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An alternative method to access diverse *N,N'*-diquaternised-3,3'-biquinoxalinium "Biquinoxen" dications

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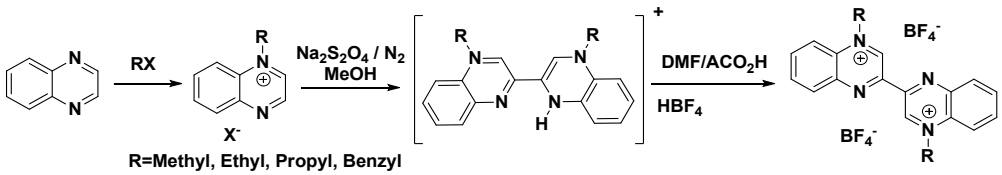
Supporting Information

A. Synthesis

A_1- Synthesis of *N,N'*-diquaternised biquinoxens



A_{11}- General Procedure

As detailed in the table hereafter, in a Schlenk round bottom flask were mixed the corresponding *N*-alkylquinoxalinium salt (RQ^+, X^-; R= Methyl (M), Et (E), Prop (P), Benzyl (Bz)), an excess of $Na_2S_2O_4$ and MeOH. The Schlenk was then purged with nitrogen, closed and inserted in an ultrasound bath for 15 min, thus giving a mixture which was left standing 7 days. The obtained purple crystalline powder was filtered, washed first with MeOH and then with distillate water and dried, leading to the direduced monoprotonated intermediate (**I**). The solid **I** was then dissolved in DMF under aerial conditions and left under agitation until the colour turned from dark blue/purple to "blood" red. Glacial acetic acid was added to the solution whilst stirring thus giving a mixture which, after 30 min stirring, was filtered and washed with glacial acetic acid until the filtrate turned dark yellow. To the dark yellow solution was added HBF_4 thus giving a precipitate of the title compound. The precipitation could be completed by adding THF. The solid was then filtered, washed with THF and dried under vacuum leading to the expected salts as a yellowish/off-white crystalline powder.

RQ^+,X^-	$Na_2S_2O_4$ (100%)	MeOH	Intermediate (I)	DMF	ACO_2H	HBF_4 50%	$RBqn(BF_4)_2$	Yield
MQ^+,I^- (2.18 g, 8 mmol)	2.18 g, 16.5 mmol	160 mL	0.769 g	14 mL	14 mL	35 mL	$MBqn(BF_4)_2$ 0.193 g	10 %
MQ^+,PF_6^-(1.15 g, 4 mmol)	1.45 g, 8.3 mmol	80 mL	0.333 g	6 mL	6 mL	15 mL	$MBqn(BF_4)_2$ 0.275 g	30 %
EQ^+,PF_6^-(1.23 g, 4 mmol)	1.45 g, 8.3 mmol	80 mL	0.683 g	12 mL	12 mL	30 mL	$EBqn(BF_4)_2$ 0.310 g	31 %
PQ^+,I^- (0.2 g, 0.7 mmol)	0.24 g, 1.4 mmol	17 mL	0.089 g	1.5 mL	1.5 mL	4 mL	$PBqn(BF_4)_2$ 0.016 g	9 %
PQ^+,PF_6^- (0.9 g, 2.8 mmol)	0.97 g, 5.6 mmol	70 mL	0.229 g	4 mL	4 mL	10 mL	$PBqn(BF_4)_2$ Fine powder very difficult to isolate	n.a
BzQ^+,Br^-(4.87 g, 16.2 mmol)	5.9 g, 33.9 mmol	320 mL	2.584 g	45 mL	45 mL	115 mL	$BzBqn(BF_4)_2$ 1.232 g	24 %
BzQ^+,PF_6^-(2.5 g, 6.8 mmol)	2.5 g, 14.3 mmol	140 mL	1.031 g	18 mL	18 mL	46 mL	$BzBqn(BF_4)_2$ 0.689 g	32 %

***N*-methylquinoxalinium iodide (MQ)[I].** Quinoxaline (5 mL, 4.32 10^{-2} mol) and methyliodide (4 mL, 6.42 10^{-2} mol) are mixed with 10 mL of DCM and the solution is left standing 3 weeks after sealing. The orange-red crystals formed are filtered, washed with Et_2O and dried under vacuum to afford 9.263 g (79%) of the tittle compound.

^1H NMR (500 MHz, DMSO-d^6): δ= 9.73 (d, J= 2.8 Hz, 1H), 9.67 (d, J= 2.8 Hz, 1H), 8.64 (d, J=8.5 Hz, 1H), 8.54 (dd, J=8.4, 1.3 Hz, 1H), 8.37 (ddd, J =8.7, 7.1, 1.5 Hz, 1H), 8.31 (ddd, J = 8.3, 7.1, 1.2 Hz, 1H), 4.73 (s, 3H).

***N*-ethylquinoxalinium iodide (EQ)[I].** In a round-bottomed flask is mixed quinoxaline (2 mL, 1.73 10^{-2} mol) with ethyliodide (2mL, 2.5 10^{-2} mol). After sealing, the solution is heated 48h at 60°C under stirring. After cooling down, Et_2O is added and the orange precipitate is then filtered, washed with Et_2O and dried, affording 2.525 g (51%) of the tittle compound.

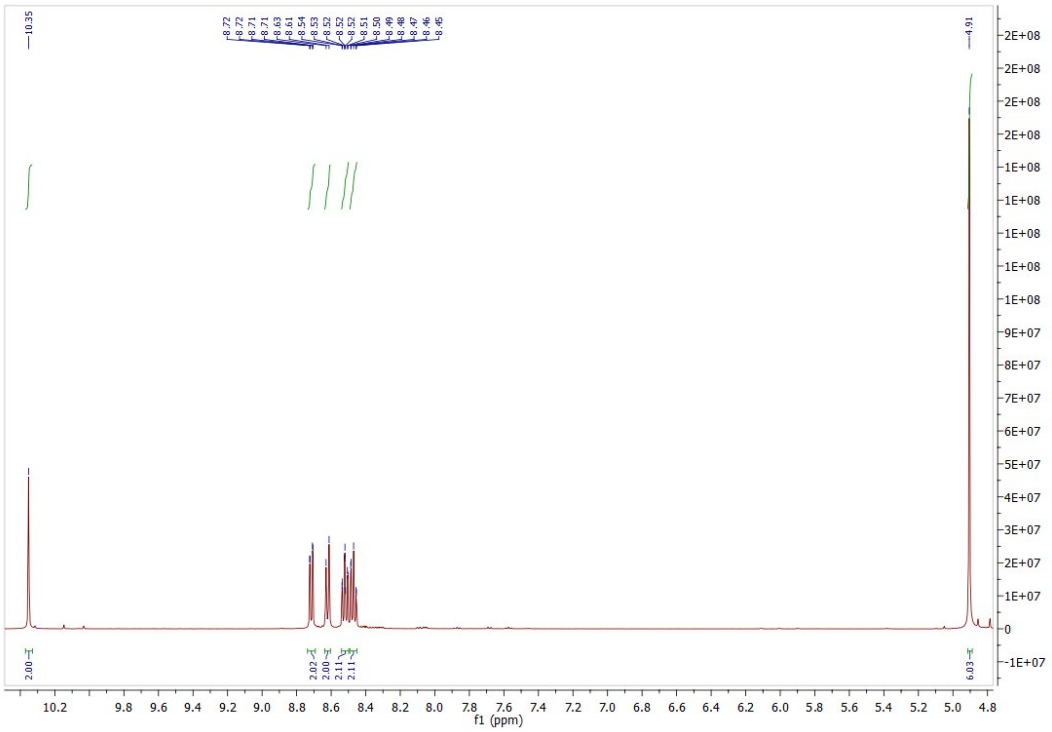
^{1}H NMR (500 MHz, DMSO-d^6): δ= 9.72 (d, J= 2.9 Hz, 1H), 9.69 (d, J= 2.9 Hz, 1H), 8.74 (d, J=9 Hz, 1H), 8.55 (dd, J=8.4, 1.4 Hz, 1H), 8.35 (ddd, J =8.7, 7.0, 1.5 Hz, 1H), 8.29 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 5.17 (q, J=7.2 Hz, 2H), 1.67 (t, J=7.3 Hz, 3H).

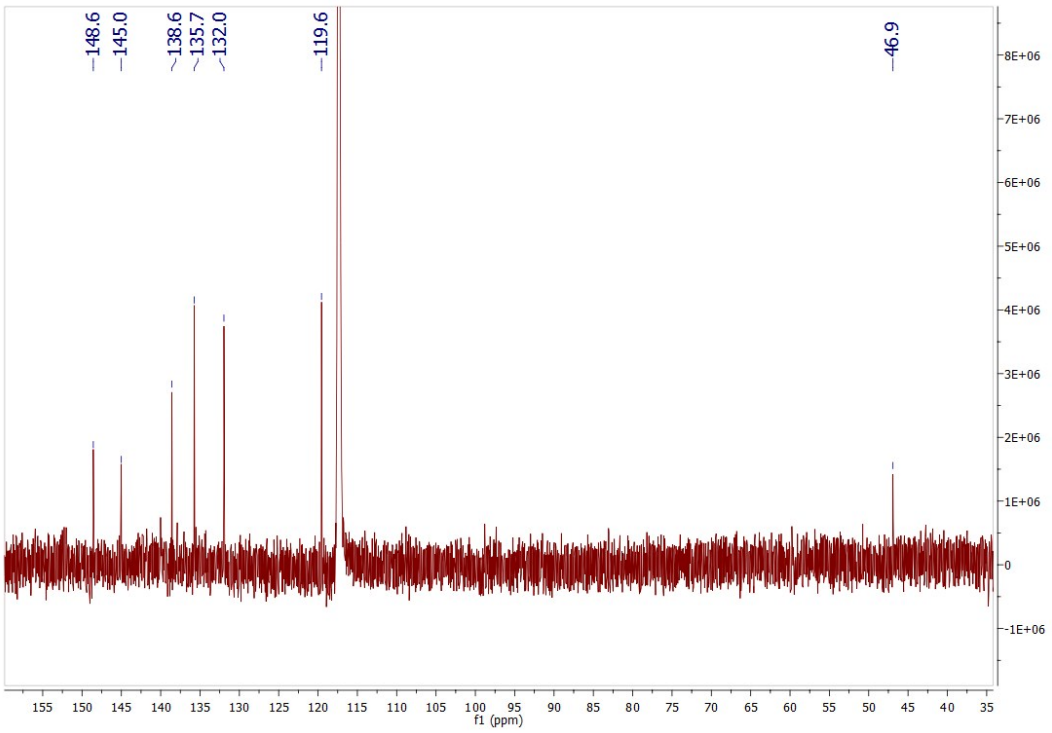
***N*-propylquinoxalinium iodide (PQ)[I].** In a round-bottomed flask is mixed quinoxaline (2 mL, 1.73 10^{-2} mol) with 1-iodopropane (6mL, 6.15 10^{-2} mol). After sealing, the system is purged with nitrogen and the solution is heated 48h at 70°C under stirring. After cooling down, Et_2O is added and the orange precipitate is then filtered, washed with Et_2O and dried, affording 1.56 g (30%) of the tittle compound.
^{1}H NMR (500 MHz, DMSO-d^6): δ= 9.73 (d, J= 2.6 Hz, 1H), 9.66 (d, J= 2.6 Hz, 1H), 8.77 (d, J=8.7 Hz, 1H), 8.55 (d J=7.8, 1H), 8.35 (ddd, J =7.3 Hz, 1H), 8.30 (ddd, J = 7.4, 1H), 5.10 (t, J=7.5 Hz, 2H), 2.07 (m, 7.4 Hz, 2H), 1.05 (t, J=7.3 Hz, 3H).

***N*-benzylquinoxalinium hexafluorophosphate (BzQ)[PF_6]**: A solution of quinoxaline (2.35 ml, 20 mmol) and benzylbromide (5 ml, 20mmol) is left standing 3 days, after what the dark yellow crystals are filtered, washed with Et_2O and dried affording *N*-benzylquinoxalinium bromide (BzQ)[Br] in a pure phase (3.34 g, 55%). (BzQ)[Br] (1 g, 3.3 mmol) is then dissolved in 30 ml of warm distillate water and subsequently poured into a stirring saturated aqueous solution of KPF_6 (1.22 g in 100 ml). The white crystalline precipitate is then filtered, washed with water and dried, leading to (BzQ)[PF_6] in a pure phase (0.98 g, 80 %). ^{1}H NMR (500 MHz, DMSO-d^6): δ = 9.79 (d, *J* = 2.8 Hz, 1H), 9.69 (d, *J* = 2.8 Hz, 1H), 8.63 (d, *J* = 8.3 Hz, 1H), 8.58 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.39 – 8.19 (m, 2H), 7.55 (d, *J* = 6.5 Hz, 2H), 7.49 – 7.40 (m, 3H), 6.44 (s, 2H).

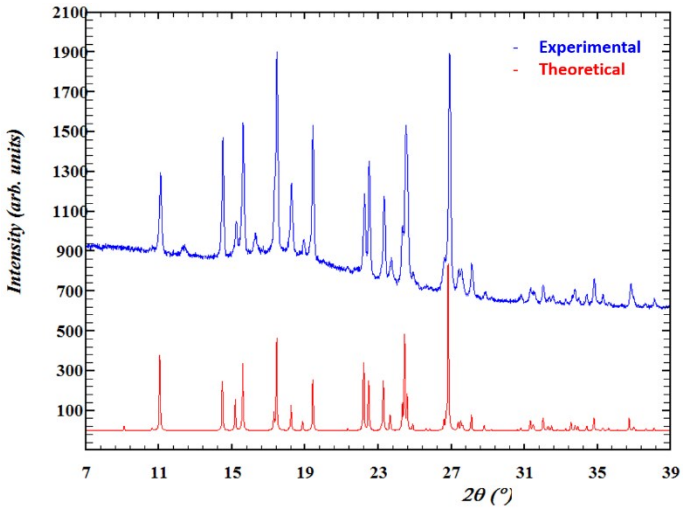
The ion exchange procedure aforementioned has been similarly applied to the other compounds.

