

Dibenzylimidazolium Halides: From Complex Molecular Network in Solid State to Simple Dimer in Solution and in Gaz Phase

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General experimental details

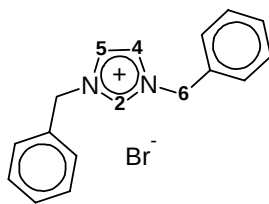
All the reagents were purchased and used without further purification. NMR spectra were recorded in the indicated solvents. NMR spectra were recorded on spectrometer operating at 400 MHz or 300 MHz for ^1H NMR and at 100 MHz or 75 MHz for ^{13}C NMR locked to the deuterated solvent. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane. The following abbreviations are used to explain the multiplicities: s= singlet, d= doublet, t= triplet, q= quartet, p= pentet, m= multiplet. Accurate mass measurements were performed on a LC-MSD-Tof instrument in positive electrospray mode.

All reactions were carried in oven-dried glassware under nitrogen, using standard Schlenk and vacuum line techniques. Calculations were performed on a Windows® XP workstation with the GaussView interface that allows running Gaussian 03® semi-empirical calculation. The structures are optimized using the PM3 parameterization in the gas phase (RHF, using keywords: # opt rpm3 geom=connectivity).

Materials.

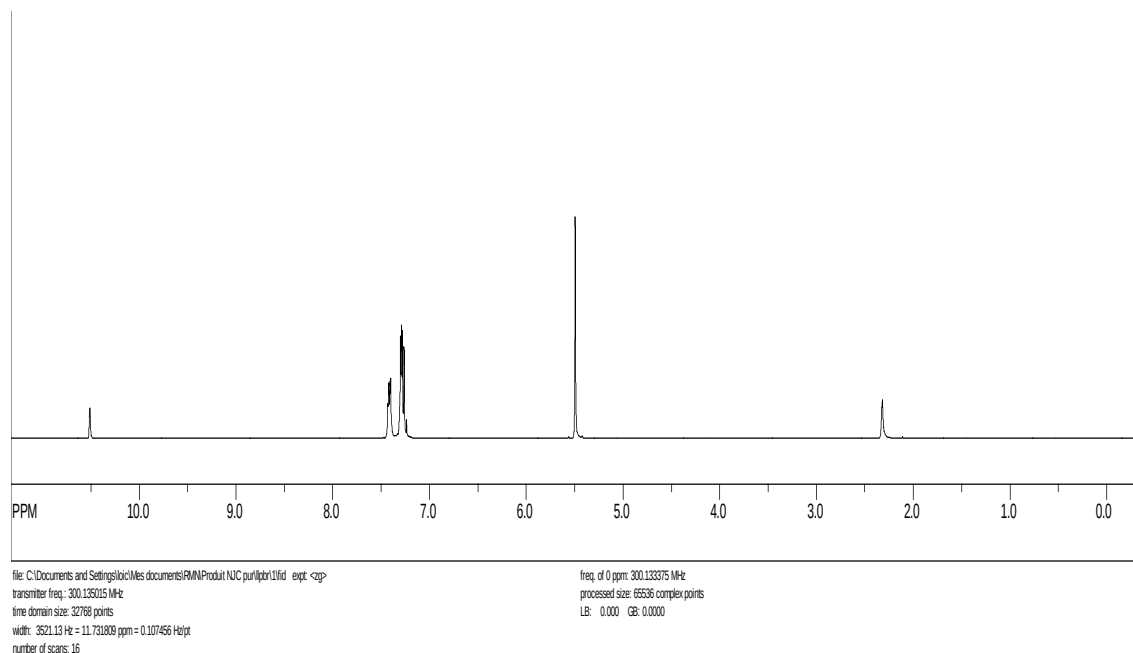
D₂O (99.95 % isotopic purity), CDCl₃ and all other chemicals were purchased and used without further purification. Anhydrous solvents (Toluene) were dried and deoxygenated.

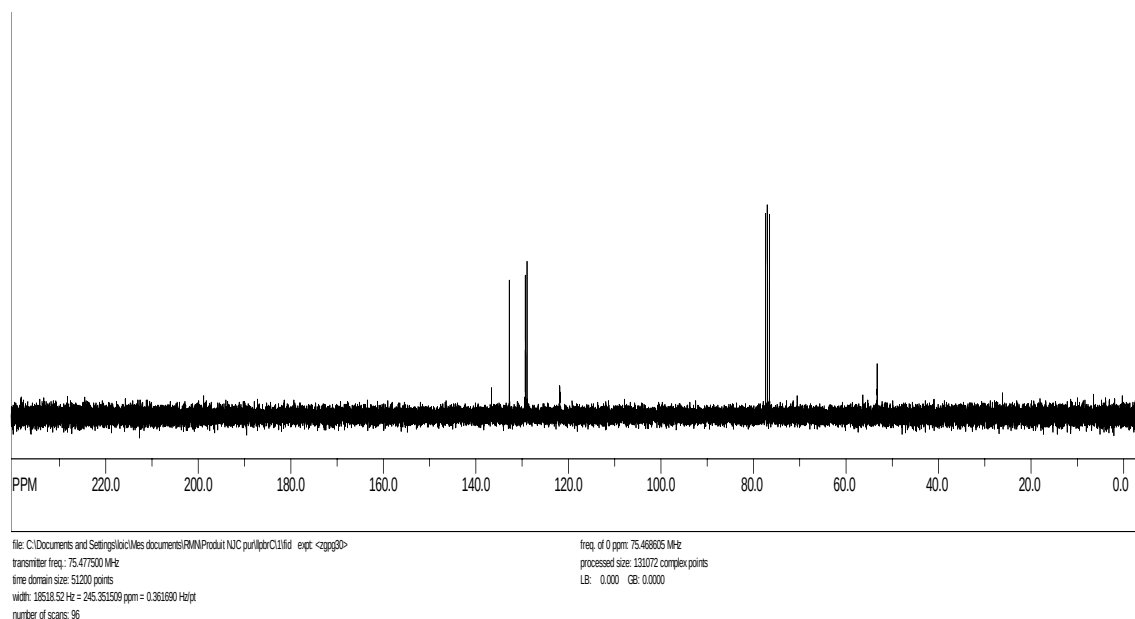
Synthesis of 1,3-dibenzylimidazolium bromide [1][Br].



A dry flask (250mL), equipped with a magnetic stir bar and a septum-inlet for nitrogen, was charged with a solution of (bromomethyl)benzene (1.44 g, 8.42 mmol) in toluene (50mL). In a Schlenk, a solution of 1-benzylimidazole in toluene (1.60g, 10.1 mmol) was added to the other flask in a dropwise fashion by cannulation at 0°C. The reaction mixture was stirred for 20 min minutes to 0°C at room temperature, then filtered under gravity. The solid are washed with diethylether to remove unreacted 1-benzylimidazole. The white solid was dried overnight at 120°C in a vacuum. The product was stored under dry nitrogen (2.6g, 95%).

