P2_1/n$
Z	4	4
a, Å	13.3666(2)	10.0344(3)
b, Å	11.5570(3)	18.0759(5)
c, Å	12.6759(3)	20.3609(6)
a, deg	90	90
b, deg	105.455(2)	90.797(2)
g, deg	90	90
Volume, $Å^3$	1887.34(7)	3692.7(2)
Density, (calcd), g/cm^3	1.212	1.194
F(000)	744	1420
Crystal size, mm	0.40 × 0.15 × 0.15	0.38 × 0.32 × 0.26
Reflections collected	8080	17467
Independent reflections [a]	4070 (0.0398)	8111 (0.0253)
Final R index [b]	0.0635	0.0468
wR index (all data)	0.1832	0.1077
Goodness-of-fit on F^2	1.038	1.024
Data / restraints / parameters	4068 / 175 / 334	8110 / 0 / 461
Largest dif. Map peaks, $eÅ^{-3}$	0.270 / -0.199	0.277 / -0.173

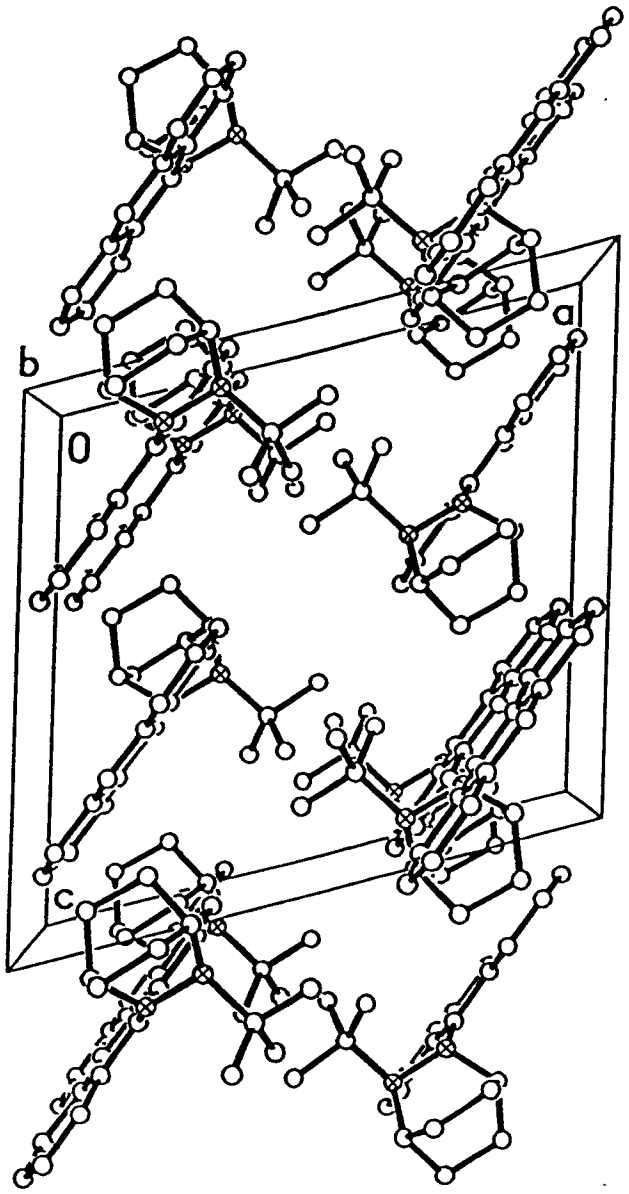
[a] In parenthesis: R_{int}.