A_{12}- $MBqn(BF_4)_2$



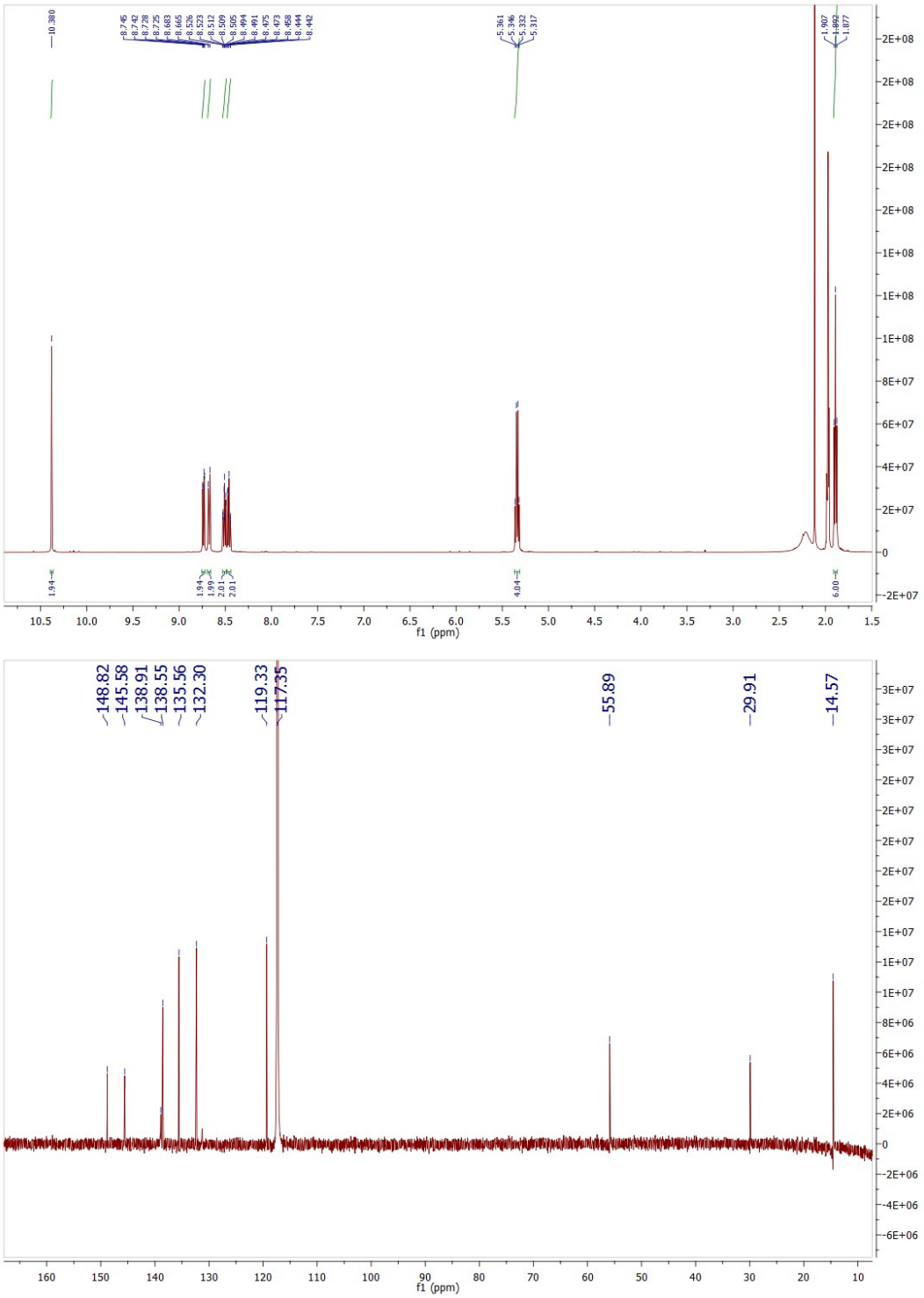


^{1}H NMR (500 MHz, CD_3CN): δ = 10.35 (s, 2H), 8.72 (dd, *J* = 8.3, 1.3 Hz, 2H), 8.62 (d, *J* = 8.6 Hz, 2H), 8.52 (ddd, *J* = 8.7, 7.1, 1.5 Hz, 2H), 8.49 – 8.45 (m, 1H), 4.91 (s, 6H). ^{13}C NMR (125 MHz, CD_3CN): δ = 148.6, 145.0, 138.6, 135.7, 132.0, 119.6, 46.9.

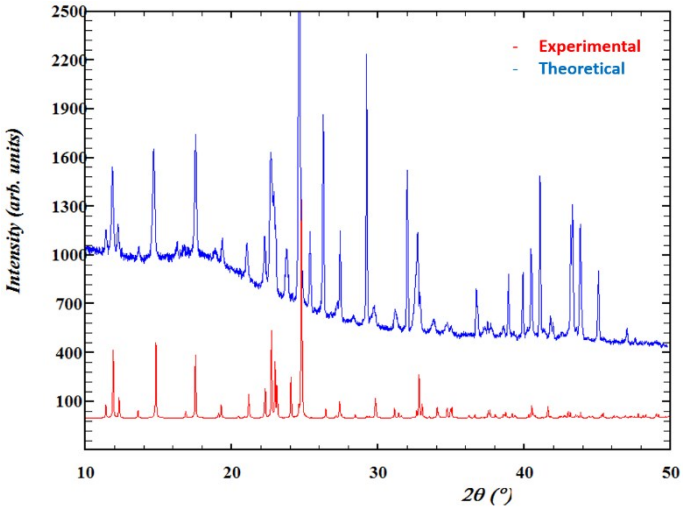


PXRD pattern of (Mbqn)$[BF_4]_2$. 2 MeCN

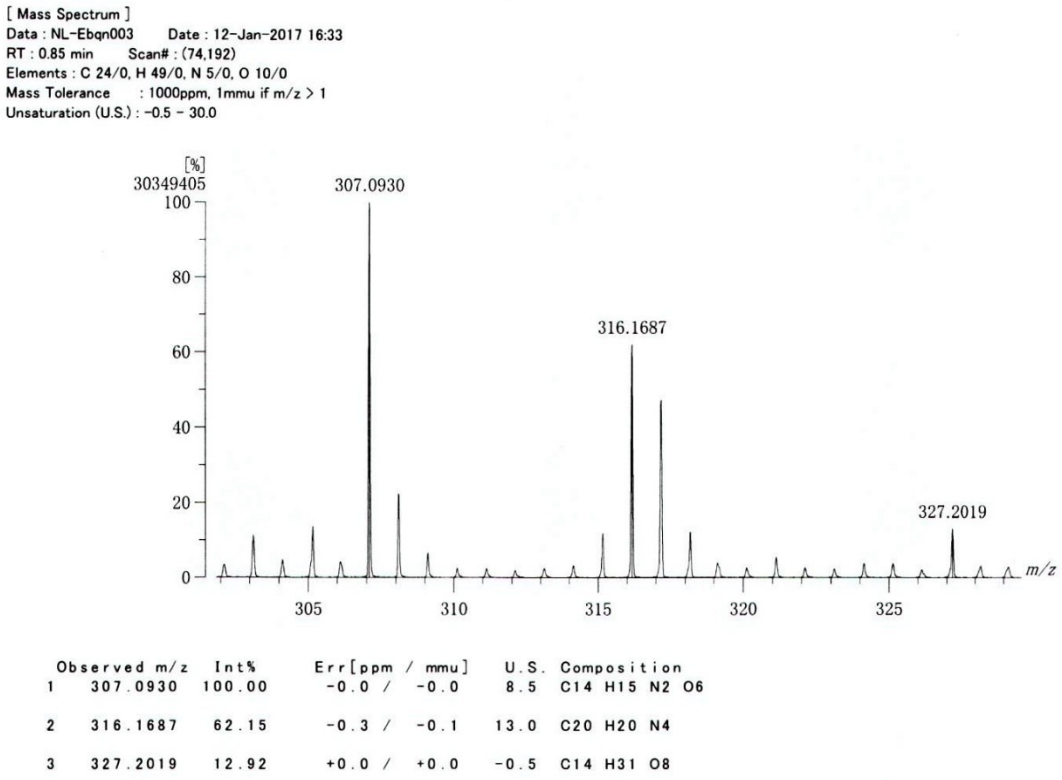
A_{13} - (Ebqn)$[BF_4]_2$



^{1}H NMR (500 MHz, CD_3CN): δ = 10.38 (s, 2H), 8.73 (dd, *J* = 8.3, 1.4 Hz, 2H), 8.67 (d, *J* = 8.6 Hz, 2H), 8.51 (ddd, *J* = 8.7, 7.1, 1.5 Hz, 2H), 8.46 (ddd, *J* = 8, 7.5, 1.5 Hz, 2H), 5.34 (q, *J* = 7.3 Hz, 4H), 1.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, CD_3CN): δ = 148.8, 145.6, 138.9, 138.5, 135.6, 132.3, 131.3, 119.3, 55.9, 14.6.



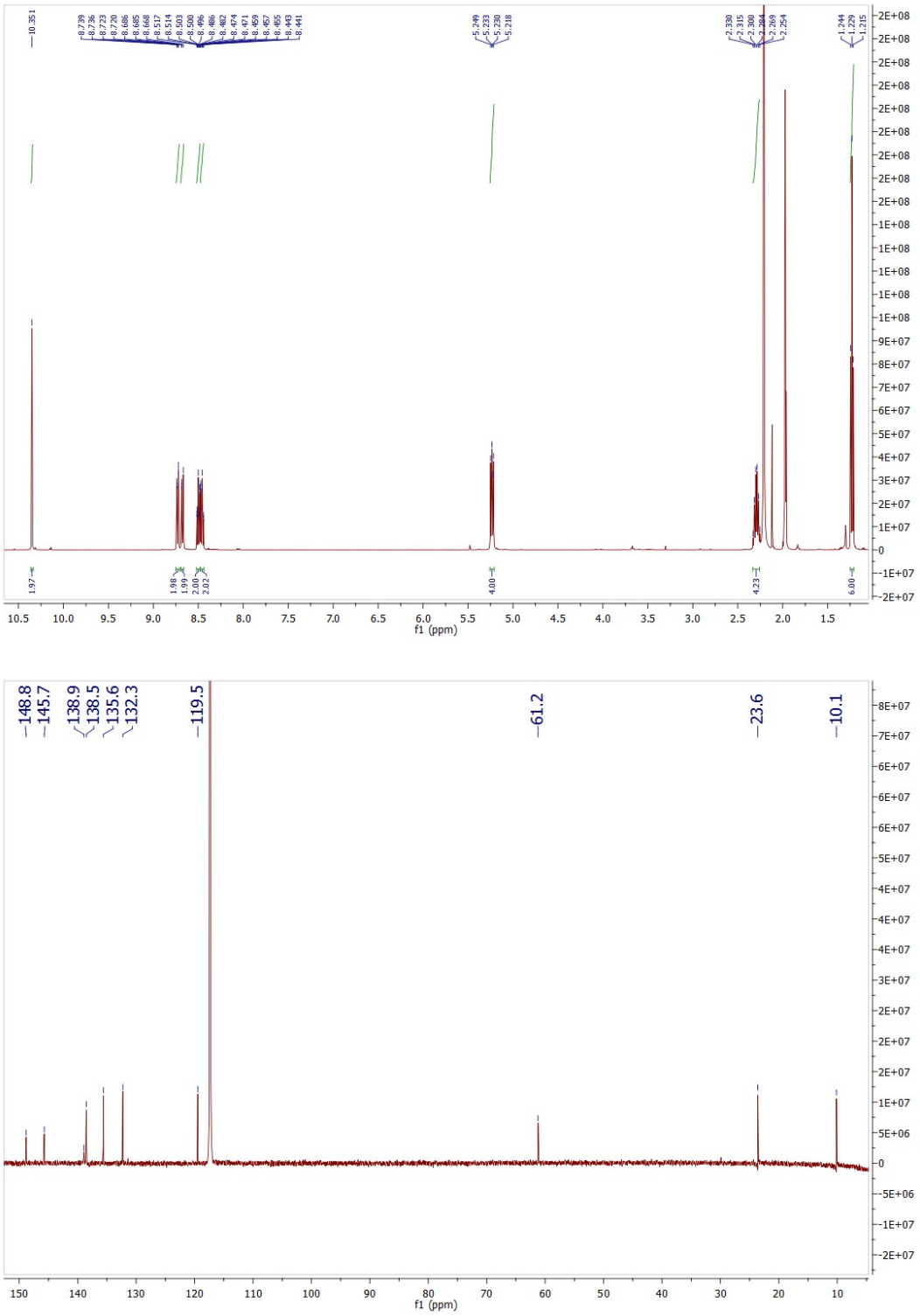
PXRD pattern of $(Ebqn)[BF_4]_2$



	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	307.0930	100.00	-0.0 / -0.0	8.5	C14 H15 N2 O6
2	316.1687	62.15	-0.3 / -0.1	13.0	C20 H20 N4
3	327.2019	12.92	+0.0 / +0.0	-0.5	C14 H31 O8

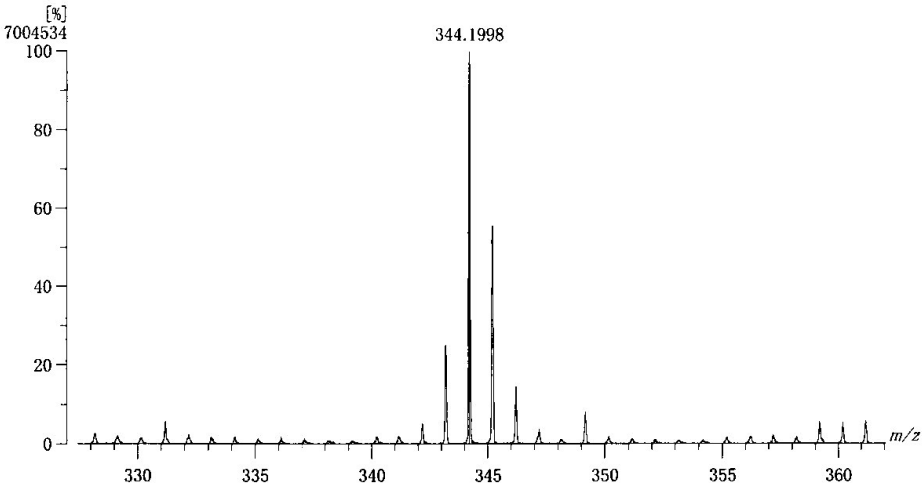
FAB mass spectrum of $(Ebqn)[BF_4]_2$. $M_{theo}(Ebqn^{2+})$=316.17 m/z

A_{13} - (Pbqn)$[BF_4]_2$



^{1}H NMR (500 MHz, CD_3CN): δ = 10.35 (s, 2H), 8.73 (dd, *J* = 8.3, 1.5 Hz, 2H), 8.68 (d, *J* = 8.5, 2H), 8.50 (ddd, *J* = 8.8, 7.0, 1.6 Hz, 2H), 8.46 (ddd, *J* = 8.1, 7.1, 1.2 Hz, 2H), 5.23 (t, *J* = 8.3 Hz, 4H), 2.29 (sex, *J* = 8, 7.5 Hz, 4H), 1.23 (t, *J* = 7.4 Hz, 6H) . ^{13}C NMR (125 MHz, CD_3CN): δ = 148.8, 145.7, 138.9, 138.5, 135.6, 132.3, 131.4, 119.5, 61.2, 23.6, 10.1.