¹H NMR (300 MHz, CDCl₃, 20°C, TMS): δ = 5.5 ppm (s, 4H, 6), 7.2-7.3 ppm (m, 2H, 4, 5), 7.3-7.4 ppm (m, 10H; H_{aro}), 10.5 ppm (s, 1H; 2); ¹³C NMR (75 MHz, CDCl₃, 20°C): δ = 53.2 ppm (6), 121.8 ppm (4/5), 128.9 ppm (C_m), 129.3 ppm (C_o), 129.3 ppm (C_p), 132.7 ppm (2), 136.6 ppm (C_{aro}-CH₂). Anal. Calc. for C₁₇H₁₇BrN₂ · 2H₂O: C, 55.90%; H, 5.79%; N, 7.67%. Found: C, 54.84%; H, 5.77%; N, 7.87%. MP: 85°C.

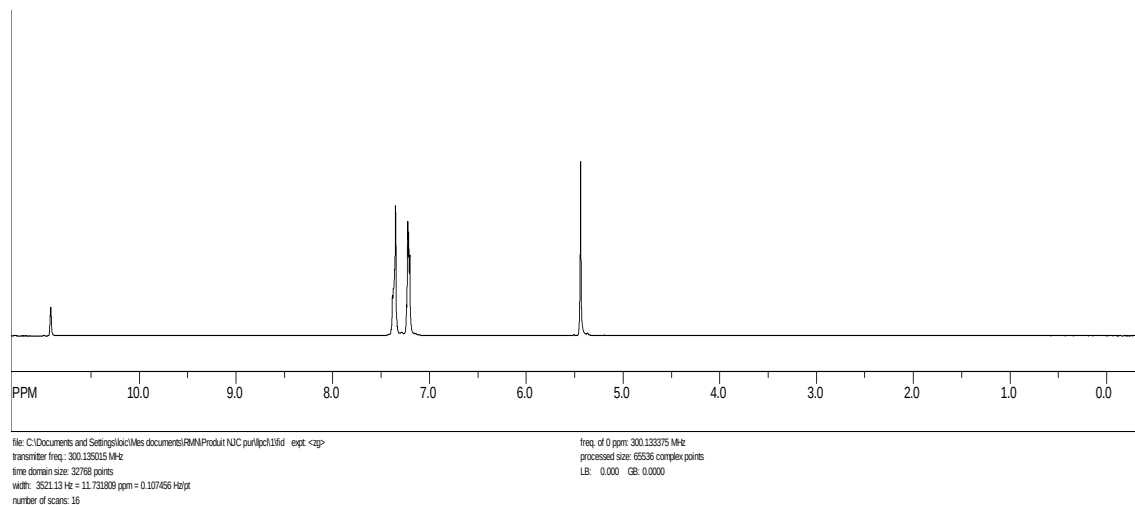


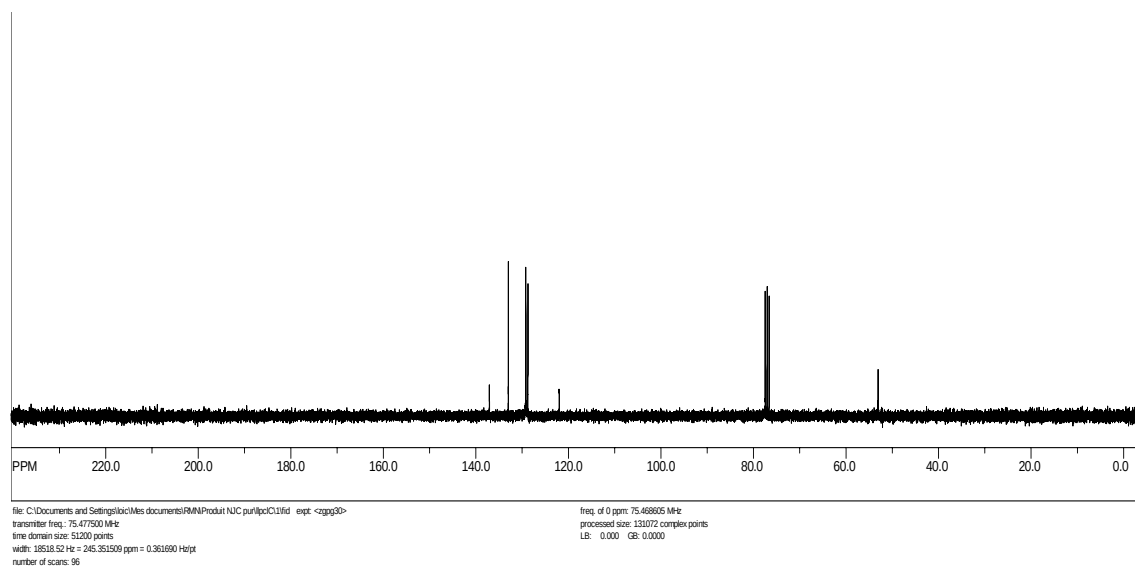


Synthesis of 1,3-dibenzylimidazolium chloride [1][Cl].

The procedure is identical to the one which presented above.

^1H NMR (300 MHz, CDCl_3 , 20°C , TMS): δ = 5.4 (s, 4H, 6), 7.2-7.3 ppm (m, 7H, H_{aro} , 4, 5), 7.3-7.4 ppm (m, 7H, H_{aro}), 10.9 ppm (s, 1H, 2); ^{13}C NMR (75 MHz, CDCl_3 , 20°C): δ = 53.0 ppm (6), 122.0 ppm (4/5), 128.7 ppm (C_m), 129.1 ppm (C_o), 129.2 ppm (C_p), 133.0 ppm (2), 137.0 ppm ($\text{C}_{\text{aro-CH}_2}$). Anal. Calc. for $\text{C}_{17}\text{H}_{17}\text{ClN}_2$: C, 70.11%; H, 6.13%; N, 9.76%. Found: C, 69.89%; H, 6.01%; N, 9.75%. MP: 63°C .

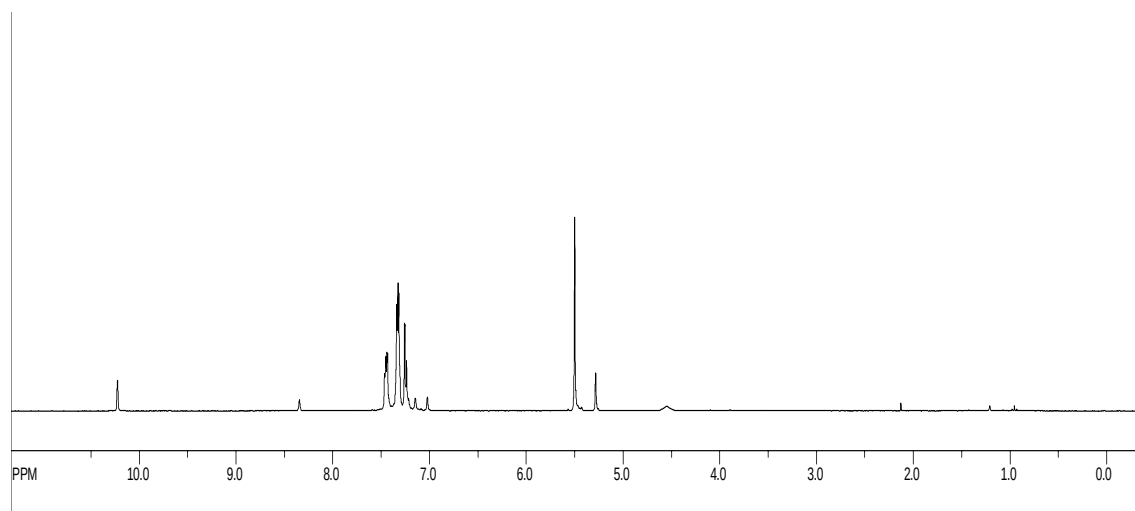




Synthesis of 1,3-dibenzylimidazolium iodide [1][I].