[b] 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 **3**

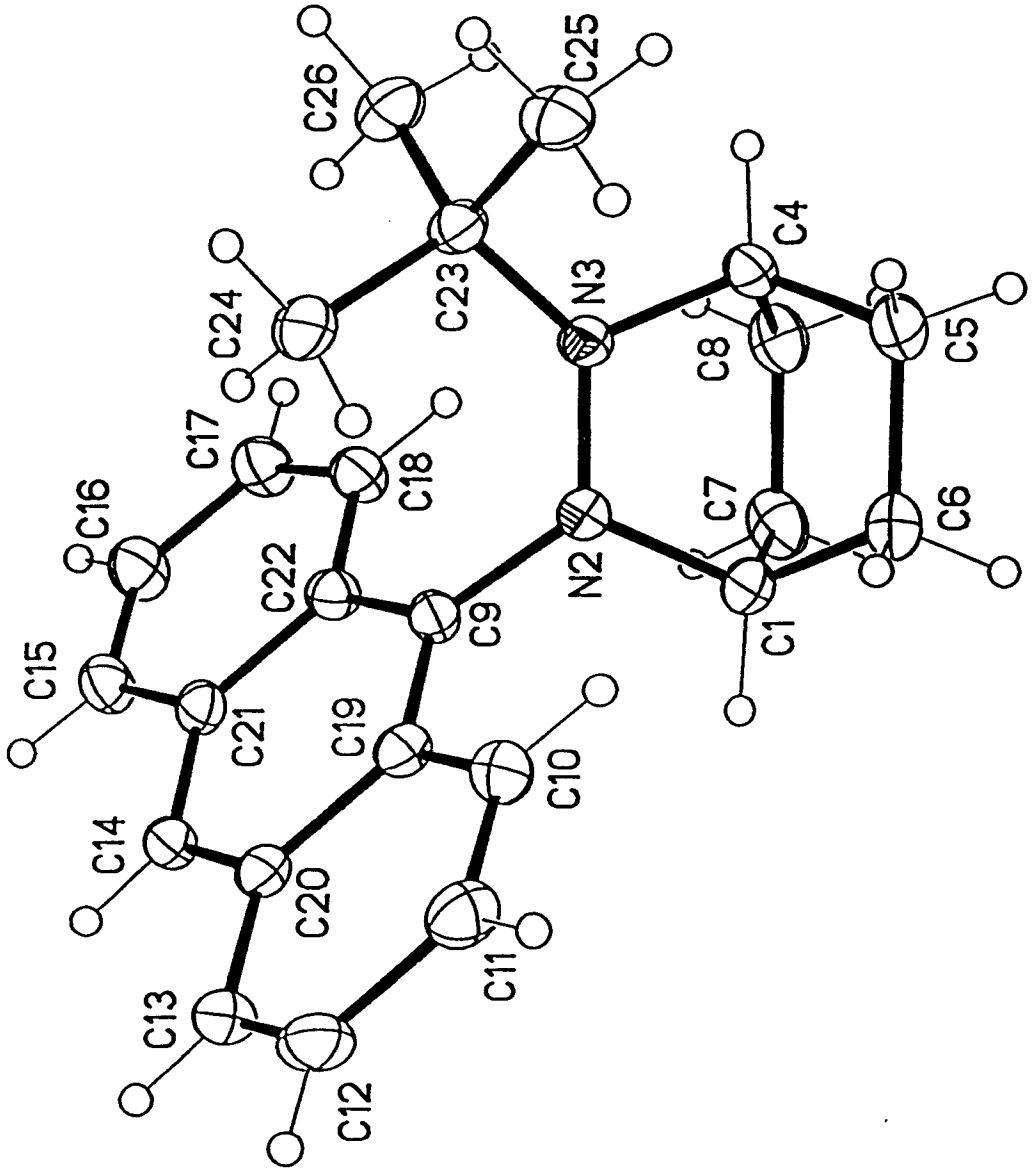


Packing Diagram for **3**

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

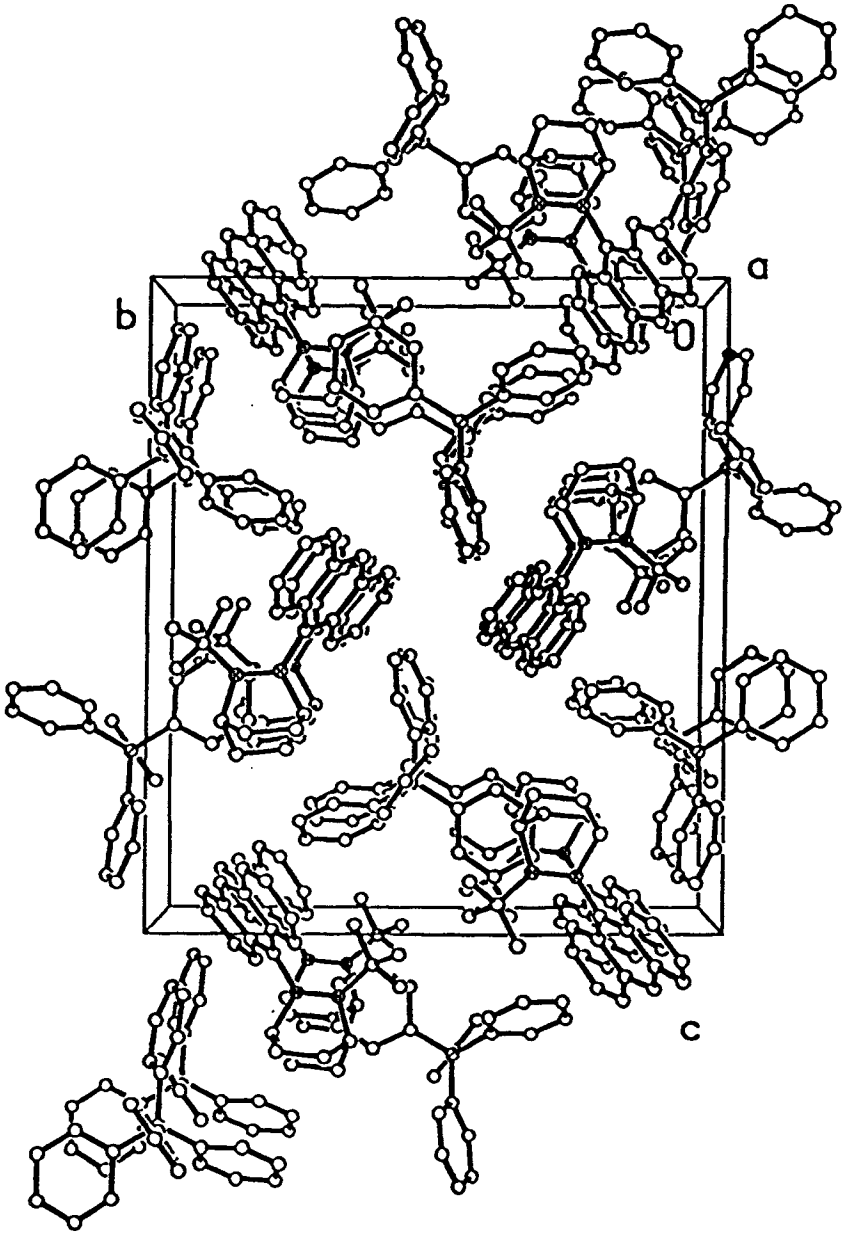
	x	y	z	U(eq)
C(1)	0.8533(2)	0.5880(3)	0.4575(2)	0.0295(7)
N(2)	0.7621(2)	0.5298(2)	0.3813(2)	0.0259(6)
N(3)	0.6679(3)	0.5508(2)	0.4149(3)	0.0247(8)
C(4)	0.6884(2)	0.6292(3)	0.5104(3)	0.0329(8)
C(5)	0.7364(3)	0.7451(3)	0.4922(3)	0.0401(8)
C(6)	0.8353(3)	0.7179(3)	0.4523(3)	0.0347(8)
C(7)	0.8665(2)	0.5417(4)	0.5729(4)	0.0328(10)
C(8)	0.7635(3)	0.5666(3)	0.6059(3)	0.0340(8)
C(1')	0.5732(14)	0.475(2)	0.309(2)	0.041(6)
N(2')	0.6867(11)	0.4804(13)	0.3779(14)	0.032(5)
N(3')	0.7206(9)	0.5991(12)	0.3813(9)	0.021(4)
C(4')	0.643(2)	0.679(2)	0.323(2)	0.059(8)