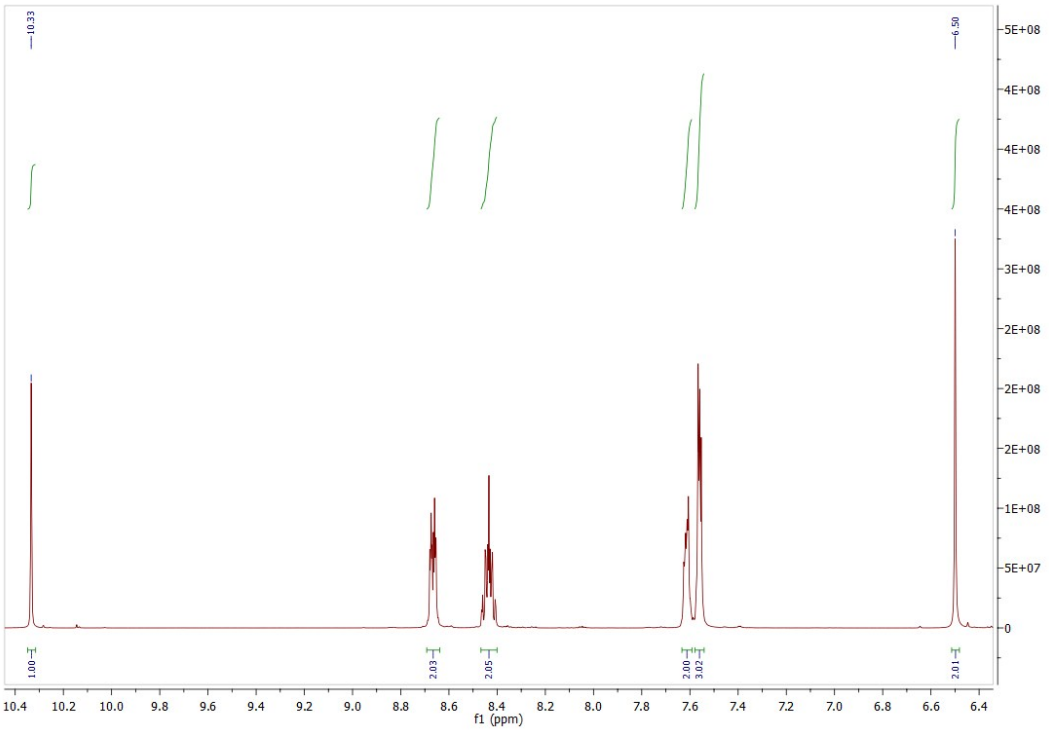
[Mass Spectrum]
Data : NL-PBqn001 Date : 12-Jan-2017 16:46
RT : 1.57 min Scan# : (65,96)
Elements : C 24/0, H 49/0, N 5/0
Mass Tolerance : 1000ppm, 1mmu if m/z > 1
Unsaturation (U.S.) : -0.5 - 30.0

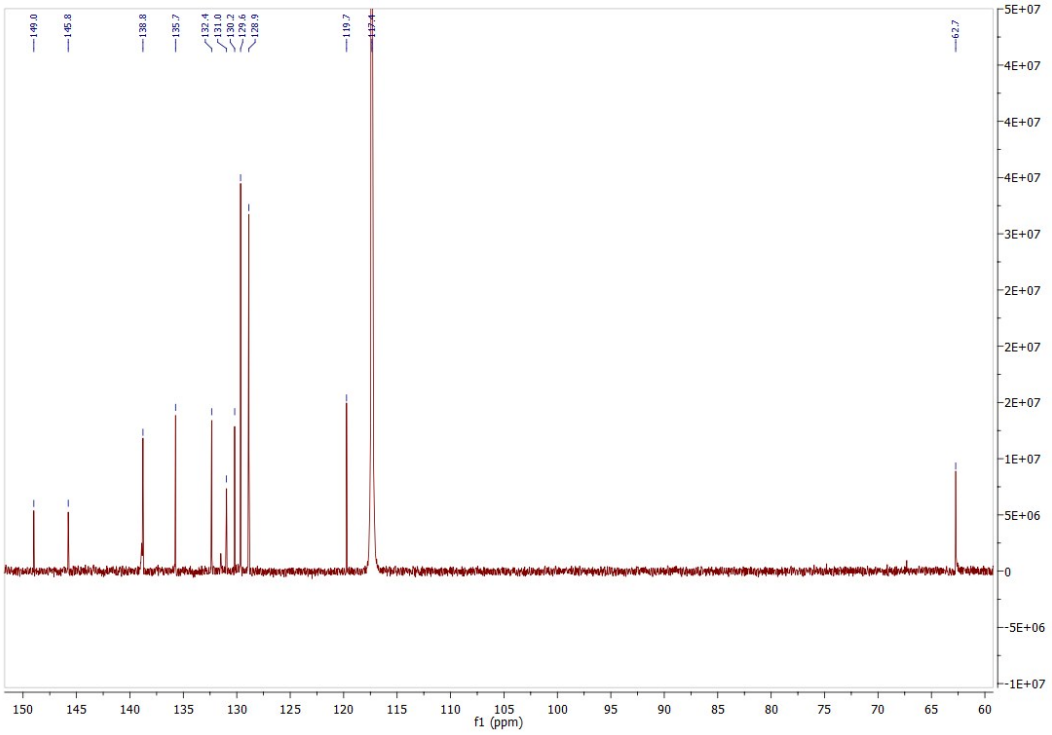


	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	344.1998	100.00	-0.9 / -0.3	13.0	C22 H24 N4

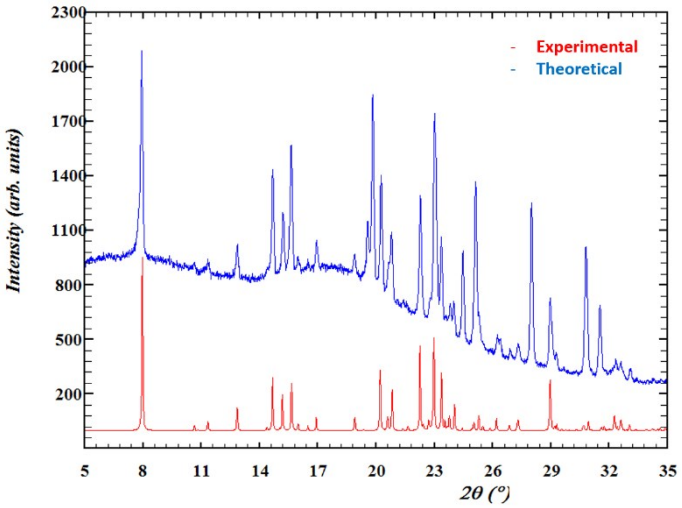
FAB mass spectrum of (Pbqn)$[BF_4]_2$. $M_{theo}(Pbqn^{2+})$=344.20 m/z

A_{14} - (Bzbqn)$[BF_4]_2$



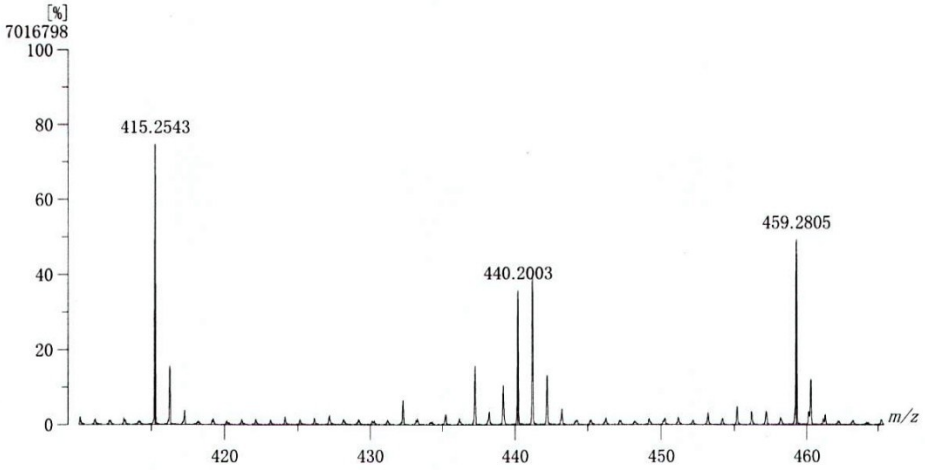


(Bzbqn)$[BF_4]_2$. 2MECN: ^{1}H NMR (500 MHz, CD_3CN): δ = 10.33 (s, 2H), 8.67 (m, 4H), 8.43 (m, 4H), 7.61 (dt, *J* = 6.1, 3.6 Hz, 4H), 7.56 (dd, *J* = 6.8, 3.5 Hz, 6H), 6.50 (s, 4H). ^{13}C NMR (125 MHz, CD_3CN): δ = 149.0, 145.8, 138.8, 138.5, 135.7, 132.3, 131.0, 130.2, 129.6, 128.9, 119.7, 62.7.



PXRD pattern of (Bzbqn)$[BF_4]_2$ .2 MeCN

[Mass Spectrum]
Data : NL-BzBqn002 Date : 12-Jan-2017 17:03
RT : 0.83 min Scan# : (35,47)
Elements : C 30/18, H 49/0, N 5/0, O 15/0
Mass Tolerance : 1000ppm, 1mmu if m/z > 1
Unsaturation (U.S.) : -0.5 - 30.0



	Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
1	415.2543	74.70	-0.1 / -0.0	-0.5	C18 H39 O10
2	440.2003	35.76	+0.5 / +0.2	21.0	C30 H24 N4
3	459.2805	49.29	-0.1 / -0.0	-0.5	C20 H43 O11

FAB mass spectrum of $(Bzbqn)[BF_4]_2$. $M_{theo}(Bzbqn^{2+})$=440.20 m/z

B. Single crystal X-ray diffraction analysis for $(Mbqn)[BF_4]_2$. MeCN, $(Ebqn)[BF_4]_2$ and $(Bzbqn)[BF_4]_2$. 2 MeCN

B_{11} - $(Mbqn)[BF_4]_2$. MeCN

Empirical formula	C20 H16 B2 F8 N5
Formula weight	500.00
Temperature	291(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 2/c
Unit cell dimensions	a = 19.372(2) A alpha = 90 deg. b = 12.2295(10) A beta = 124.421(8) deg. c = 11.3742(14) A gamma = 90 deg.
Volume	2222.8(5) A^3
Z, Calculated density	4, 1.494 Mg/m^3
Absorption coefficient	0.137 mm^-1
F(000)	1012
Crystal size	0.385 x 0.367 x 0.344 mm
Theta range for data collection	2.097 to 27.415 deg.
Limiting indices	-24<=h<=18, -15<=k<=13, -14<=l<=14
Reflections collected / unique	5009 / 2438 [R(int) = 0.0217]
Completeness to theta = 25.242	96.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2438 / 0 / 194
Goodness-of-fit on F^2	1.124
Final R indices [I>2sigma(I)]	R1 = 0.0617, wR2 = 0.1976
R indices (all data)	R1 = 0.0760, wR2 = 0.2127
Extinction coefficient	n/a
Largest diff. peak and hole	0.308 and -0.233 e.A^-3

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

	x	y	z	U(eq)
C(1)	6380(2)	3605(2)	7139(3)	70(1)
C(2)	7016(1)	3100(1)	5901(2)	53(1)
C(3)	7263(1)	2318(1)	5293(2)	51(1)
C(4)	6676(1)	951(1)	5815(2)	54(1)
C(5)	6498(1)	-168(2)	5791(2)	63(1)
C(6)	6099(1)	-518(2)	6391(2)	67(1)
C(7)	5864(1)	235(2)	7038(2)	69(1)
C(8)	6015(1)	1322(2)	7077(2)	64(1)
C(9)	6424(1)	1697(1)	6456(2)	53(1)
C(10)	5000	2969(3)	2500	78(1)
C(11)	5000	4148(3)	2500	122(2)
N(1)	6611(1)	2784(1)	6457(2)	53(1)
N(2)	7092(1)	1275(1)	5241(2)	55(1)
N(3)	5000	2058(3)	2500	115(1)
B(1)	8671(2)	1537(2)	9571(2)	70(1)
F(1)	8373(2)	598(2)	9715(3)	140(1)
F(2A)	8642(5)	1578(5)	8393(6)	143(2)
F(2B)	8358(11)	1924(16)	8379(13)	218(11)
F(3A)	8095(2)	2321(2)	9432(5)	107(1)
F(3B)	9395(7)	960(11)	9700(17)	214(6)
F(4A)	9359(2)	1837(6)	10743(5)	150(2)
F(4B)	9030(20)	2223(13)	10570(20)	198(10)

Table 3. Bond lengths [A] and angles [deg] for mbqn.

C(1)-N(1)	1.484(2)
C(2)-N(1)	1.313(2)
C(2)-C(3)	1.414(2)
C(3)-N(2)	1.311(2)
C(3)-C(3)#1	1.473(3)
C(4)-N(2)	1.353(2)
C(4)-C(5)	1.407(3)
C(4)-C(9)	1.415(3)
C(5)-C(6)	1.357(3)
C(6)-C(7)	1.406(3)
C(7)-C(8)	1.357(3)
C(8)-C(9)	1.405(3)
C(9)-N(1)	1.377(2)
C(10)-N(3)	1.115(5)
C(10)-C(11)	1.442(5)
B(1)-F(2B)	1.225(10)
B(1)-F(4B)	1.262(10)
B(1)-F(4A)	1.296(4)
B(1)-F(2A)	1.309(4)
B(1)-F(1)	1.336(3)
B(1)-F(3A)	1.411(4)
B(1)-F(3B)	1.502(10)
F(2A)-F(2B)	0.69(3)
F(2A)-F(3B)	1.568(15)
F(2B)-F(3A)	1.62(3)
F(3A)-F(4B)	1.53(3)
F(3B)-F(4A)	1.630(13)
F(4A)-F(4B)	0.72(3)
N(1)-C(2)-C(3)	119.75(16)
N(2)-C(3)-C(2)	122.21(16)
N(2)-C(3)-C(3)#1	118.68(18)
C(2)-C(3)-C(3)#1	119.11(19)
N(2)-C(4)-C(5)	118.78(16)
N(2)-C(4)-C(9)	122.15(16)

C(5)-C(4)-C(9)	119.06(17)
C(6)-C(5)-C(4)	119.94(18)
C(5)-C(6)-C(7)	120.16(19)
C(8)-C(7)-C(6)	122.01(19)
C(7)-C(8)-C(9)	118.49(19)
N(1)-C(9)-C(8)	122.51(16)
N(1)-C(9)-C(4)	117.16(15)
C(8)-C(9)-C(4)	120.32(17)
N(3)-C(10)-C(11)	180.0
C(2)-N(1)-C(9)	120.78(14)
C(2)-N(1)-C(1)	119.41(15)
C(9)-N(1)-C(1)	119.78(15)
C(3)-N(2)-C(4)	117.94(15)
F(2B)-B(1)-F(4B)	114.7(13)
F(2B)-B(1)-F(4A)	127.3(6)
F(4B)-B(1)-F(4A)	32.9(13)
F(2B)-B(1)-F(2A)	31.2(13)
F(4B)-B(1)-F(2A)	125.5(5)
F(4A)-B(1)-F(2A)	117.7(5)
F(2B)-B(1)-F(1)	119.4(6)
F(4B)-B(1)-F(1)	121.2(5)
F(4A)-B(1)-F(1)	112.5(3)
F(2A)-B(1)-F(1)	112.7(3)
F(2B)-B(1)-F(3A)	75.4(15)
F(4B)-B(1)-F(3A)	69.4(15)
F(4A)-B(1)-F(3A)	102.2(4)
F(2A)-B(1)-F(3A)	106.6(4)
F(1)-B(1)-F(3A)	103.2(3)
F(2B)-B(1)-F(3B)	98.0(15)
F(4B)-B(1)-F(3B)	102.4(15)
F(4A)-B(1)-F(3B)	70.8(6)
F(2A)-B(1)-F(3B)	67.4(6)
F(1)-B(1)-F(3B)	91.7(6)
F(3A)-B(1)-F(3B)	165.1(6)
F(2B)-F(2A)-B(1)	67.6(12)
F(2B)-F(2A)-F(3B)	128.6(14)
B(1)-F(2A)-F(3B)	62.2(5)
F(2A)-F(2B)-B(1)	81.2(9)
F(2A)-F(2B)-F(3A)	138.6(12)
B(1)-F(2B)-F(3A)	57.5(11)
B(1)-F(3A)-F(4B)	50.7(5)
B(1)-F(3A)-F(2B)	47.1(5)
F(4B)-F(3A)-F(2B)	83.4(6)
B(1)-F(3B)-F(2A)	50.4(4)
B(1)-F(3B)-F(4A)	48.7(4)
F(2A)-F(3B)-F(4A)	88.4(6)
F(4B)-F(4A)-B(1)	71.0(13)
F(4B)-F(4A)-F(3B)	128.9(15)
B(1)-F(4A)-F(3B)	60.5(5)
F(4A)-F(4B)-B(1)	76.1(8)
F(4A)-F(4B)-F(3A)	135.9(13)
B(1)-F(4B)-F(3A)	59.9(11)

Symmetry transformations used to generate equivalent atoms:
#1 -x+3/2,-y+1/2,-z+1

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for mbqn.
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
C(1)	84(1)	56(1)	96(1)	-7(1)	67(1)	2(1)
C(2)	56(1)	48(1)	60(1)	2(1)	36(1)	1(1)
C(3)	56(1)	48(1)	52(1)	2(1)	32(1)	2(1)
C(4)	57(1)	50(1)	55(1)	2(1)	33(1)	0(1)
C(5)	74(1)	50(1)	70(1)	1(1)	44(1)	-2(1)
C(6)	73(1)	55(1)	77(1)	4(1)	45(1)	-7(1)
C(7)	70(1)	70(1)	79(1)	7(1)	49(1)	-6(1)
C(8)	66(1)	65(1)	73(1)	1(1)	46(1)	-1(1)
C(9)	53(1)	51(1)	56(1)	4(1)	32(1)	0(1)
C(10)	76(2)	68(2)	92(2)	0	48(2)	0
C(11)	161(5)	60(2)	146(4)	0	88(4)	0
N(1)	57(1)	49(1)	60(1)	1(1)	37(1)	4(1)
N(2)	64(1)	50(1)	60(1)	0(1)	39(1)	0(1)
N(3)	125(3)	69(2)	183(4)	0	107(3)	0
B(1)	81(2)	59(1)	65(1)	1(1)	38(1)	-3(1)
F(1)	211(3)	67(1)	185(2)	-6(1)	137(2)	-26(1)
F(2A)	213(6)	154(4)	116(3)	-17(3)	126(4)	-21(3)
F(2B)	141(9)	209(12)	97(7)	96(8)	-57(7)	-92(8)
F(3A)	105(2)	74(2)	127(3)	6(2)	56(2)	29(1)
F(3B)	147(7)	238(12)	270(13)	-31(11)	125(9)	24(8)
F(4A)	68(2)	212(5)	105(2)	-17(3)	9(2)	-14(2)
F(4B)	400(30)	130(8)	182(12)	-106(8)	240(17)	-150(12)

Table 5. Torsion angles [deg] for mbqn.