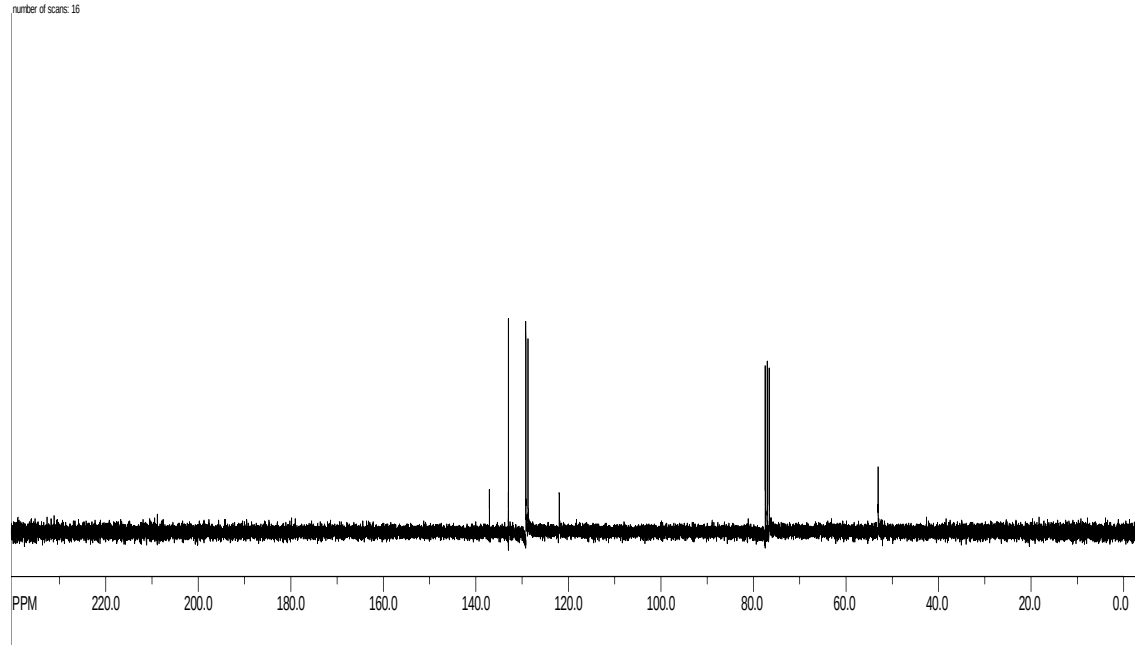
The procedure is identical to the one which presented above.

^1H NMR (300 MHz, CDCl_3 , 20°C, TMS): δ 5.5 ppm (s, 4H, 6), 7.2-7.5 ppm (m, 12H, H_{aro} , 4, 5), 10.2 ppm (s, 1H, 2); ^{13}C NMR (75 MHz, CDCl_3 , 20°C): δ 53.4 ppm (6), 121.6 ppm (4/5), 129.0 ppm (C_m), 129.4 ppm (C_o), 129.5 ppm (C_p), 132.3 ppm (2), 136.0 ppm ($\text{C}_{\text{aro-CH}_2}$).
 Anal. Calc. for $\text{C}_{17}\text{H}_{17}\text{IN}_2$: C, 54.56%; H, 4.04%; N, 7.49. Found: C, 54.28%; H, 4.86%; N, 8.53%. MP < 25°C.



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 number of scans: 16

freq. of 0 ppm: 300.133375 MHz
 processed size: 65536 complex points
 LB: 0.000 GB: 0.0000



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 number of scans: 96

freq. of 0 ppm: 75.468605 MHz
 processed size: 131072 complex points
 LB: 0.000 GB: 0.0000

CRYSTAL AND MOLECULAR STRUCTURE OF [1][Br]

Table 1. Crystal data and structure refinement for C₁₇ H₁₉ Br N₂ O.

Empirical formula	C ₁₇ H ₁₉ Br N ₂ O
Formula weight	347.25
Temperature	150(2)K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	a = 12.9952(4) Å α = 90° b = 11.6158(3) Å β = 91.6770(10)° c = 10.5961(3) Å γ = 90°
Volume	1598.79(8)Å ³
Z	4
Density (calculated)	1.443 g/cm ³
Absorption coefficient	3.500 mm ⁻¹
F(000)	712
Crystal size	0.20 x 0.18 x 0.16 mm
Theta range for data collection	3.40 to 73.05°
Index ranges	-14 ≤ h ≤ 15, -14 ≤ k ≤ 14, -12 ≤ l ≤ 13
Reflections collected	21728
Independent reflections	3146 [R _{int} = 0.036]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.470 and 0.568
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3146 / 3 / 197
Goodness-of-fit on F ²	1.246
Final R indices [I>2σ(I)]	R ₁ = 0.0453, wR ₂ = 0.1062
R indices (all data)	R ₁ = 0.0455, wR ₂ = 0.1063
Extinction coefficient	0.0457(13)
Largest diff. peak and hole	0.489 and -1.266 e/Å ³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for C17 H19 Br N2 O.

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Br(1)	7667(1)	8584(1)	215(1)	29(1)
O(1)	8315(1)	6378(1)	-1644(2)	39(1)
N(1)	7812(1)	5174(1)	1031(1)	20(1)
N(3)	9252(1)	5402(1)	2066(1)	21(1)
C(2)	8295(1)	5798(2)	1920(2)	23(1)
C(4)	9386(1)	4492(2)	1244(2)	22(1)
C(5)	8479(1)	4347(2)	604(2)	22(1)
C(6)	6746(1)	5358(2)	559(2)	25(1)
C(7)	5983(1)	4587(2)	1204(2)	23(1)
C(8)	5603(2)	3606(2)	599(2)	26(1)
C(9)	4875(2)	2913(2)	1175(2)	33(1)
C(10)	4525(2)	3213(2)	2352(2)	38(1)
C(11)	4903(2)	4180(2)	2962(2)	41(1)
C(12)	5640(2)	4865(2)	2395(2)	33(1)
C(13)	10033(2)	5858(2)	2966(2)	25(1)
C(14)	10796(2)	6655(2)	2350(2)	21(1)
C(15)	10467(1)	7519(2)	1524(2)	23(1)
C(16)	11183(2)	8274(2)	1020(2)	27(1)
C(17)	12221(2)	8171(2)	1338(2)	29(1)
C(18)	12551(2)	7307(2)	2163(2)	29(1)
C(19)	11843(2)	6542(2)	2668(2)	24(1)

Table 3. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for C17 H19 Br N2 O.

	x	y	z	Ueq
H(1A)	8068(18)	6928(15)	-1238(19)	58
H(1B)	8050(20)	6440(20)	-2373(10)	58
H(2)	8006	6420	2372	27
H(4)	9996	4054	1148	26
H(5)	8329	3782	-23	26
H(6A)	6709	5208	-361	30
H(6B)	6554	6172	695	30
H(8)	5841	3406	-211	31
H(9)	4621	2240	761	40
H(10)	4021	2750	2741	45
H(11)	4662	4379	3771	49
H(12)	5907	5523	2824	39
H(13A)	10412	5207	3363	30
H(13B)	9684	6283	3641	30
H(15)	9757	7596	1303	28
H(16)	10957	8862	453	32
H(17)	12704	8689	995	35
H(18)	13262	7236	2384	34
H(19)	12071	5947	3224	28

Table 4. Anisotropic parameters ($\text{\AA}^2 \times 10^3$) for C17 H19 Br N2 O.