C(5')	0.606(2)	0.648(2)	0.199(2)	0.028(6)
C(6')	0.572(2)	0.520(2)	0.1976(14)	0.039(6)
C(7')	0.5107(11)	0.548(2)	0.3693(14)	0.015(4)
C(8')	0.546(2)	0.678(2)	0.366(2)	0.056(8)
C(1")	0.6400(9)	0.5533(10)	0.2332(10)	0.038(3)
N(2")	0.7226(8)	0.5233(9)	0.3355(9)	0.030(3)
N(3")	0.6877(11)	0.5439(13)	0.4325(12)	0.094(12)
C(4")	0.5819(10)	0.5917(11)	0.4045(10)	0.043(4)
C(5")	0.5074(9)	0.5029(12)	0.3357(11)	0.040(3)
C(6")	0.552(2)	0.469(2)	0.240(2)	0.054(12)
C(7")	0.6057(12)	0.6789(11)	0.228(2)	0.008(3)
C(8")	0.5701(14)	0.7046(12)	0.3386(13)	0.068(5)
C(9)	0.7784(2)	0.4114(2)	0.3480(2)	0.0359(5)
C(10)	0.6879(2)	0.2963(2)	0.4650(2)	0.0409(6)
C(11)	0.6653(2)	0.1909(2)	0.5025(2)	0.0475(7)
C(12)	0.7008(2)	0.0861(2)	0.4669(2)	0.0461(7)
C(13)	0.7583(2)	0.0894(2)	0.3938(2)	0.0425(6)