N(1)-C(2)-C(3)-N(2)	1.0(3)
N(1)-C(2)-C(3)-C(3)#1	-178.42(18)
N(2)-C(4)-C(5)-C(6)	178.40(17)
C(9)-C(4)-C(5)-C(6)	-0.7(3)
C(4)-C(5)-C(6)-C(7)	-0.1(3)
C(5)-C(6)-C(7)-C(8)	0.7(3)
C(6)-C(7)-C(8)-C(9)	-0.4(3)
C(7)-C(8)-C(9)-N(1)	-179.36(18)
C(7)-C(8)-C(9)-C(4)	-0.4(3)
N(2)-C(4)-C(9)-N(1)	0.9(3)
C(5)-C(4)-C(9)-N(1)	179.99(16)
N(2)-C(4)-C(9)-C(8)	-178.16(16)
C(5)-C(4)-C(9)-C(8)	0.9(3)
C(3)-C(2)-N(1)-C(9)	0.1(3)
C(3)-C(2)-N(1)-C(1)	177.87(17)
C(8)-C(9)-N(1)-C(2)	178.05(17)
C(4)-C(9)-N(1)-C(2)	-1.0(2)
C(8)-C(9)-N(1)-C(1)	0.3(3)
C(4)-C(9)-N(1)-C(1)	-178.74(17)
C(2)-C(3)-N(2)-C(4)	-1.1(3)
C(3)#1-C(3)-N(2)-C(4)	178.34(18)
C(5)-C(4)-N(2)-C(3)	-178.97(17)
C(9)-C(4)-N(2)-C(3)	0.1(3)
F(4B)-B(1)-F(2A)-F(2B)	-79(2)
F(4A)-B(1)-F(2A)-F(2B)	-116.9(13)
F(1)-B(1)-F(2A)-F(2B)	109.6(12)
F(3A)-B(1)-F(2A)-F(2B)	-3.0(13)
F(3B)-B(1)-F(2A)-F(2B)	-168.5(14)
F(2B)-B(1)-F(2A)-F(3B)	168.5(14)
F(4B)-B(1)-F(2A)-F(3B)	89(2)
F(4A)-B(1)-F(2A)-F(3B)	51.6(7)
F(1)-B(1)-F(2A)-F(3B)	-81.9(6)
F(3A)-B(1)-F(2A)-F(3B)	165.5(6)
F(3B)-F(2A)-F(2B)-B(1)	-13.0(16)
B(1)-F(2A)-F(2B)-F(3A)	3.8(16)
F(3B)-F(2A)-F(2B)-F(3A)	-9(3)

F(4B)-B(1)-F(2B)-F(2A)	118.4(19)
F(4A)-B(1)-F(2B)-F(2A)	82.7(19)
F(1)-B(1)-F(2B)-F(2A)	-85.8(13)
F(3A)-B(1)-F(2B)-F(2A)	177.1(13)
F(3B)-B(1)-F(2B)-F(2A)	10.7(13)
F(4B)-B(1)-F(2B)-F(3A)	-58.6(15)
F(4A)-B(1)-F(2B)-F(3A)	-94.4(13)
F(2A)-B(1)-F(2B)-F(3A)	-177.1(13)
F(1)-B(1)-F(2B)-F(3A)	97.2(9)
F(3B)-B(1)-F(2B)-F(3A)	-166.4(6)
F(2B)-B(1)-F(3A)-F(4B)	-124.0(7)
F(4A)-B(1)-F(3A)-F(4B)	1.7(6)
F(2A)-B(1)-F(3A)-F(4B)	-122.4(6)
F(1)-B(1)-F(3A)-F(4B)	118.6(5)
F(3B)-B(1)-F(3A)-F(4B)	-59(2)
F(4B)-B(1)-F(3A)-F(2B)	124.0(7)
F(4A)-B(1)-F(3A)-F(2B)	125.7(6)
F(2A)-B(1)-F(3A)-F(2B)	1.6(7)
F(1)-B(1)-F(3A)-F(2B)	-117.4(5)
F(3B)-B(1)-F(3A)-F(2B)	65(2)
F(2A)-F(2B)-F(3A)-B(1)	-4.4(19)
F(2A)-F(2B)-F(3A)-F(4B)	36(2)
B(1)-F(2B)-F(3A)-F(4B)	40.2(6)
F(2B)-B(1)-F(3B)-F(2A)	-6.0(8)
F(4B)-B(1)-F(3B)-F(2A)	-123.6(7)
F(4A)-B(1)-F(3B)-F(2A)	-132.8(6)
F(1)-B(1)-F(3B)-F(2A)	114.0(4)
F(3A)-B(1)-F(3B)-F(2A)	-69(2)
F(2B)-B(1)-F(3B)-F(4A)	126.8(7)
F(4B)-B(1)-F(3B)-F(4A)	9.2(8)
F(2A)-B(1)-F(3B)-F(4A)	132.8(6)
F(1)-B(1)-F(3B)-F(4A)	-113.3(4)
F(3A)-B(1)-F(3B)-F(4A)	64(3)
F(2B)-F(2A)-F(3B)-B(1)	13.6(17)
F(2B)-F(2A)-F(3B)-F(4A)	-19.8(19)
B(1)-F(2A)-F(3B)-F(4A)	-33.5(4)
F(2B)-B(1)-F(4A)-F(4B)	78(2)
F(2A)-B(1)-F(4A)-F(4B)	113.3(11)
F(1)-B(1)-F(4A)-F(4B)	-113.0(10)
F(3A)-B(1)-F(4A)-F(4B)	-3.0(11)
F(3B)-B(1)-F(4A)-F(4B)	163.3(13)
F(2B)-B(1)-F(4A)-F(3B)	-85.5(19)
F(4B)-B(1)-F(4A)-F(3B)	-163.3(13)
F(2A)-B(1)-F(4A)-F(3B)	-50.0(7)
F(1)-B(1)-F(4A)-F(3B)	83.6(7)
F(3A)-B(1)-F(4A)-F(3B)	-166.3(7)
B(1)-F(3B)-F(4A)-F(4B)	-20.4(16)
F(2A)-F(3B)-F(4A)-F(4B)	14.1(18)
F(2A)-F(3B)-F(4A)-B(1)	34.5(4)
F(3B)-F(4A)-F(4B)-B(1)	18.7(14)
B(1)-F(4A)-F(4B)-F(3A)	3.9(14)
F(3B)-F(4A)-F(4B)-F(3A)	23(3)
F(2B)-B(1)-F(4B)-F(4A)	-121.1(18)
F(2A)-B(1)-F(4B)-F(4A)	-87.1(16)
F(1)-B(1)-F(4B)-F(4A)	83.5(13)
F(3A)-B(1)-F(4B)-F(4A)	176.9(11)
F(3B)-B(1)-F(4B)-F(4A)	-16.1(12)
F(2B)-B(1)-F(4B)-F(3A)	62.0(15)
F(4A)-B(1)-F(4B)-F(3A)	-176.9(11)
F(2A)-B(1)-F(4B)-F(3A)	96.1(12)
F(1)-B(1)-F(4B)-F(3A)	-93.3(10)
F(3B)-B(1)-F(4B)-F(3A)	167.0(7)
B(1)-F(3A)-F(4B)-F(4A)	-4.4(16)
F(2B)-F(3A)-F(4B)-F(4A)	-42.0(19)
F(2B)-F(3A)-F(4B)-B(1)	-37.7(5)

Symmetry transformations used to generate equivalent atoms:
#1 -x+3/2,-y+1/2,-z+1