The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$$

	U11	U22	U33	U23	U13	U12
Br(1)	33(1)	30(1)	25(1)	-1(1)	3(1)	-2(1)
O(1)	38(1)	47(1)	31(1)	-1(1)	1(1)	15(1)
N(1)	20(1)	21(1)	20(1)	1(1)	2(1)	-1(1)
N(3)	21(1)	22(1)	20(1)	-1(1)	2(1)	-3(1)
C(2)	23(1)	21(1)	25(1)	-2(1)	2(1)	0(1)
C(4)	24(1)	21(1)	20(1)	0(1)	5(1)	0(1)
C(5)	26(1)	21(1)	20(1)	-2(1)	4(1)	-1(1)
C(6)	21(1)	26(1)	28(1)	6(1)	-2(1)	-1(1)
C(7)	18(1)	24(1)	26(1)	4(1)	-2(1)	1(1)
C(8)	22(1)	28(1)	28(1)	2(1)	-3(1)	0(1)
C(9)	26(1)	31(1)	42(1)	6(1)	-8(1)	-5(1)
C(10)	22(1)	41(1)	51(1)	17(1)	6(1)	-2(1)
C(11)	43(1)	42(1)	38(1)	6(1)	17(1)	5(1)
C(12)	38(1)	28(1)	33(1)	-1(1)	6(1)	2(1)
C(13)	25(1)	30(1)	20(1)	-1(1)	-2(1)	-5(1)
C(14)	22(1)	23(1)	18(1)	-6(1)	1(1)	-2(1)
C(15)	24(1)	26(1)	21(1)	-5(1)	1(1)	2(1)
C(16)	37(1)	23(1)	19(1)	-3(1)	2(1)	-1(1)
C(17)	33(1)	31(1)	23(1)	-7(1)	6(1)	-11(1)
C(18)	22(1)	38(1)	26(1)	-8(1)	-1(1)	-6(1)
C(19)	25(1)	27(1)	20(1)	-4(1)	-2(1)	0(1)

Table 5. Bond lengths [Å] and angles [°] for C17 H19 Br N2 O

N(1)-C(2)	1.331(2)
N(1)-C(5)	1.379(2)
N(1)-C(6)	1.475(2)
N(3)-C(2)	1.331(3)
N(3)-C(4)	1.384(2)
N(3)-C(13)	1.471(2)
C(4)-C(5)	1.353(3)
C(6)-C(7)	1.514(3)
C(7)-C(12)	1.389(3)
C(7)-C(8)	1.391(3)
C(8)-C(9)	1.397(3)
C(9)-C(10)	1.384(4)
C(10)-C(11)	1.379(4)
C(11)-C(12)	1.394(3)
C(13)-C(14)	1.517(3)
C(14)-C(15)	1.391(3)
C(14)-C(19)	1.398(3)
C(15)-C(16)	1.395(3)
C(16)-C(17)	1.386(3)
C(17)-C(18)	1.391(3)
C(18)-C(19)	1.397(3)
C(2)-N(1)-C(5)	108.94(15)
C(2)-N(1)-C(6)	125.47(15)
C(5)-N(1)-C(6)	125.57(16)
C(2)-N(3)-C(4)	108.98(15)
C(2)-N(3)-C(13)	125.14(16)
C(4)-N(3)-C(13)	125.87(16)
N(1)-C(2)-N(3)	108.26(16)
C(5)-C(4)-N(3)	106.66(16)
C(4)-C(5)-N(1)	107.16(16)
N(1)-C(6)-C(7)	112.49(15)
C(12)-C(7)-C(8)	119.32(18)
C(12)-C(7)-C(6)	120.37(18)
C(8)-C(7)-C(6)	120.30(18)
C(7)-C(8)-C(9)	120.5(2)
C(10)-C(9)-C(8)	119.5(2)
C(11)-C(10)-C(9)	120.4(2)
C(10)-C(11)-C(12)	120.1(2)
C(7)-C(12)-C(11)	120.1(2)
N(3)-C(13)-C(14)	112.82(15)
C(15)-C(14)-C(19)	119.85(18)
C(15)-C(14)-C(13)	121.25(17)
C(19)-C(14)-C(13)	118.84(18)
C(14)-C(15)-C(16)	119.90(18)
C(17)-C(16)-C(15)	120.52(19)
C(16)-C(17)-C(18)	119.67(18)
C(17)-C(18)-C(19)	120.36(18)
C(18)-C(19)-C(14)	119.69(19)

Table 6. Torsion angles [°] for C17 H19 Br N2 O.

C(5)-N(1)-C(2)-N(3)	0.5(2)
C(6)-N(1)-C(2)-N(3)	-178.03(15)
C(4)-N(3)-C(2)-N(1)	-0.1(2)
C(13)-N(3)-C(2)-N(1)	-179.65(16)
C(2)-N(3)-C(4)-C(5)	-0.3(2)
C(13)-N(3)-C(4)-C(5)	179.18(16)
N(3)-C(4)-C(5)-N(1)	0.7(2)
C(2)-N(1)-C(5)-C(4)	-0.8(2)
C(6)-N(1)-C(5)-C(4)	177.82(15)
C(2)-N(1)-C(6)-C(7)	-96.2(2)
C(5)-N(1)-C(6)-C(7)	85.4(2)
N(1)-C(6)-C(7)-C(12)	79.5(2)
N(1)-C(6)-C(7)-C(8)	-101.7(2)
C(12)-C(7)-C(8)-C(9)	0.8(3)
C(6)-C(7)-C(8)-C(9)	-177.96(18)
C(7)-C(8)-C(9)-C(10)	0.5(3)
C(8)-C(9)-C(10)-C(11)	-1.0(3)
C(9)-C(10)-C(11)-C(12)	0.2(4)
C(8)-C(7)-C(12)-C(11)	-1.5(3)
C(6)-C(7)-C(12)-C(11)	177.2(2)
C(10)-C(11)-C(12)-C(7)	1.0(4)
C(2)-N(3)-C(13)-C(14)	-100.4(2)
C(4)-N(3)-C(13)-C(14)	80.2(2)
N(3)-C(13)-C(14)-C(15)	46.5(2)
N(3)-C(13)-C(14)-C(19)	-136.29(17)
C(19)-C(14)-C(15)-C(16)	-0.2(3)
C(13)-C(14)-C(15)-C(16)	176.90(17)
C(14)-C(15)-C(16)-C(17)	-0.2(3)
C(15)-C(16)-C(17)-C(18)	0.3(3)
C(16)-C(17)-C(18)-C(19)	0.1(3)
C(17)-C(18)-C(19)-C(14)	-0.6(3)
C(15)-C(14)-C(19)-C(18)	0.7(3)
C(13)-C(14)-C(19)-C(18)	-176.55(17)

Table 7. Bond lengths [Å] and angles [°] related to the hydrogen bonding for C17 H19 Br N2 O.