C(14)	0.8489(2)	0.1986(2)	0.2816(2)	0.0365(6)
C(15)	0.9442(2)	0.3039(2)	0.1694(2)	0.0404(6)
C(16)	0.9702(2)	0.4046(2)	0.1284(2)	0.0429(6)
C(17)	0.9307(2)	0.5106(2)	0.1552(2)	0.0387(6)
C(18)	0.8687(2)	0.5135(2)	0.2254(2)	0.0327(5)
C(19)	0.7494(2)	0.3048(2)	0.3885(2)	0.0339(5)
C(20)	0.7858(2)	0.1966(2)	0.3532(2)	0.0349(5)
C(21)	0.8784(2)	0.3016(2)	0.2419(2)	0.0334(5)
C(22)	0.8404(2)	0.4102(2)	0.2724(2)	0.0312(5)
C(23)	0.5800(2)	0.5856(2)	0.3133(2)	0.0326(7)
C(24)	0.6129(5)	0.6786(5)	0.2449(4)	0.062(3)
C(25)	0.5450(4)	0.4789(5)	0.2420(5)	0.053(3)
C(26)	0.4877(2)	0.6299(3)	0.3510(3)	0.0494(10)
C(23')	0.7838(10)	0.6231(13)	0.5007(10)	0.044(9)
C(24')	0.720(2)	0.592(2)	0.5802(13)	0.038(7)
C(25')	0.8831(13)	0.552(2)	0.529(2)	0.038(9)
C(26')	0.813(2)	0.751(2)	0.515(2)	0.085(12)