Datablock: I

```
Bond precision:      C-C = 0.0033 A              Wavelength=0.71073
Cell:        a=19.372(2)    b=12.2295(10)   c=11.3742(14)
             alpha=90       beta=124.421(8) gamma=90
Temperature: 291 K
                   Calculated                      Reported
Volume             2222.8(5)                       2222.8(5)
Space group        C 2/c                           C 2/c
Hall group         -C 2yc                          -C 2yc
Moiety formula     C18 H16 N4, 2(B F4), C2 N       C18 H16 N4, 2(B F4), C2 N
Sum formula        C20 H16 B2 F8 N5                C20 H16 B2 F8 N5
Mr                 500.00                          500.00
Dx,g cm-3          1.494                           1.494
Z                  4                               4
Mu (mm-1)          0.137                           0.137
F000               1012.0                          1012.0
F000'              1012.73
h,k,lmax           25,15,14                        24,15,14
Nref               2530                            2438
Tmin,Tmax          0.949,0.954
Tmin'              0.949
Correction method= Not given
Data completeness= 0.964       Theta(max)= 27.415
R(reflections)= 0.0617( 1793)      wR2(reflections)= 0.2111( 2438)
S = 1.132             Npar= 194
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low ..... 0.967 Note
PLAT234_ALERT_4_C Large Hirshfeld Difference F3B -- B1 .. 0.17 Ang.
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of B1 Check
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C10 Check
PLAT761_ALERT_1_C CIF Contains no X-H Bonds ..... Please Check
PLAT762_ALERT_1_C CIF Contains no X-Y-H or H-Y-H Angles ..... Please Check

Alert level G

PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large. 0.13 Report
PLAT128_ALERT_4_G Alternate Setting for Input Space Group C2/c I2/a Note
PLAT302_ALERT_4_G Anion/Solvent Disorder ..... Percentage = 38 Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms (1.50) in Resd. # 3 Check
PLAT344_ALERT_2_G Unusual sp? Angle Range in Solvent/Ion for . C11 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact F2B .. C2 .. 2.91 Ang.
PLAT432_ALERT_2_G Short Inter X...Y Contact F2B .. C3 .. 2.94 Ang.
PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) . 1.27 Ratio
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 22 Check
F4B -B1 -F4A 1.555 1.555 1.555 32.80 Deg.

PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... # 23
Check
F2B -B1 -F2A 1.555 1.555 1.555 31.20 Deg.

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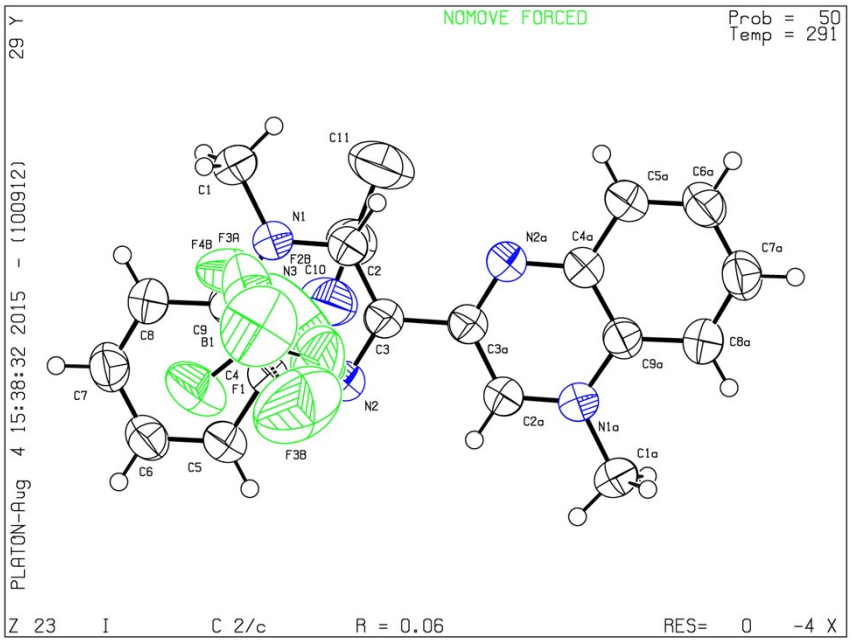
0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
6 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
10 **ALERT level G** = General information/check it is not something unexpected



B_{12} - (Ebqn)$[BF_4]_2$

Table 1. Crystal data and structure refinement.

Empirical formula	C20 H20 B2 F8 N4
Formula weight	490.02
Temperature	180(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 2/c
Unit cell dimensions	a = 9.371(4) A alpha = 90 deg. b = 14.361(7) A beta = 101.28(3) deg. c = 15.685(6) A gamma = 90 deg.
Volume	2069.9(15) A^3
Z, Calculated density	4, 1.572 Mg/m^3
Absorption coefficient	0.144 mm^-1
F(000)	1000
Crystal size	0.319 x 0.193 x 0.127 mm
Theta range for data collection	2.631 to 25.624 deg.
Limiting indices	-11<=h<=10, -17<=k<=17, -17<=l<=19
Reflections collected / unique	7293 / 1932 [R(int) = 0.0373]
Completeness to theta = 25.242	98.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1932 / 0 / 155
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0981
R indices (all data)	R1 = 0.0486, wR2 = 0.1082
Extinction coefficient	n/a
Largest diff. peak and hole	0.416 and -0.311 e.A^-3

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

	x	y	z	U(eq)
C(1)	5524(2)	1653(1)	6247(1)	33(1)
C(2)	8009(2)	1519(1)	7023(1)	30(1)
C(3)	9513(2)	1379(1)	7071(1)	29(1)
C(4)	9159(2)	1240(1)	5592(1)	29(1)
C(5)	9741(2)	1108(1)	4836(1)	33(1)
C(6)	8838(2)	1083(1)	4038(1)	36(1)
C(7)	7324(2)	1200(1)	3966(1)	35(1)
C(8)	6717(2)	1338(1)	4684(1)	32(1)
C(9)	7630(2)	1356(1)	5507(1)	28(1)
C(10)	4736(2)	733(1)	6234(1)	40(1)
N(1)	7108(1)	1507(1)	6262(1)	28(1)
N(2)	10083(2)	1252(1)	6378(1)	30(1)
F(1)	7929(2)	-552(1)	6796(1)	85(1)
F(2)	8326(1)	-2077(1)	6809(1)	57(1)
F(3)	6089(1)	-1544(1)	6864(1)	49(1)
F(4)	6938(2)	-1391(2)	5632(1)	89(1)
B(1)	7321(2)	-1397(1)	6520(1)	35(1)

Table 3. Bond lengths [A] and angles [deg].

C(1)-N(1)	1.495(2)
C(1)-C(10)	1.511(2)
C(2)-N(1)	1.320(2)
C(2)-C(3)	1.411(2)
C(3)-N(2)	1.315(2)
C(3)-C(3)#1	1.470(3)
C(4)-N(2)	1.360(2)
C(4)-C(5)	1.411(2)
C(4)-C(9)	1.423(2)
C(5)-C(6)	1.368(3)
C(6)-C(7)	1.411(3)
C(7)-C(8)	1.371(2)
C(8)-C(9)	1.402(2)
C(9)-N(1)	1.385(2)
F(1)-B(1)	1.374(3)
F(2)-B(1)	1.370(2)
F(3)-B(1)	1.383(2)
F(4)-B(1)	1.368(3)
N(1)-C(1)-C(10)	111.02(14)
N(1)-C(2)-C(3)	120.12(15)
N(2)-C(3)-C(2)	122.59(16)
N(2)-C(3)-C(3)#1	118.49(18)
C(2)-C(3)-C(3)#1	118.91(18)
N(2)-C(4)-C(5)	118.73(15)
N(2)-C(4)-C(9)	122.33(15)
C(5)-C(4)-C(9)	118.93(15)
C(6)-C(5)-C(4)	120.12(16)
C(5)-C(6)-C(7)	120.10(16)
C(8)-C(7)-C(6)	121.62(16)
C(7)-C(8)-C(9)	118.78(16)
N(1)-C(9)-C(8)	122.46(15)
N(1)-C(9)-C(4)	117.08(15)

C(8)-C(9)-C(4)	120.44(15)
C(2)-N(1)-C(9)	120.36(14)
C(2)-N(1)-C(1)	118.06(14)
C(9)-N(1)-C(1)	121.58(14)
C(3)-N(2)-C(4)	117.48(14)
F(4)-B(1)-F(2)	111.61(17)
F(4)-B(1)-F(1)	108.97(18)
F(2)-B(1)-F(1)	108.02(16)
F(4)-B(1)-F(3)	108.95(16)
F(2)-B(1)-F(3)	109.55(15)
F(1)-B(1)-F(3)	109.72(17)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y,-z+3/2

Table 4. Anisotropic displacement parameters (A^2 x 10^3).
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
C(1)	27(1)	35(1)	37(1)	-2(1)	6(1)	4(1)
C(2)	32(1)	27(1)	30(1)	-1(1)	6(1)	0(1)
C(3)	31(1)	26(1)	30(1)	1(1)	5(1)	-1(1)
C(4)	31(1)	25(1)	31(1)	1(1)	5(1)	-2(1)
C(5)	33(1)	34(1)	34(1)	1(1)	9(1)	-1(1)
C(6)	44(1)	34(1)	31(1)	0(1)	12(1)	-4(1)
C(7)	40(1)	32(1)	30(1)	1(1)	1(1)	-7(1)
C(8)	32(1)	29(1)	34(1)	2(1)	3(1)	-3(1)
C(9)	31(1)	23(1)	30(1)	1(1)	5(1)	-2(1)
C(10)	35(1)	42(1)	43(1)	0(1)	10(1)	-5(1)
N(1)	28(1)	25(1)	30(1)	0(1)	4(1)	0(1)
N(2)	30(1)	29(1)	31(1)	1(1)	5(1)	-1(1)
F(1)	66(1)	42(1)	143(2)	6(1)	6(1)	-7(1)
F(2)	41(1)	53(1)	80(1)	19(1)	17(1)	16(1)
F(3)	32(1)	74(1)	42(1)	4(1)	12(1)	5(1)
F(4)	48(1)	184(2)	36(1)	16(1)	11(1)	7(1)
B(1)	28(1)	43(1)	34(1)	9(1)	7(1)	4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3).

	x	y	z	U(eq)
H(1A)	5100	2011	5736	39
H(1B)	5405	2005	6756	39
H(2)	7652	1620	7528	35
H(5)	10739	1039	4881	40
H(6)	9223	989	3541	43
H(7)	6723	1182	3419	42
H(8)	5718	1419	4626	39
H(1C)	5170	372	6732	59
H(10A)	4807	399	5714	59
H(10C)	3731	844	6247	59

Table 6. Torsion angles [deg].

N(1)-C(2)-C(3)-N(2)	1.4(2)
N(1)-C(2)-C(3)-C(3)#1	-178.89(10)
N(2)-C(4)-C(5)-C(6)	179.32(15)
C(9)-C(4)-C(5)-C(6)	-0.8(2)
C(4)-C(5)-C(6)-C(7)	0.8(2)
C(5)-C(6)-C(7)-C(8)	-0.1(3)
C(6)-C(7)-C(8)-C(9)	-0.5(2)
C(7)-C(8)-C(9)-N(1)	178.95(14)
C(7)-C(8)-C(9)-C(4)	0.5(2)
N(2)-C(4)-C(9)-N(1)	1.5(2)
C(5)-C(4)-C(9)-N(1)	-178.38(13)
N(2)-C(4)-C(9)-C(8)	-179.95(14)
C(5)-C(4)-C(9)-C(8)	0.2(2)
C(3)-C(2)-N(1)-C(9)	0.1(2)
C(3)-C(2)-N(1)-C(1)	179.61(14)
C(8)-C(9)-N(1)-C(2)	-179.92(14)
C(4)-C(9)-N(1)-C(2)	-1.4(2)
C(8)-C(9)-N(1)-C(1)	0.5(2)
C(4)-C(9)-N(1)-C(1)	179.07(13)
C(10)-C(1)-N(1)-C(2)	-95.52(17)
C(10)-C(1)-N(1)-C(9)	84.02(18)
C(2)-C(3)-N(2)-C(4)	-1.3(2)
C(3)#1-C(3)-N(2)-C(4)	178.99(9)
C(5)-C(4)-N(2)-C(3)	179.72(14)
C(9)-C(4)-N(2)-C(3)	-0.2(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y,-z+3/2

Datablock: I

Bond precision: C-C = 0.0026 A Wavelength=0.71073
Cell: a=9.371(4) b=14.361(7) c=15.685(6)
alpha=90 beta=101.28(3) gamma=90
Temperature: 180 K

	Calculated	Reported
Volume	2070.1(16)	2069.9(15)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C20 H20 N4, 2(B F4)	C20 H20 N4, 2(B F4)
Sum formula	C20 H20 B2 F8 N4	C20 H20 B2 F8 N4
Mr	490.02	490.02
Dx,g cm-3	1.572	1.572
Z	4	4
Mu (mm-1)	0.144	0.144
F000	1000.0	1000.0
F000'	1000.73	
h,k,lmax	11,17,19	11,17,19
Nref	1968	1932
Tmin,Tmax	0.967,0.982	
Tmin'	0.955	

Correction method= Not given
Data completeness= 0.982 Theta(max)= 25.624
R(reflections)= 0.0389(1621) wR2(reflections)= 0.1082(1932)
S = 1.071 Npar= 155

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

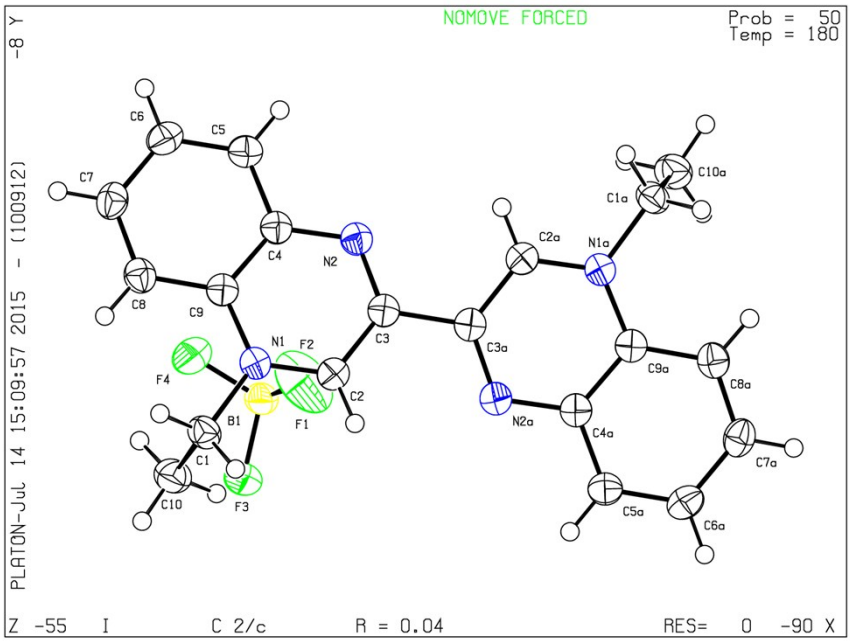
Alert level C

PLAT761_ALERT_1_C CIF Contains no X-H Bonds ..... Please Check
PLAT762_ALERT_1_C CIF Contains no X-Y-H or H-Y-H Angles ..... Please Check

Alert level G

PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of B1 Check
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 2 Note
B F4

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
2 **ALERT level G** = General information/check it is not something unexpected



B_{14} -(Bzbqn)[BF_4]$_2$.2 MeCN

Table 1. Crystal data and structure refinement.

Empirical formula	C34 H30 B2 F8 N6
Formula weight	696.26
Temperature	291(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 8.6630(10) A alpha = 90 deg. b = 8.7810(10) A beta = 95.376(6) deg. c = 22.282(2) A gamma = 90 deg.
Volume	1687.5(3) A^3
Z, Calculated density	2, 1.370 Mg/m^3
Absorption coefficient	0.113 mm^-1
F(000)	716
Crystal size	0.341 x 0.316 x 0.309 mm
Theta range for data collection	2.452 to 27.389 deg.
Limiting indices	-11<=h<=11, -10<=k<=11, -24<=l<=28
Reflections collected / unique	7569 / 3732 [R(int) = 0.0258]
Completeness to theta = 25.242	97.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3732 / 0 / 275
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0595, wR2 = 0.1801
R indices (all data)	R1 = 0.0874, wR2 = 0.1985
Extinction coefficient	n/a
Largest diff. peak and hole	0.411 and -0.379 e.A^-3

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

	x	y	z	U(eq)
C(1)	1904(3)	956(2)	4263(1)	62(1)
C(2)	701(2)	3153(2)	4687(1)	60(1)
C(3)	665(2)	4710(2)	4848(1)	58(1)
C(4)	2984(2)	5112(2)	4470(1)	57(1)
C(5)	4197(2)	6116(3)	4357(1)	64(1)
C(6)	5487(3)	5564(3)	4128(1)	68(1)
C(7)	5635(3)	4016(3)	4011(1)	69(1)
C(8)	4481(2)	3005(3)	4109(1)	64(1)
C(9)	3132(2)	3546(2)	4330(1)	56(1)
C(10)	1804(2)	742(2)	3592(1)	59(1)
C(11)	587(3)	1328(3)	3223(1)	74(1)
C(12)	545(4)	1098(4)	2604(1)	96(1)
C(13)	1682(5)	302(4)	2363(1)	98(1)
C(14)	2869(4)	-298(4)	2725(1)	92(1)
C(15)	2942(3)	-94(3)	3339(1)	73(1)
C(16)	-929(6)	7197(5)	2745(2)	132(1)
C(17)	-882(4)	5933(4)	3165(2)	99(1)
B(1)	2678(3)	351(3)	5875(1)	71(1)
N(1)	1893(2)	2608(2)	4436(1)	56(1)
N(2)	1751(2)	5667(2)	4734(1)	59(1)
N(3)	-844(4)	4945(4)	3487(2)	127(1)
F(1)	3129(3)	245(5)	6457(1)	182(1)
F(2)	1542(3)	1412(3)	5774(1)	133(1)
F(3)	2062(3)	-968(2)	5666(2)	170(1)
F(4)	3918(2)	683(2)	5564(1)	101(1)

Table 3. Bond lengths [A] and angles [deg].

C(1)-C(10)	1.501(3)
C(1)-N(1)	1.501(2)
C(2)-N(1)	1.311(3)
C(2)-C(3)	1.415(3)
C(3)-N(2)	1.304(3)
C(3)-C(3)#1	1.479(4)
C(4)-N(2)	1.356(3)
C(4)-C(5)	1.413(3)
C(4)-C(9)	1.418(3)
C(5)-C(6)	1.361(3)
C(6)-C(7)	1.392(3)
C(7)-C(8)	1.370(3)
C(8)-C(9)	1.393(3)
C(9)-N(1)	1.390(3)
C(10)-C(11)	1.375(3)
C(10)-C(15)	1.390(3)
C(11)-C(12)	1.390(4)
C(12)-C(13)	1.360(5)
C(13)-C(14)	1.353(5)
C(14)-C(15)	1.376(4)
C(16)-C(17)	1.450(5)
C(17)-N(3)	1.124(4)
B(1)-F(1)	1.323(3)
B(1)-F(3)	1.341(3)
B(1)-F(2)	1.358(3)
B(1)-F(4)	1.364(3)
C(10)-C(1)-N(1)	112.06(16)
N(1)-C(2)-C(3)	119.91(19)
N(2)-C(3)-C(2)	122.61(19)
N(2)-C(3)-C(3)#1	118.3(2)
C(2)-C(3)-C(3)#1	119.0(2)
N(2)-C(4)-C(5)	118.82(18)
N(2)-C(4)-C(9)	122.32(17)
C(5)-C(4)-C(9)	118.80(19)
C(6)-C(5)-C(4)	119.7(2)
C(5)-C(6)-C(7)	120.8(2)
C(8)-C(7)-C(6)	121.4(2)
C(7)-C(8)-C(9)	119.0(2)
N(1)-C(9)-C(8)	122.98(18)
N(1)-C(9)-C(4)	116.73(17)
C(8)-C(9)-C(4)	120.28(18)
C(11)-C(10)-C(15)	119.2(2)
C(11)-C(10)-C(1)	121.2(2)
C(15)-C(10)-C(1)	119.56(19)
C(10)-C(11)-C(12)	119.1(3)
C(13)-C(12)-C(11)	120.9(3)
C(14)-C(13)-C(12)	120.2(3)
C(13)-C(14)-C(15)	120.3(3)
C(14)-C(15)-C(10)	120.3(3)
N(3)-C(17)-C(16)	179.4(4)
F(1)-B(1)-F(3)	110.6(3)
F(1)-B(1)-F(2)	110.8(3)
F(3)-B(1)-F(2)	106.1(2)
F(1)-B(1)-F(4)	109.8(2)
F(3)-B(1)-F(4)	108.3(3)
F(2)-B(1)-F(4)	111.2(2)
C(2)-N(1)-C(9)	120.51(16)
C(2)-N(1)-C(1)	119.12(17)
C(9)-N(1)-C(1)	120.37(17)
C(3)-N(2)-C(4)	117.72(17)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1

Table 4. Anisotropic displacement parameters (A^2 x 10^3).
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
C(1)	75(1)	52(1)	62(1)	-2(1)	13(1)	-3(1)
C(2)	65(1)	59(1)	57(1)	-3(1)	12(1)	-6(1)
C(3)	63(1)	59(1)	53(1)	-4(1)	9(1)	-3(1)
C(4)	62(1)	58(1)	53(1)	-1(1)	7(1)	-5(1)
C(5)	69(1)	59(1)	64(1)	-2(1)	9(1)	-8(1)
C(6)	63(1)	74(1)	67(1)	2(1)	6(1)	-12(1)
C(7)	59(1)	82(1)	67(1)	-6(1)	9(1)	-3(1)
C(8)	62(1)	66(1)	63(1)	-7(1)	7(1)	-1(1)
C(9)	61(1)	58(1)	49(1)	-1(1)	5(1)	-3(1)
C(10)	63(1)	51(1)	64(1)	-6(1)	10(1)	-6(1)
C(11)	71(1)	75(1)	76(1)	-4(1)	2(1)	-1(1)
C(12)	101(2)	104(2)	77(2)	3(2)	-18(2)	-11(2)
C(13)	120(2)	108(2)	66(2)	-17(2)	13(2)	-20(2)
C(14)	103(2)	94(2)	84(2)	-28(1)	30(2)	-10(2)
C(15)	73(1)	71(1)	76(1)	-12(1)	12(1)	2(1)
C(16)	154(3)	105(2)	145(3)	24(2)	51(3)	8(2)
C(17)	102(2)	89(2)	112(2)	-3(2)	37(2)	0(2)
B(1)	65(1)	72(2)	75(2)	6(1)	5(1)	-7(1)
N(1)	63(1)	53(1)	52(1)	-2(1)	9(1)	-4(1)
N(2)	64(1)	57(1)	58(1)	-3(1)	9(1)	-4(1)
N(3)	144(3)	111(2)	131(2)	18(2)	43(2)	11(2)
F(1)	106(2)	351(4)	87(1)	53(2)	8(1)	32(2)
F(2)	124(2)	132(2)	147(2)	34(1)	22(1)	49(1)
F(3)	127(2)	99(1)	294(3)	-49(2)	67(2)	-48(1)
F(4)	85(1)	124(1)	95(1)	1(1)	20(1)	-26(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3).

	x	y	z	U(eq)
H(16A)	106	7443	2657	199
H(16B)	-1386	8067	2920	199
H(16C)	-1538	6919	2379	199
H(1A)	2850(30)	560(30)	4459(11)	69(6)
H(1B)	990(30)	590(30)	4406(12)	75(7)
H(2)	-90(30)	2490(30)	4755(12)	75(7)
H(5)	4060(30)	7110(30)	4459(10)	65(6)
H(6)	6340(30)	6260(30)	4064(12)	85(7)
H(7)	6630(40)	3650(30)	3857(13)	94(8)
H(8)	4610(30)	1980(30)	4052(11)	73(6)
H(11)	-170(30)	1950(30)	3414(12)	87(8)
H(12)	-250(40)	1610(40)	2377(15)	106(9)
H(13)	1780(40)	260(40)	1963(17)	105(10)
H(14)	3710(40)	-1010(40)	2545(16)	120(11)
H(15)	3850(30)	-480(30)	3598(13)	80(7)

Table 6. Torsion angles [deg].

N(1)-C(2)-C(3)-N(2)	3.1(3)
N(1)-C(2)-C(3)-C(3)#1	-177.8(2)
N(2)-C(4)-C(5)-C(6)	176.01(18)
C(9)-C(4)-C(5)-C(6)	-1.2(3)
C(4)-C(5)-C(6)-C(7)	-1.0(3)
C(5)-C(6)-C(7)-C(8)	1.6(3)
C(6)-C(7)-C(8)-C(9)	0.0(3)
C(7)-C(8)-C(9)-N(1)	179.19(17)
C(7)-C(8)-C(9)-C(4)	-2.2(3)
N(2)-C(4)-C(9)-N(1)	4.4(3)
C(5)-C(4)-C(9)-N(1)	-178.52(16)
N(2)-C(4)-C(9)-C(8)	-174.30(17)
C(5)-C(4)-C(9)-C(8)	2.8(3)
N(1)-C(1)-C(10)-C(11)	-57.5(3)
N(1)-C(1)-C(10)-C(15)	124.0(2)
C(15)-C(10)-C(11)-C(12)	-1.4(3)
C(1)-C(10)-C(11)-C(12)	-179.9(2)
C(10)-C(11)-C(12)-C(13)	0.2(4)
C(11)-C(12)-C(13)-C(14)	0.8(5)
C(12)-C(13)-C(14)-C(15)	-0.6(5)
C(13)-C(14)-C(15)-C(10)	-0.6(4)
C(11)-C(10)-C(15)-C(14)	1.6(4)
C(1)-C(10)-C(15)-C(14)	-179.8(2)
C(3)-C(2)-N(1)-C(9)	0.5(3)
C(3)-C(2)-N(1)-C(1)	-179.43(17)
C(8)-C(9)-N(1)-C(2)	174.70(18)
C(4)-C(9)-N(1)-C(2)	-4.0(2)
C(8)-C(9)-N(1)-C(1)	-5.3(3)
C(4)-C(9)-N(1)-C(1)	175.98(16)
C(10)-C(1)-N(1)-C(2)	112.9(2)
C(10)-C(1)-N(1)-C(9)	-67.1(2)
C(2)-C(3)-N(2)-C(4)	-2.6(3)
C(3)#1-C(3)-N(2)-C(4)	178.2(2)
C(5)-C(4)-N(2)-C(3)	-178.20(17)
C(9)-C(4)-N(2)-C(3)	-1.1(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1

Datablock: I

Bond precision: C-C = 0.0035 A Wavelength=0.71073
Cell: a=8.663(1) b=8.781(1) c=22.282(2)
alpha=90 beta=95.376(6) gamma=90
Temperature: 291 K

	Calculated	Reported
Volume	1687.5(3)	1687.5(3)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C30 H24 N4, 2(B F4), 2(C2 H3 N)	C30 H24 N4, 2(B F4), 2(C2 H3 N)
Sum formula	C34 H30 B2 F8 N6	C34 H30 B2 F8 N6
Mr	696.26	696.26
Dx,g cm-3	1.370	1.370
Z	2	2
Mu (mm-1)	0.113	0.113
F000	716.0	716.0
F000'	716.44	
h,k,lmax	11,11,28	11,11,28
Nref	3827	3732
Tmin,Tmax	0.962,0.966	
Tmin'	0.962	
Correction method=	Not given	