D-H	..A	d(D-H)	d(H..A)	d(D..A)	<DHA
O(1)-H(1A)	BR1	0.8399(1)	2.528(5)	3.3554(16)	169(2)
O(1)-H(1B)	BR1#1	0.840(1)	2.590(7)	3.4092(18)	165(2)

Symmetry transformations used to generate equivalent atoms:

#1 x, -y+3/2, z-1/2

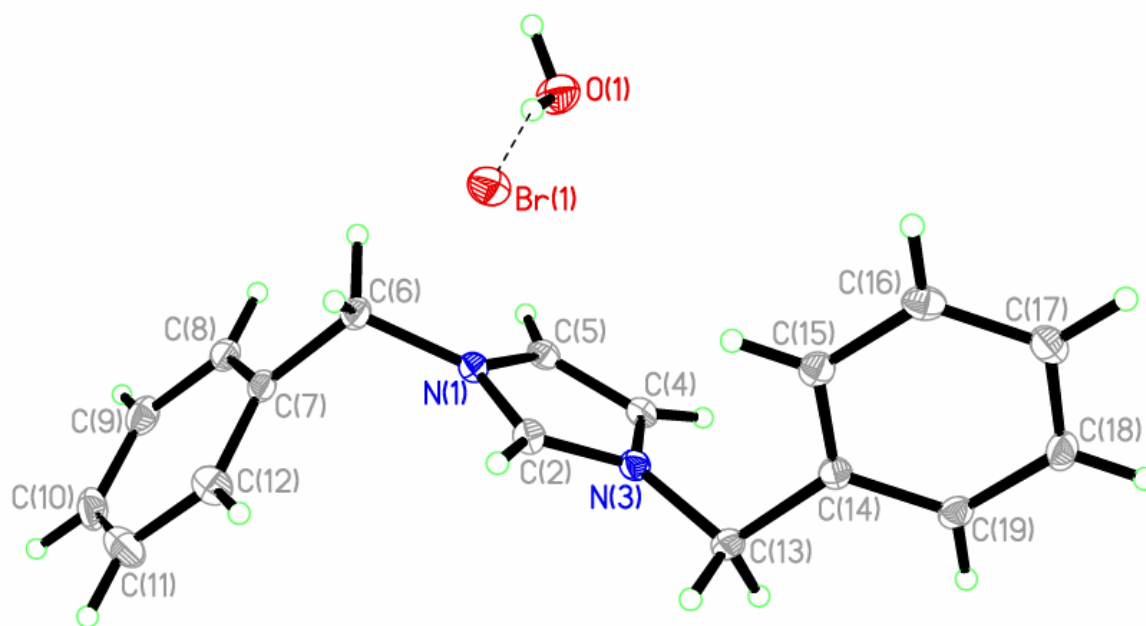


Figure S1 ORTEP view of the **[1][Br]** compound with the numbering scheme adopted. Ellipsoids drawn at 50% probability level. Hydrogen atoms are represented by sphere of arbitrary size.

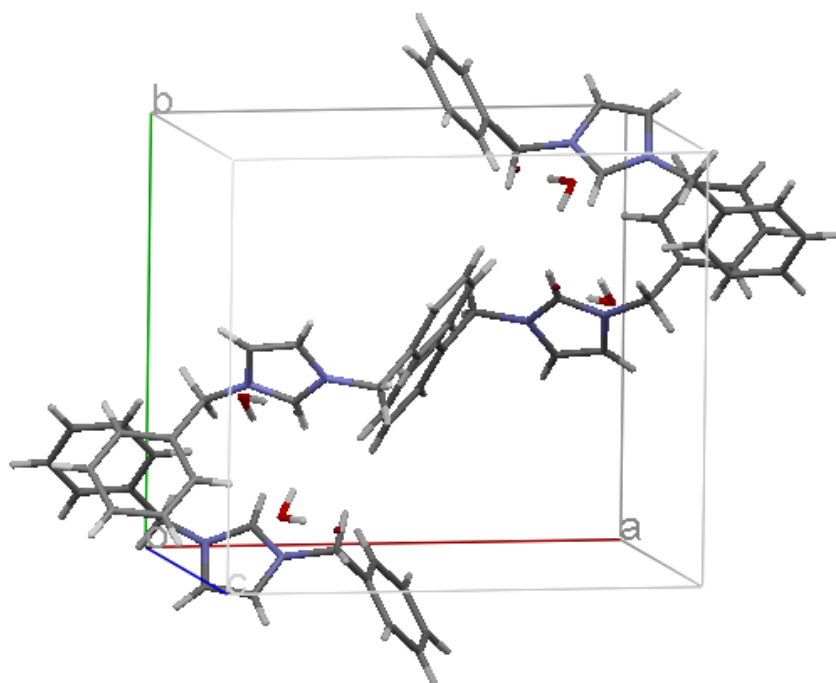


Figure S2 Unit cell of **[1][Br]** obtained by X-ray diffraction structure analysis.