C(23")	0.7758(8)	0.6076(9)	0.5168(8)	0.038(4)
C(24")	0.7439(14)	0.631(2)	0.6215(10)	0.067(5)
C(25")	0.8740(10)	0.534(2)	0.545(2)	0.065(14)
C(26")	0.800(2)	0.7227(12)	0.4702(14)	0.055(6)



Thermal Ellipsoid Drawing (50% Probability Level)

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



Packing Diagram for $3^{+}BPh_4^{-}$

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

	x	y	z	U(eq)
C(1)	0.3310(2)	0.71931(8)	0.66041(7)	0.0255(3)
N(2)	0.30645(11)	0.76067(6)	0.59795(6)	0.0188(3)
N(3)	0.32993(11)	0.83425(6)	0.60334(6)	0.0184(3)
C(4)	0.37716(14)	0.85559(8)	0.67019(7)	0.0216(3)
C(5)	0.2710(2)	0.83420(9)	0.72069(8)	0.0260(3)
C(6)	0.2410(2)	0.75111(9)	0.71336(8)	0.0298(4)
C(7)	0.4777(2)	0.72953(9)	0.67954(8)	0.0312(4)
C(8)	0.5060(2)	0.81314(9)	0.68540(8)	0.0274(4)
C(9)	0.31171(14)	0.71957(8)	0.53719(7)	0.0192(3)
C(10)	0.07816(14)	0.68093(8)	0.55825(8)	0.0245(3)
C(11)	-0.0313(2)	0.64074(9)	0.54020(8)	0.0270(3)
C(12)	-0.0271(2)	0.59148(9)	0.48603(8)	0.0272(3)
C(13)	0.0864(2)	0.58455(8)	0.45096(8)	0.0246(3)
C(14)	0.31576(14)	0.62557(8)	0.42785(7)	0.0214(3)
C(15)	0.5378(2)	0.67138(9)	0.39853(8)	0.0261(3)
C(16)	0.6464(2)	0.71367(9)	0.41164(8)	0.0295(4)
C(17)	0.6497(2)	0.75871(9)	0.46892(8)	0.0281(4)
C(18)	0.54412(14)	0.76170(8)	0.51013(8)	0.0237(3)
C(19)	0.19888(14)	0.67616(8)	0.52217(7)	0.0197(3)
C(20)	0.20229(14)	0.62737(8)	0.46672(7)	0.0204(3)
C(21)	0.42505(14)	0.67138(8)	0.44076(7)	0.0205(3)
C(22)	0.42608(14)	0.71926(8)	0.49757(7)	0.0200(3)
C(23)	0.27407(14)	0.89259(8)	0.55687(7)	0.0208(3)
C(24)	0.1991(2)	0.85961(9)	0.49836(8)	0.0274(4)
C(25)	0.1756(2)	0.94059(9)	0.59530(8)	0.0265(3)
C(26)	0.3923(2)	0.93925(9)	0.53425(8)	0.0288(4)
B(30)	0.7111(2)	0.53585(9)	0.77485(8)	0.0187(3)
C(31)	0.87453(14)	0.54214(8)	0.77123(7)	0.0211(3)
C(32)	0.9456(2)	0.50279(9)	0.72362(8)	0.0263(3)
C(33)	1.0834(2)	0.50738(10)	0.71770(9)	0.0326(4)
C(34)	1.1575(2)	0.55026(10)	0.76123(9)	0.0341(4)
C(35)	1.0922(2)	0.58637(10)	0.81126(9)	0.0334(4)
C(36)	0.9538(2)	0.58210(9)	0.81602(8)	0.0266(3)
C(37)	0.64374(13)	0.60734(8)	0.81240(7)	0.0180(3)
C(38)	0.52208(14)	0.60113(8)	0.84507(7)	0.0218(3)
C(39)	0.4578(2)	0.66143(9)	0.87301(8)	0.0275(4)
C(40)	0.5142(2)	0.73140(9)	0.87012(8)	0.0294(4)
C(41)	0.6332(2)	0.74016(9)	0.83719(8)	0.0275(4)
C(42)	0.69515(14)	0.67951(8)	0.80860(7)	0.0225(3)
C(43)	0.63806(13)	0.53643(8)	0.70179(7)	0.0186(3)
C(44)	0.50530(14)	0.51217(8)	0.69397(7)	0.0219(3)
C(45)	0.43501(14)	0.51797(9)	0.63485(8)	0.0248(3)
C(46)	0.4951(2)	0.54826(8)	0.58005(8)	0.0246(3)
C(47)	0.6253(2)	0.57319(8)	0.58571(8)	0.0244(3)
C(48)	0.69437(14)	0.56746(8)	0.64550(7)	0.0218(3)
C(49)	0.68318(13)	0.45881(8)	0.81528(7)	0.0193(3)