```
Data completeness= 0.975        Theta(max)= 27.389
R(reflections)= 0.0595( 2296)      wR2(reflections)= 0.1985( 3732)
S = 1.071              Npar= 275
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

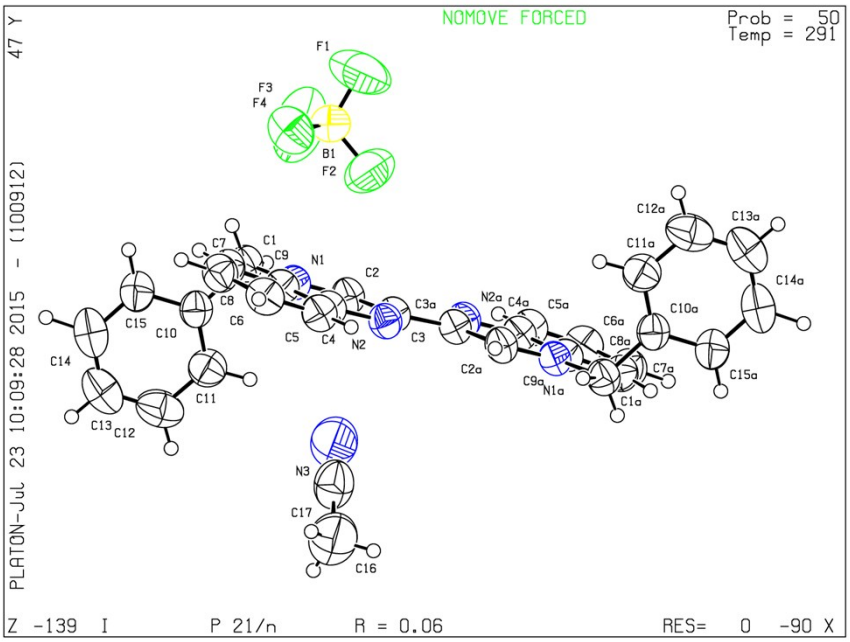
Alert level C

PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low ..... 0.979 Note
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C17 Check
PLAT761_ALERT_1_C CIF Contains no X-H Bonds ..... Please Check
PLAT762_ALERT_1_C CIF Contains no X-Y-H or H-Y-H Angles ..... Please Check

Alert level G

PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large. 0.12 Report
PLAT244_ALERT_4_G Low 'Solvent' Ueq as Compared to Neighbors of B1 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact F2 .. C2 .. 2.90 Ang.

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
3 **ALERT level G** = General information/check it is not something unexpected



C. Additional characterisations

C_1 – Single crystal X-Ray structure of $[Pbqn^0\text{-}H^+]_2(S_4O_6^{2-})$

Empirical formula	2(C22 H25 N4), O6 S4
Formula weight	915.16
Temperature	150(2) K
Wavelength	1.54184 A
Crystal system, space group	Triclinic, P -1

Unit cell dimensions	a = 13.375(2) A alpha = 67.600(16) deg. b = 13.596(2) A beta = 70.371(15) deg. c = 13.843(2) A gamma = 69.377(15) deg.
Volume	2118.2(6) A^3
Z, Calculated density	2, 1.435 Mg/m^3
Absorption coefficient	2.557 mm^-1
F(000)	964
Crystal size	0.070 x 0.060 x 0.050 mm
Theta range for data collection	3.551 to 37.290 deg.
Limiting indices	-10<=h<=10, -10<=k<=10, -10<=l<=10
Reflections collected / unique	5154 / 2076 [R(int) = 0.0247]
Completeness to theta = 37.290	96.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.78270
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2076 / 0 / 304
Goodness-of-fit on F^2	1.072
Final R indices [I>2sigma(I)]	R1 = 0.0541, wR2 = 0.1321
R indices (all data)	R1 = 0.0593, wR2 = 0.1365
Extinction coefficient	0.0022(2)
Largest diff. peak and hole	0.544 and -0.413 e.A^-3

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

	x	y	z	U(eq)
C(1)	-6008(6)	-1491(6)	6006(5)	32(2)
C(2)	-6193(6)	-1042(5)	6923(5)	23(2)
C(3)	-5869(6)	38(5)	6497(5)	20(2)
C(4)	-5086(6)	357(5)	7668(5)	18(2)
C(5)	-5115(5)	820(5)	8395(5)	13(2)
C(6)	-7063(5)	1616(5)	8533(5)	14(2)
C(7)	-8043(5)	2252(5)	8958(5)	17(2)
C(8)	-8991(6)	2378(5)	8679(5)	20(2)
C(9)	-8953(6)	1873(5)	7977(5)	18(2)
C(10)	-7977(5)	1241(5)	7535(5)	18(2)
C(11)	-7012(5)	1110(5)	7798(5)	14(2)
C(12)	640(6)	-719(6)	6854(6)	42(2)
C(13)	-511(5)	-35(6)	7179(5)	27(2)
C(14)	-1173(5)	-693(5)	8186(5)	18(2)
C(15)	-3135(6)	66(5)	8350(5)	18(2)
C(16)	-4155(5)	738(5)	8700(5)	14(2)
C(17)	-3352(6)	1320(5)	9550(5)	15(2)
C(18)	-3434(6)	2006(5)	10123(5)	21(2)
C(19)	-2517(6)	2053(6)	10329(5)	23(2)
C(20)	-1500(6)	1395(5)	9985(5)	25(2)
C(21)	-1389(6)	709(6)	9429(5)	23(2)
C(22)	-2311(5)	668(5)	9193(5)	13(2)
C(23)	949(6)	6341(6)	9131(6)	32(2)
C(24)	1028(6)	5512(5)	8601(5)	25(2)
C(25)	785(6)	6115(5)	7503(5)	21(2)
C(26)	-67(6)	5123(5)	6997(5)	17(2)
C(27)	-50(5)	4417(5)	6500(5)	15(2)
C(28)	1902(5)	4096(5)	5899(5)	12(2)
C(29)	2898(5)	3531(5)	5401(5)	20(2)
C(30)	3863(6)	3676(6)	5408(5)	25(2)
C(31)	3845(6)	4386(5)	5902(5)	22(2)
C(32)	2865(6)	4944(5)	6410(5)	20(2)
C(33)	1878(5)	4809(5)	6418(5)	13(2)
C(34)	-5719(6)	5746(6)	8304(6)	43(2)
C(35)	-4700(5)	5368(6)	7493(5)	25(2)
C(36)	-3901(5)	4379(5)	8061(5)	22(2)
C(37)	-2002(5)	4394(5)	7234(5)	17(2)
C(38)	-995(6)	4112(5)	6559(5)	16(2)
C(39)	-1696(5)	3120(5)	6007(5)	12(2)
C(40)	-1549(6)	2466(5)	5379(5)	18(2)
C(41)	-2402(6)	2099(5)	5420(5)	22(2)
C(42)	-3409(6)	2376(5)	6089(5)	20(2)
C(43)	-3590(6)	3013(5)	6723(5)	19(2)
C(44)	-2728(5)	3396(5)	6680(5)	12(2)
N(1)	-5989(4)	506(4)	7336(4)	17(2)
N(2)	-6091(4)	1472(4)	8807(4)	18(2)
N(3)	-2241(4)	12(4)	8598(4)	14(2)
N(4)	-4289(4)	1349(4)	9321(4)	16(2)
N(5)	852(4)	5361(4)	6936(4)	16(2)
N(6)	918(4)	3973(4)	5893(4)	18(2)
N(7)	-2849(4)	4040(4)	7324(4)	16(2)
N(8)	-814(4)	3457(4)	5942(4)	17(2)
O(1)	-2725(4)	9522(4)	6100(4)	49(2)
O(2)	-1829(4)	8393(4)	4889(4)	52(2)
O(3)	-1096(5)	8106(5)	6372(4)	61(2)
O(4)	-2579(5)	5401(5)	9161(4)	60(2)
O(5)	-1688(5)	6737(5)	8938(4)	66(2)
O(6)	-3383(4)	6597(4)	10308(5)	48(2)
S(1)	-2027(2)	8484(2)	5943(2)	34(1)
S(2)	-3008(2)	7325(2)	6856(2)	43(1)
S(3)	-2709(2)	6450(2)	9260(2)	49(1)
S(4)	-3708(2)	7607(2)	8259(2)	55(1)

Table 3. Bond lengths [A] and angles [deg] for pbqni.