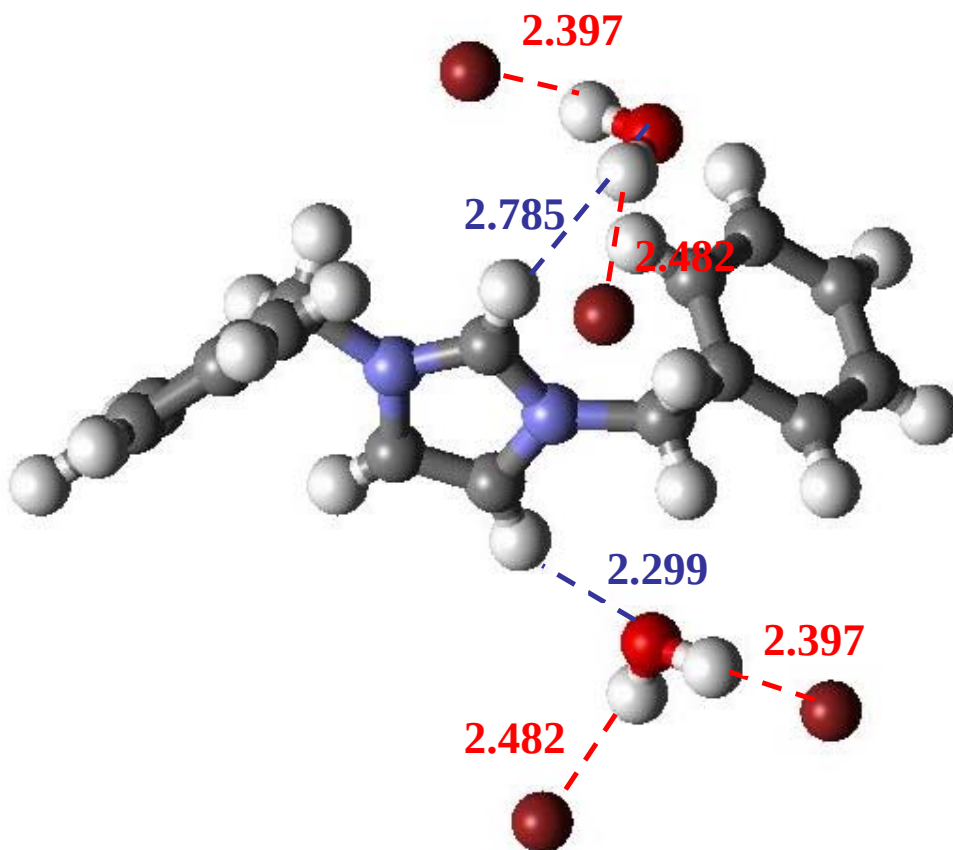


Figure S3 The cation coordination environment in **[1][Br]** obtained by X-ray diffraction structure analysis.

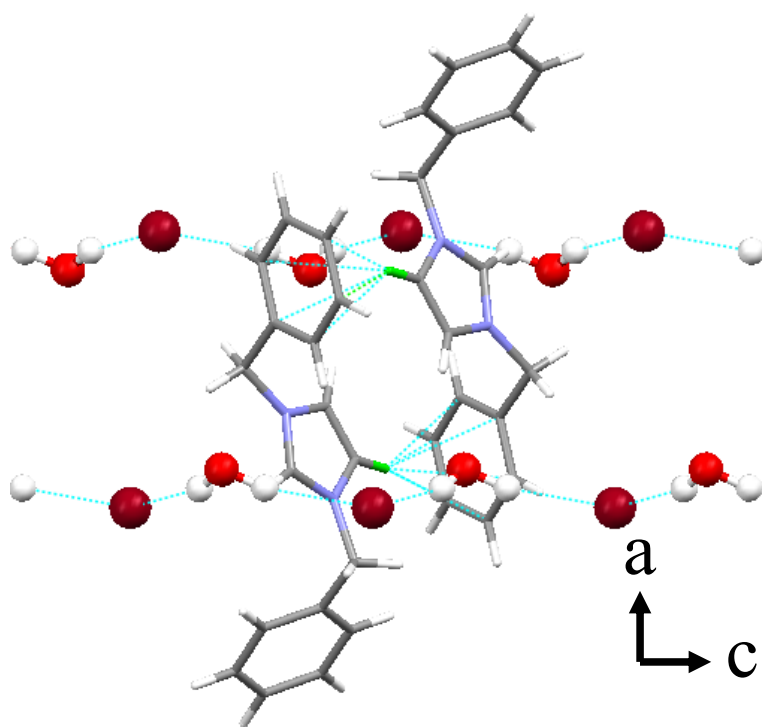


Figure S4 Another view of [1][Br] dimer obtained by X-ray diffraction analysis.

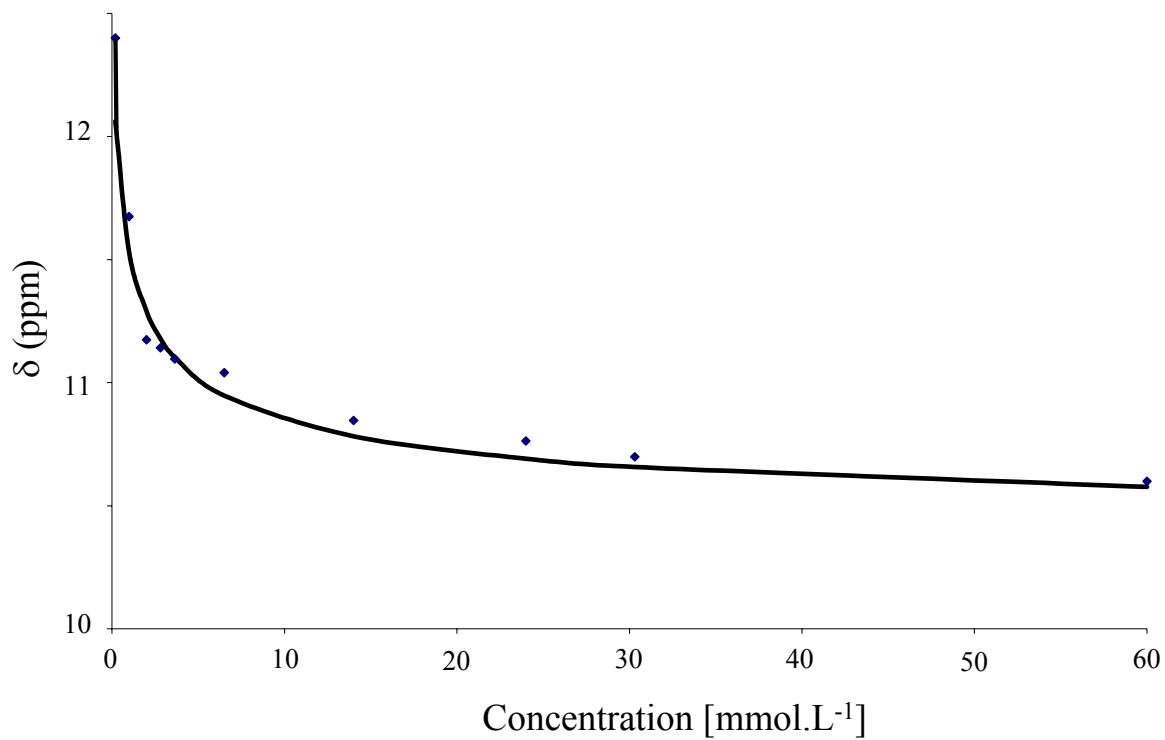


Figure S5 Binding isotherms for the H₂ of imidazolium ring of **[1][Br]** in CDCl₃ at 298K. The solid lines show the curve fitting for a 1:1 dimerisation ($K_{\text{dim}} = 700 \text{ M}^{-1}$).