C(50)	0.64979(14)	0.39074(8)	0.78657(8)	0.0229(3)
C(51)	0.63619(14)	0.32591(9)	0.82312(9)	0.0277(4)
C(52)	0.6560(2)	0.32681(9)	0.89049(9)	0.0288(4)
C(53)	0.6904(2)	0.39317(9)	0.92070(8)	0.0287(4)
C(54)	0.70406(14)	0.45693(8)	0.88362(7)	0.0237(3)

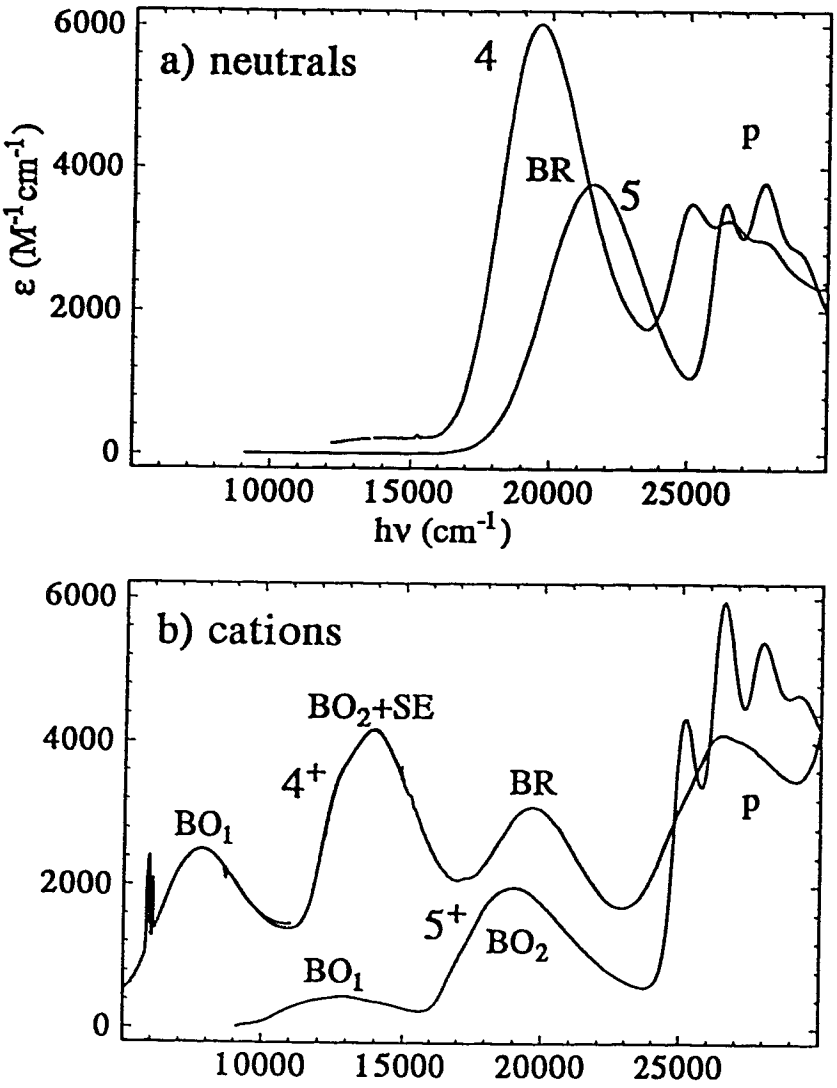


Figure 2. Optical spectra in CH_2Cl_2. a) Neutral **2** and **3**. b) $2^+NO_3^-$ and 3^+TsO^-.

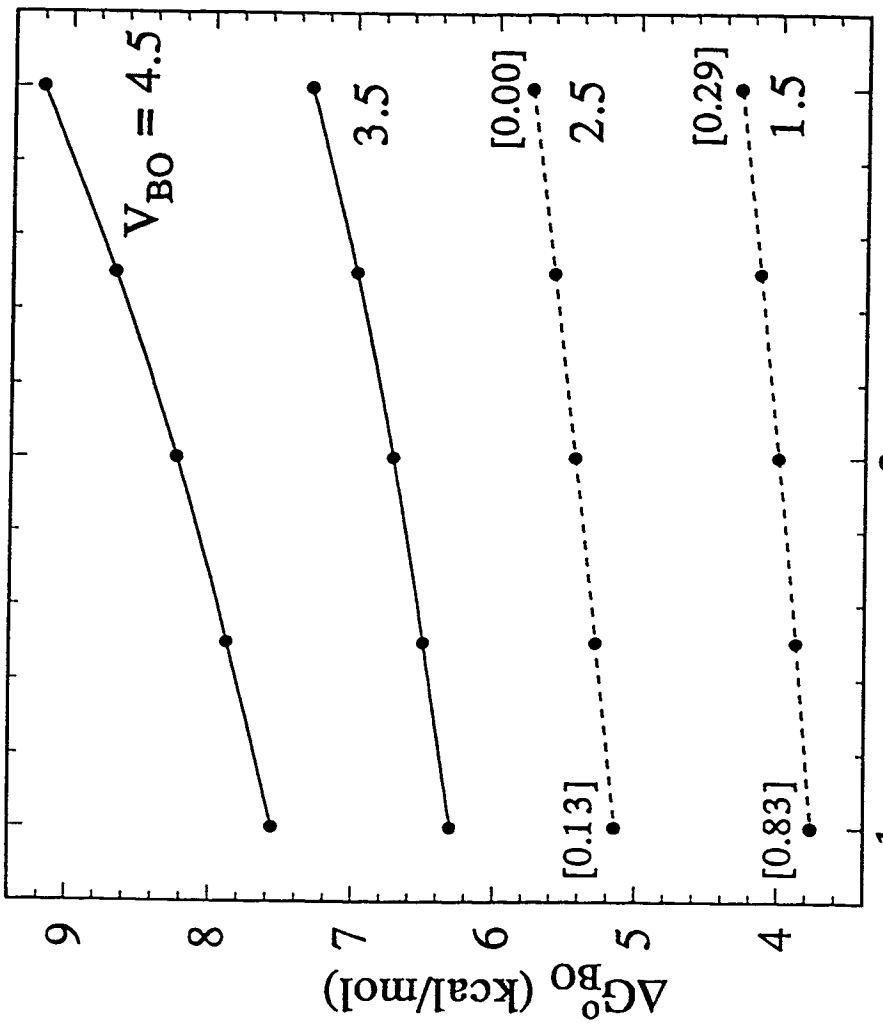


Figure 3. Three state model fits[11] for 2^{+} using $\lambda_{BO} + \Delta G^{o}_{BO} = 25.7$ kcal/mol which give $\Delta G^{\ddagger} = 4.2$ kcal/mol. The broken lines are for fits having $2^{+}(BO)$ as an intermediate which is more stable than the transition state by the number shown in brackets (kcal/mol).