C(1)-C(2)	1.522(8)
C(2)-C(3)	1.520(8)
C(3)-N(1)	1.465(7)
C(4)-N(1)	1.356(7)
C(4)-C(5)	1.360(8)
C(5)-N(2)	1.373(7)
C(5)-C(16)	1.437(8)
C(6)-C(7)	1.371(8)
C(6)-N(2)	1.402(7)
C(6)-C(11)	1.403(8)
C(7)-C(8)	1.383(8)
C(8)-C(9)	1.367(8)
C(9)-C(10)	1.376(8)
C(10)-C(11)	1.391(8)
C(11)-N(1)	1.405(7)
C(12)-C(13)	1.511(9)
C(13)-C(14)	1.518(9)
C(14)-N(3)	1.480(7)
C(15)-N(3)	1.322(7)
C(15)-C(16)	1.395(8)
C(16)-N(4)	1.342(7)
C(17)-N(4)	1.377(7)
C(17)-C(18)	1.395(8)
C(17)-C(22)	1.404(8)
C(18)-C(19)	1.376(8)
C(19)-C(20)	1.381(8)
C(20)-C(21)	1.363(8)
C(21)-C(22)	1.401(8)
C(22)-N(3)	1.390(7)
C(23)-C(24)	1.521(8)
C(24)-C(25)	1.511(9)
C(25)-N(5)	1.475(7)
C(26)-N(5)	1.347(7)
C(26)-C(27)	1.368(8)
C(27)-N(6)	1.361(7)
C(27)-C(38)	1.433(8)
C(28)-C(29)	1.380(8)
C(28)-N(6)	1.387(7)
C(28)-C(33)	1.398(8)
C(29)-C(30)	1.377(8)
C(30)-C(31)	1.370(8)
C(31)-C(32)	1.370(8)
C(32)-C(33)	1.390(8)
C(33)-N(5)	1.409(7)
C(34)-C(35)	1.517(9)
C(35)-C(36)	1.521(9)
C(36)-N(7)	1.474(7)
C(37)-N(7)	1.332(7)
C(37)-C(38)	1.378(8)
C(38)-N(8)	1.367(7)
C(39)-N(8)	1.375(7)
C(39)-C(40)	1.392(8)
C(39)-C(44)	1.397(8)
C(40)-C(41)	1.375(8)
C(41)-C(42)	1.372(8)
C(42)-C(43)	1.366(8)
C(43)-C(44)	1.399(8)
C(44)-N(7)	1.409(7)
O(1)-S(1)	1.443(5)
O(2)-S(1)	1.439(5)
O(3)-S(1)	1.407(6)
O(4)-S(3)	1.429(6)
O(5)-S(3)	1.431(6)
O(6)-S(3)	1.474(5)
S(1)-S(2)	2.151(3)
S(2)-S(4)	1.971(3)
S(3)-S(4)	2.070(3)

C(3)-C(2)-C(1)	110.6(5)

N(1)-C(3)-C(2)	113.9(5)
N(1)-C(4)-C(5)	122.6(6)
C(4)-C(5)-N(2)	119.1(6)
C(4)-C(5)-C(16)	123.5(6)
N(2)-C(5)-C(16)	117.2(6)
C(7)-C(6)-N(2)	121.1(6)
C(7)-C(6)-C(11)	120.3(6)
N(2)-C(6)-C(11)	118.5(6)
C(6)-C(7)-C(8)	120.1(6)
C(9)-C(8)-C(7)	120.1(7)
C(8)-C(9)-C(10)	120.7(7)
C(9)-C(10)-C(11)	120.1(7)
C(10)-C(11)-C(6)	118.7(6)
C(10)-C(11)-N(1)	122.1(6)
C(6)-C(11)-N(1)	119.2(6)
C(12)-C(13)-C(14)	111.5(6)
N(3)-C(14)-C(13)	111.7(5)
N(3)-C(15)-C(16)	121.7(6)
N(4)-C(16)-C(15)	122.0(6)
N(4)-C(16)-C(5)	116.7(6)
C(15)-C(16)-C(5)	121.3(6)
N(4)-C(17)-C(18)	118.4(6)
N(4)-C(17)-C(22)	123.0(6)
C(18)-C(17)-C(22)	118.5(6)
C(19)-C(18)-C(17)	120.9(7)
C(18)-C(19)-C(20)	119.9(7)
C(21)-C(20)-C(19)	120.8(7)
C(20)-C(21)-C(22)	120.1(7)
N(3)-C(22)-C(21)	122.6(6)
N(3)-C(22)-C(17)	117.7(6)
C(21)-C(22)-C(17)	119.7(6)
C(25)-C(24)-C(23)	109.5(5)
N(5)-C(25)-C(24)	112.6(5)
N(5)-C(26)-C(27)	122.0(6)
N(6)-C(27)-C(26)	119.1(6)
N(6)-C(27)-C(38)	116.5(6)
C(26)-C(27)-C(38)	124.5(6)
C(29)-C(28)-N(6)	121.3(6)
C(29)-C(28)-C(33)	119.7(6)
N(6)-C(28)-C(33)	119.0(6)
C(30)-C(29)-C(28)	120.2(7)
C(31)-C(30)-C(29)	120.4(7)
C(32)-C(31)-C(30)	120.1(7)
C(31)-C(32)-C(33)	120.6(7)
C(32)-C(33)-C(28)	118.9(6)
C(32)-C(33)-N(5)	122.5(6)
C(28)-C(33)-N(5)	118.6(6)
C(34)-C(35)-C(36)	110.4(6)
N(7)-C(36)-C(35)	112.9(5)
N(7)-C(37)-C(38)	121.8(6)
N(8)-C(38)-C(37)	121.8(6)
N(8)-C(38)-C(27)	115.1(6)
C(37)-C(38)-C(27)	123.0(6)
N(8)-C(39)-C(40)	118.3(6)
N(8)-C(39)-C(44)	123.0(6)
C(40)-C(39)-C(44)	118.7(6)
C(41)-C(40)-C(39)	120.7(6)
C(42)-C(41)-C(40)	119.7(7)
C(43)-C(42)-C(41)	121.6(7)
C(42)-C(43)-C(44)	118.9(6)
C(39)-C(44)-C(43)	120.3(6)
C(39)-C(44)-N(7)	117.5(6)
C(43)-C(44)-N(7)	122.1(6)
C(4)-N(1)-C(11)	119.4(6)
C(4)-N(1)-C(3)	118.9(5)
C(11)-N(1)-C(3)	121.7(5)
C(5)-N(2)-C(6)	121.0(6)
C(15)-N(3)-C(22)	119.3(6)
C(15)-N(3)-C(14)	119.7(5)
C(22)-N(3)-C(14)	120.9(5)
C(16)-N(4)-C(17)	116.2(5)
C(26)-N(5)-C(33)	119.6(5)
C(26)-N(5)-C(25)	119.6(5)

C(33)-N(5)-C(25)	120.6(5)
C(27)-N(6)-C(28)	120.9(6)
C(37)-N(7)-C(44)	119.3(5)
C(37)-N(7)-C(36)	118.7(5)
C(44)-N(7)-C(36)	122.0(5)
C(38)-N(8)-C(39)	116.5(5)
O(3)-S(1)-O(2)	115.6(3)
O(3)-S(1)-O(1)	112.9(4)
O(2)-S(1)-O(1)	115.2(3)
O(3)-S(1)-S(2)	106.6(3)
O(2)-S(1)-S(2)	99.6(2)
O(1)-S(1)-S(2)	104.9(2)
S(4)-S(2)-S(1)	106.25(13)
O(4)-S(3)-O(5)	112.6(4)
O(4)-S(3)-O(6)	113.7(3)
O(5)-S(3)-O(6)	113.7(3)
O(4)-S(3)-S(4)	107.0(3)
O(5)-S(3)-S(4)	108.3(3)
O(6)-S(3)-S(4)	100.4(2)
S(2)-S(4)-S(3)	104.34(14)

Symmetry transformations used to generate equivalent atoms:

CHECK CIF.

Datablock: shelx

Bond precision: C-C = 0.0102 A Wavelength=1.54184
Cell: a=13.375(2) b=13.596(2) c=13.843(2)
alpha=67.600(16) beta=70.371(15) gamma=69.377(15)
Temperature: 150 K

	Calculated	Reported
Volume	2118.2(6)	2118.2(6)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	2(C22 H25 N4), O6 S4	2(C22 H25 N4), O6 S4
Sum formula	C44 H50 N8 O6 S4	C44 H50 N8 O6 S4
Mr	915.16	915.16
Dx,g cm-3	1.435	1.435
Z	2	2
Mu (mm-1)	2.557	2.557
F000	964.0	964.0
F000'	969.19	
h,k,lmax	10,10,10	10,10,10
Nref	2148	2076
Tmin,Tmax	0.836,0.880	0.783,1.000
Tmin'	0.836	

Correction method= # Reported T Limits: Tmin=0.783
Tmax=1.000 AbsCorr = MULTI-SCAN
Data completeness= 0.966 Theta(max)= 37.289
R(reflections)= 0.0541(1858) wR2(reflections)= 0.1365(2076)
S = 1.072 Npar= 304

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A
THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.3929
PLAT201_ALERT_2_A Isotropic non-H Atoms in Main Residue(s) 52
Report

Alert level B
REFNR01_ALERT_3_B Ratio of reflections to parameters is < 8 for a
centrosymmetric structure
sine(theta)/lambda 0.3929
Proportion of unique data used 1.0000
Ratio reflections to parameters 6.8289
PLAT088_ALERT_3_B Poor Data / Parameter Ratio 6.83
Note

PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.01024 Ang.

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without a literature citation. This should be contained in the _exptl_absorpt_process_details field. Absorption correction given as multi-scan

PLAT018_ALERT_1_C _diffrn_measured_fraction_theta_max .NE. *_full ! Check

PLAT214_ALERT_2_C Atom O2 (Anion/Solvent) ADP max/min Ratio 4.3 oblate

PLAT220_ALERT_2_C Non-Solvent Resd 1 C Ueq(max)/Ueq(min) Range 3.2 Ratio

PLAT220_ALERT_2_C Non-Solvent Resd 2 C Ueq(max)/Ueq(min) Range 3.6 Ratio

PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of S1 Check

PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 1 Note

C22 H25 N4

PLAT911_ALERT_3_C Missing # FCF Refl Between THmin & STh/L= 0.393 73 Report

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Alert level G

PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 2 Report

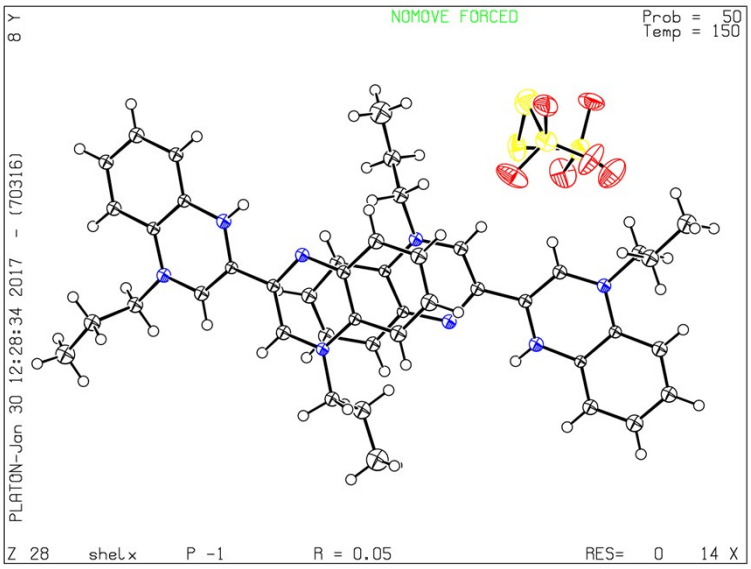
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large 6.97 Why ?

PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 3 Note

O6 S4

PLAT909_ALERT_3_G Percentage of Observed Data at Theta(Max) Still 89 % Note

PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 1 Note

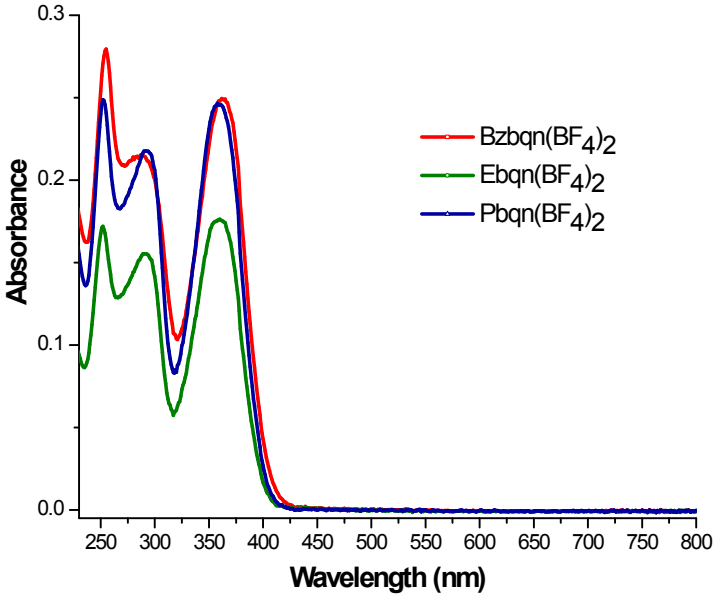


C_2 - Elemental Analysis on the intermediate purple powder made of R=Methyl, Ethyl, Propyl and Benzyl

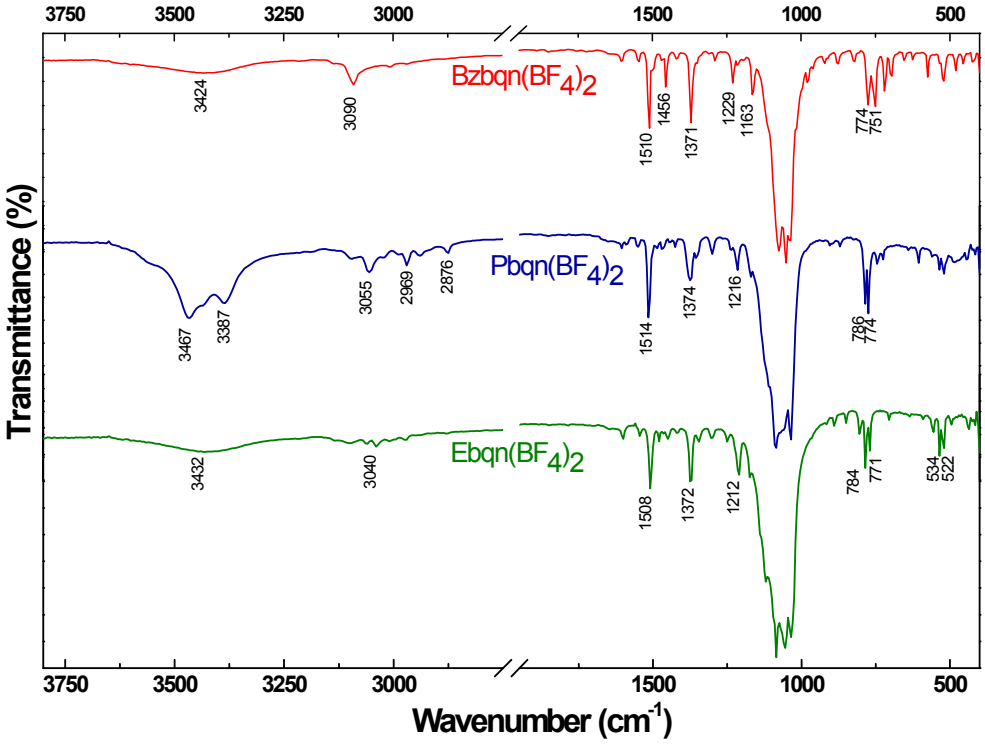
The data are the experimental one.