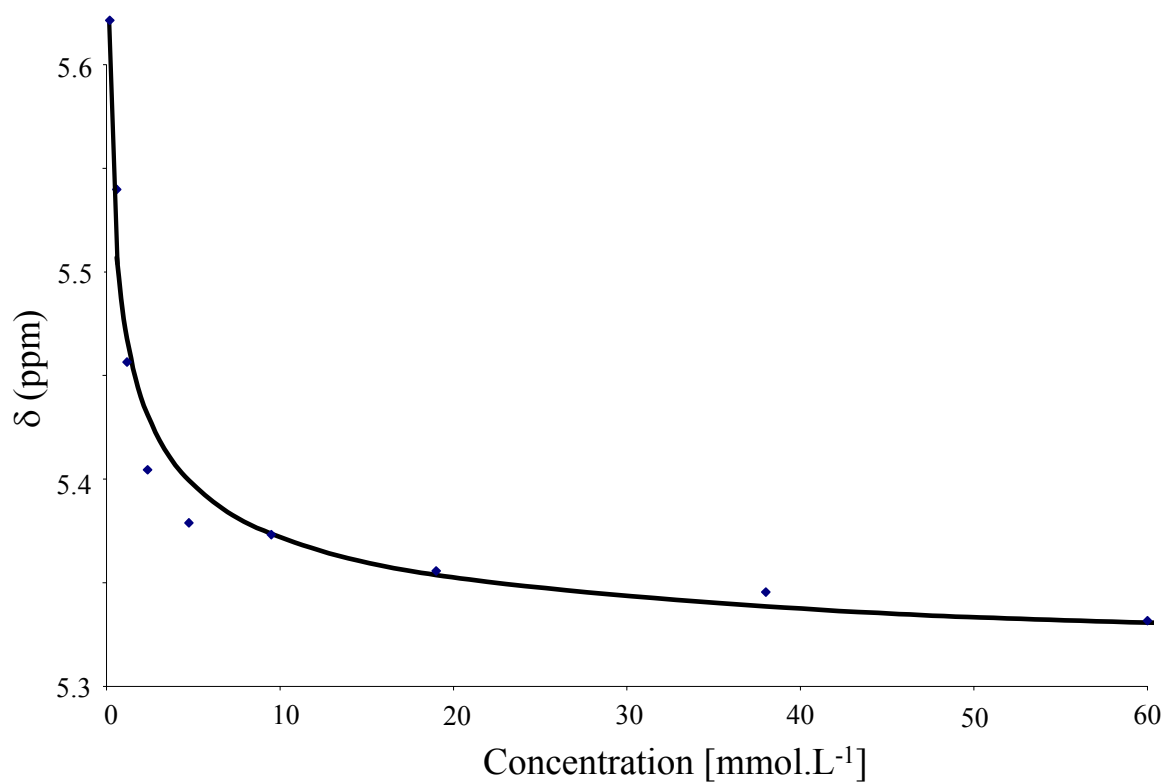


Figure S6 Binding isotherms for the H₂ of imidazolium ring of **[1][Br]** in D₂O at 298K. The solid lines show the curve fitting for a 1:1 dimerisation ($K_{\text{dim}} = 790 \text{ M}^{-1}$).

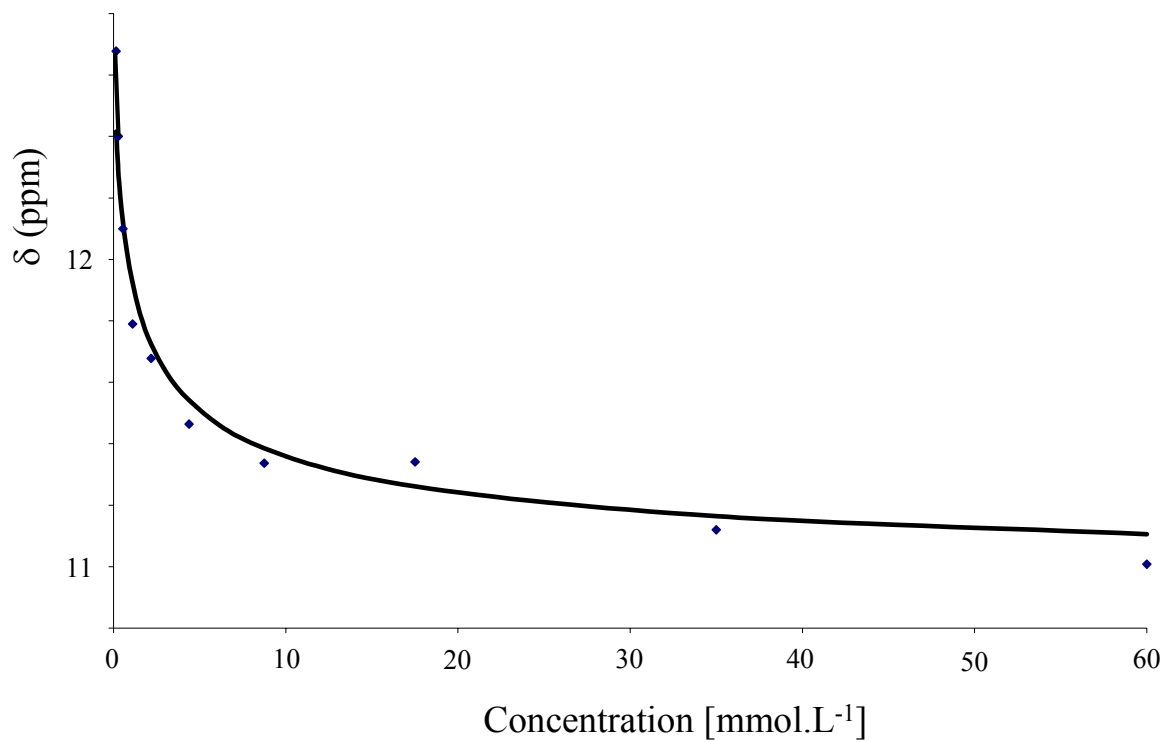


Figure S7 Binding isotherms for the H_2 of imidazolium ring of **[1][Cl]** in CDCl_3 at 298K. The solid lines show the curve fitting for a 1:1 dimerisation ($K_{\text{dim}} = 500 \text{ M}^{-1}$).