Intermediate purple powder	%C	%H	%N	**%S**
R=Methyl	48.01	4.17	12.47	**11.4**
R=Ethyl	53.76	4.83	12.76	**6.98**
R=Propyl	53.20	5.29	11.31	
R=Benzyl	68.45	4.84	10.76	

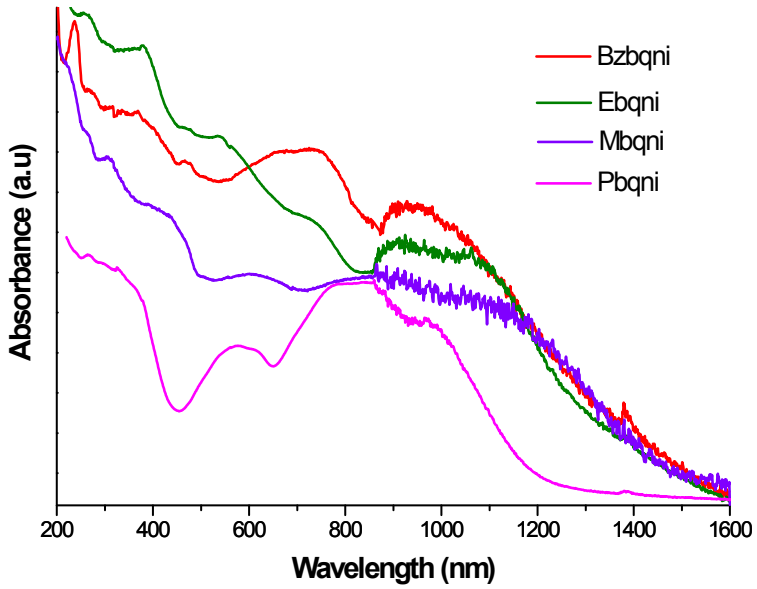
C_3 – Solution state UV-Visible spectrum of $Ebqn(BF_4)_2$, $Pbqn(BF_4)_2$ and $Bzbqn(BF_4)_2$



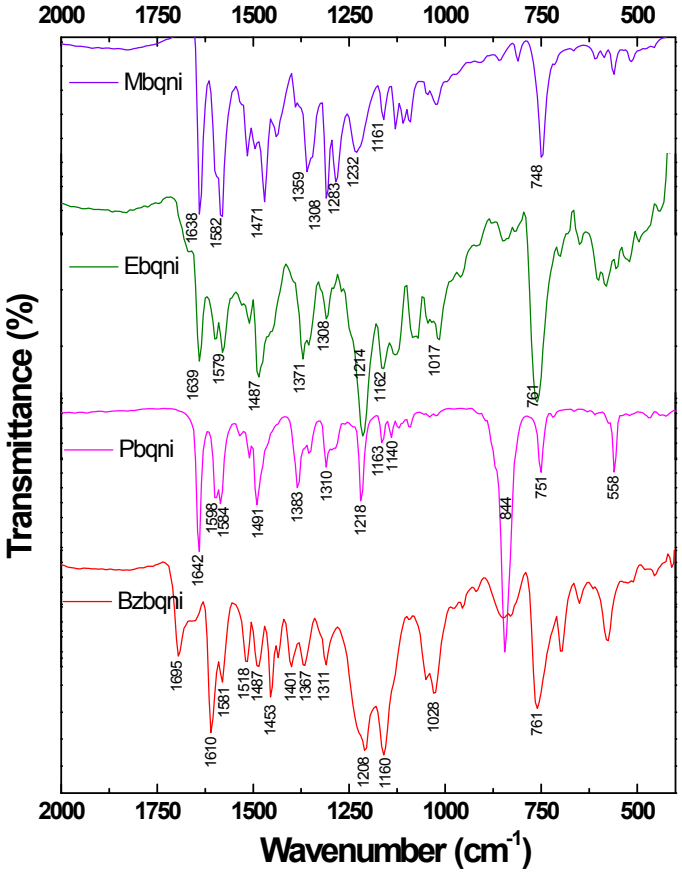
C_4 – Solid state infrared spectrum of $Ebqn(BF_4)_2$, $Pbqn(BF_4)_2$ and $Bzbqn(BF_4)_2$



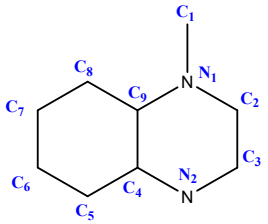
C_5 – Solid state UV-Visible spectrum of the intermediate reduced forms $Ebqn^0$-H^+, $Mbqn^0$-H^+, $Pbqn^0$-H^+ and $Bzbqn^0$-H^+



C_6 – Solid state infrared spectrum of the intermediate reduced forms Ebqn^0-H$^+$, Mbqn^0-H$^+$, Pbqn^0-H$^+$ and Bzbqn^0-H$^+$



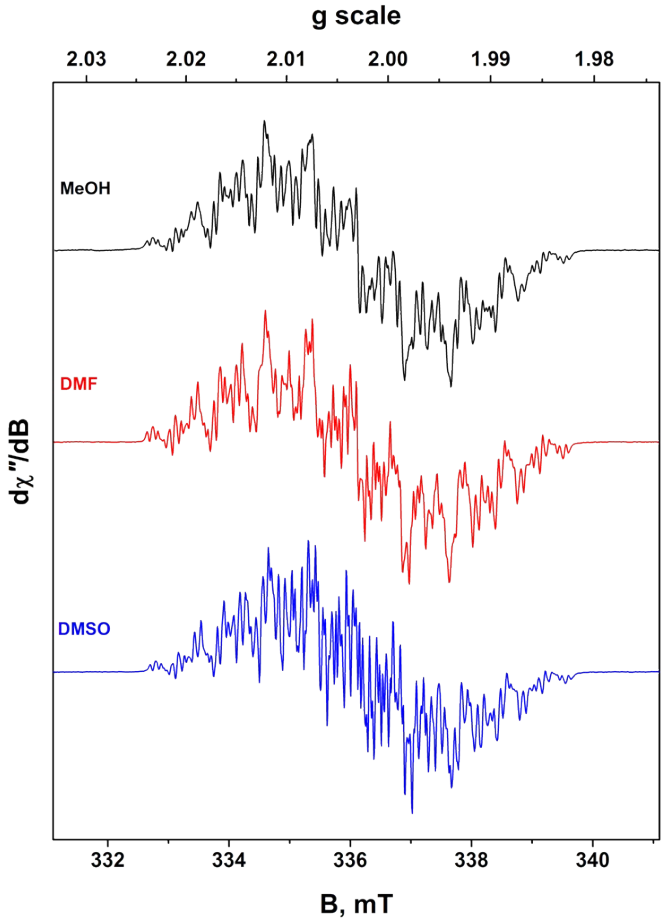
C_7 – DFT calculation on the *N*-methylquinoxalinium cation, radical and protonated radical cation (main geometrical parameters).



	N-methylquinoxalinium			
	Experimental	cation[a]	radical[a,b]	protonated radical cation[a,b]
C_1-N_1	1.479	1.481	1.458	1.465
C_9-N_1	1.370	1.382	1.395	1.398
C_8-C_9	1.385	1.405	1.398	1.398
C_7-C_8	1.361	1.377	1.393	1.387
C_6-C_7	1.363	1.413	1.395	1.397
C_5-C_6	1.341	1.370	1.387	1.385
C_5-C_4	1.402	1.415	1.407	1.395
C_4-C_9	1.389	1.435	1.430	1.418
C_4-N_2	1.357	1.350	1.376	1.383
N_2-C_3	1.295	1.314	1.347	1.356
N_1-C_2	1.305	1.332	1.376	1.365
C_2-C_3	1.393	1.401	1.370	1.361
Energy (hartree)		-457.502428589884	-457.726999544873	-458.190454548052

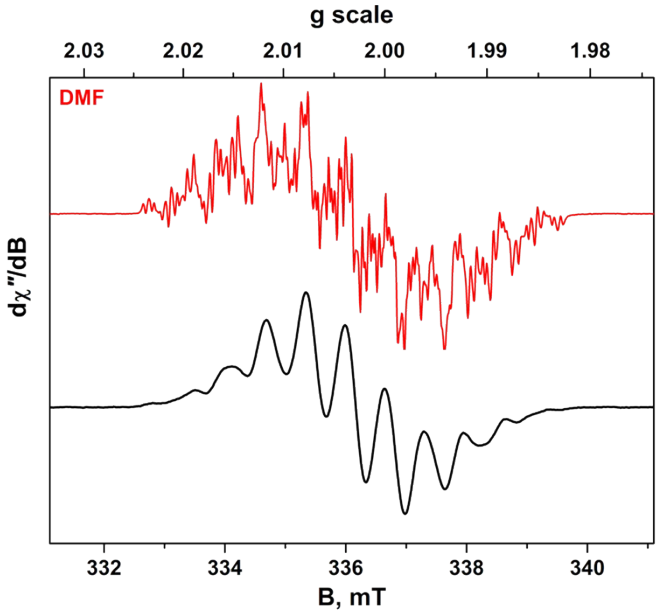
[a] All the values have been computed at the B3LYP/TZVP level of theory without symmetry restriction
[b] Solvation model using COSMO (ε=32,63, r=1.329)

C_8 – Additional EPR measurements



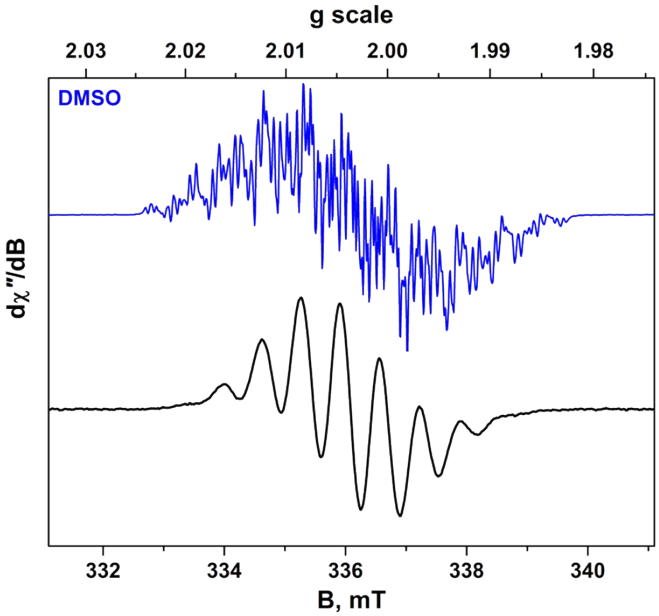
C8-1. Comparison of the radical formed from the reaction of *N*-methylquinoxalinium iodide and sodium dithionite in different solvents. Top: MeOH at 233 K; middle: DMF at 293 K; bottom: DMSO at 293 K.

This is the multiline spectrum indicative of *N*-methylquinoxalinyl radical, possibly protonated. The effect of tumbling as modulated by the solvent medium, gives a slightly sharper (narrower lines) profile in DMSO at ambient temperature. A chilled solution (-40 °C) is required for MeOH, though this was a more dilute solution. For the DMSO reaction, this spectrum was recorded 30 min after mixing; for the DMF reaction, this spectrum was recorded 48 h after initial mixing; for the MeOH reaction, this is a long-lived signal.



C8-2. Comparison of the radical formed from the reaction of *N*-methylquinoxalinium iodide and sodium dithionite in DMF after 24 h (red) and 72 h (black) at 293 K. The latter represents the spectrum for the $Mbqn^{\bullet+}$-H^+ radical,* here from coupling of two *N*-methylquinoxalinyl radicals formed initially.

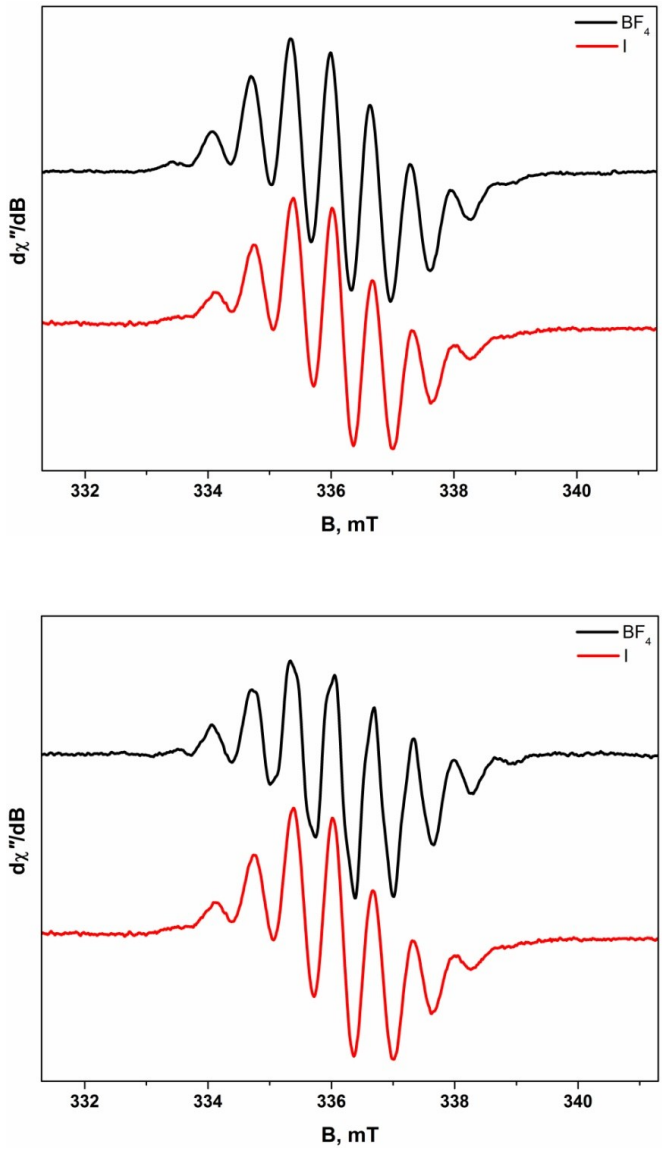
The reaction progresses more slowly here than in the DMSO reaction (vide supra). A less concentrated sample was confined to a capillary tube where mixing was perturbed.



C8-3. Comparison of the radical formed from the reaction of *N*-methylquinoxalinium iodide and sodium dithionite in DMSO after 30 min (blue) and 24 h (black) at 293 K. The latter represents the spectrum for $Mbqn^{\bullet+}$-H^+ radical,* here from coupling of two *N*-methylquinoxalinyl radicals formed initially.

The reaction progresses much quicker in DMSO with a red colour quickly becoming dark purple to dark blue within a few hours.

* N. Leblanc, S. Sproules, K. Fink, L. Sanguinet, O. Aleveque, E. Levillain, P. Rosa and A. K. Powell, *Chem. Sci.*, 2016, **7**, 3820-3828.



C8-4. Comparison of the X-band EPR spectra of the $Mbqn^{\bullet+}$-H^+ radical formed here *in situ* with BF_4^- (black) and I^- (red) counterions recorded in DMF solution at 233 K (top) and 293 K (bottom).

D. Experimental details

Single crystals X-Ray diffraction data of $[Mbqn](BF_4)_2$,MeCN, $[Ebqn](BF_4)_2$ and $[Bzqn](BF_4)_2$, 2 MeCN were collected at 180 K on a STOE IPDS II diffractometer equipped with a graphite monochromatized Mo Kα radiation (λ = 0.71073 Å), and mounted with an Oxford Nitrogen Cryostream. Data of $[Pbqn]_2$ (S_4O_6) have been collected at 150 K on an Agilent SuperNova diffractometer equipped with a Cu Kα x-ray source (λ = 1.54184 Å).

Structures were solved and refined using the Shelxl2013[†] and WingX2013[‡] packages and molecular diagrams were prepared using Diamond 4.2.2.[§] Positions, atomic displacement parameters, and hydrogens were refined by full-matrix least-squares routines against F^2.

EPR spectroscopy. X-band EPR spectra were recorded using a Bruker ELEXSYS E500 spectrometer and simulated using Bruker′s Xsophe software package.[**]

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Calculations. All calculations have been performed with the program package Orca 3.0.3.[††] In the DFT calculations[‡‡] the hybrid functional B3LYP[§§] in combination with the TZVP basis set[***] was used throughout. The influence of the MeOH solvent is considered by the conductor like screening model with a dielectric constant of 37.0.[†††] Artworks have been made with Chemissian[‡‡‡]

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