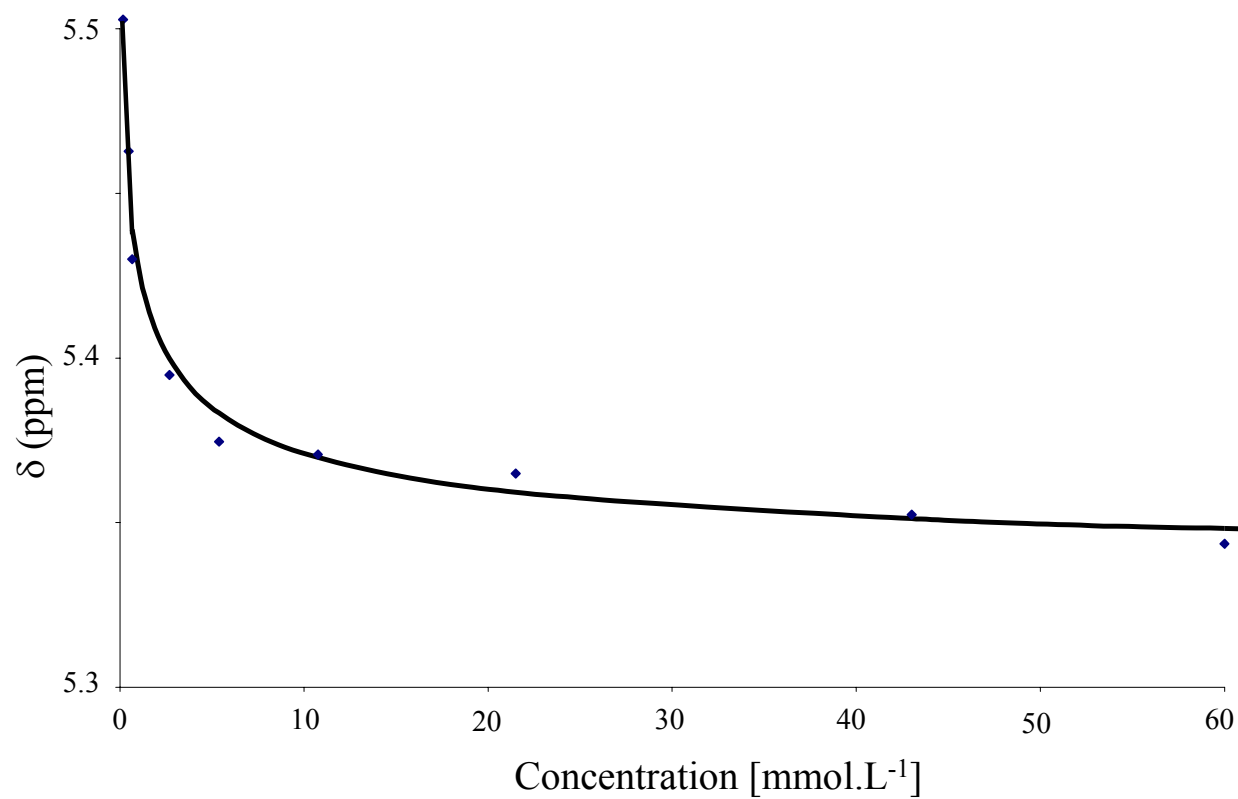


Figure S8 Binding isotherms for the H₂ of imidazolium ring of **[1][Cl]** in D₂O at 298K. The solid lines show the curve fitting for a 1:1 dimerisation ($K_{\text{dim}} = 640 \text{ M}^{-1}$).

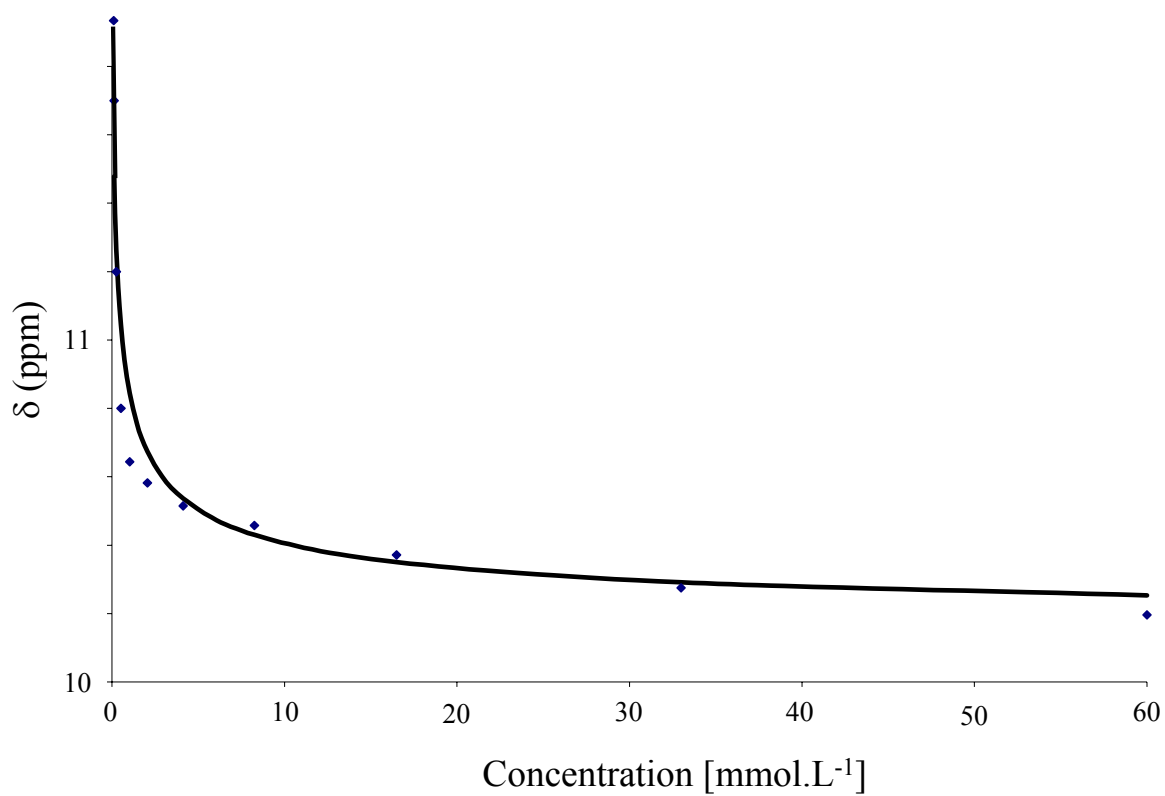
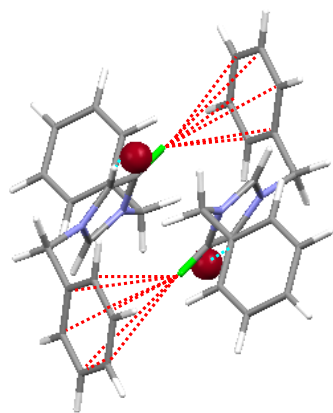
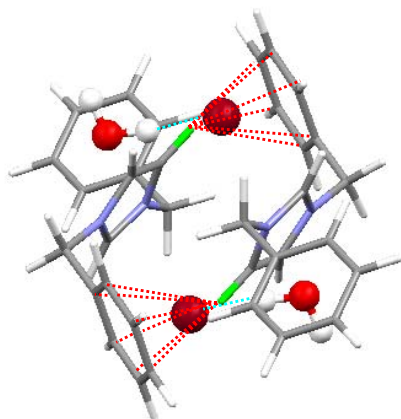


Figure S9 Binding isotherms for the H₂ of imidazolium ring of **[1][I]** in CDCl₃ at 298K. The solid lines show the curve fitting for a 1:1 dimerisation ($K_{\text{dim}} = 2100 \text{ M}^{-1}$).

PM3 without water



PM3 with water



Crystalline structure

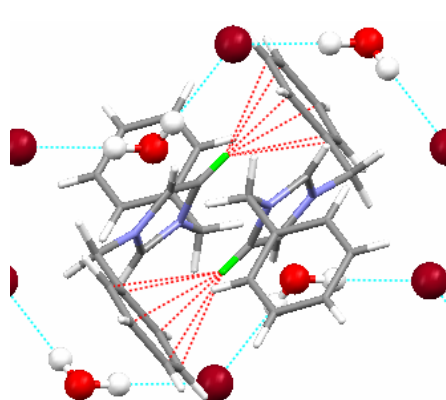


Figure S10 Dimer structure obtained after PM3 calculation (restricted shell) for **[1][Br]** without water molecules (distance H5 (green)/phenyl center approximately: 3 Å) and comparison with two water molecules and the crystalline structure. (Gaussian 03®, Restricted Shell, PM3, keywords: # opt rpm3 geom=connectivity).