C-H – π Interactions in 1-*n*-Butyl-3-methylimidazolium Tetraphenylborate Molten Salt: Solid and Solution Structures

Jairton Dupont,*[a] Paulo A. Z. Suarez,[a] Roberto F. De Souza,[a] Robert A. Burrow,[b] and Jean-Pierre Kintzinger*[c]

Abstract: The crystal structure of 1-*n*-butyl-3-methylimidazolium tetraphenylborate molten salt (**1**) shows C-H – π interactions between the hydrogens of the imidazolium cation and the phenyl rings of the tetraphenylborate anion. The imidazolium ring is surrounded by three tetraphenylborate anions that are connected with the same cation by C-H – π (phenyl rings) interactions. The nearest inter-ion interaction is found between the N-CH-N proton of the cation and the B-phenyl centroid (2.349 Å) with a nearly T-shaped geometry. The inter-ionic solution structure of **1** has been investigated by the detection of inter-ionic contacts in ^{1}H NOESY NMR spectra between the protons of the cation and the anion. The ^{1}H-NMR spectra of molten salt **1** is almost independent of its concentration in [D_6]DMSO solution, the imidazolium proton chemical shifts are in the expected region and there are no observable NOE effects between the protons of the cation with those of the anion, indicating that **1** behaves in [D_6]DMSO as a solvent-separated ion pair. In $CDCl_3$ the ^{1}H-NMR spectra of **1** are concentration dependent and all the imidazolium protons are shielded as compared with those observed in [D_6]DMSO. Moreover, the ^{1}H NOESY NMR spectra show all the peaks affected by the interaction between the protons of the imidazolium cation and those of the anion, indicating that in $CDCl_3$ **1** possesses a contact ion pair structure. The NCHN proton of the cation exhibits the greatest shielding (up to −4.5 ppm), an indication of the existence of C-H – π interactions, even in solution. The calculated distance of this proton to the phenyl centroid is 2.3 Å for a C-H – π angle of 180°. The apparent volumes for the cation and anion, calculated from the measured ^{13}C-NMR relaxation times, increase from 38 and 140 Å^3 in [D_6]DMSO to 360 and 600 Å^3 in $CDCl_3$, respectively; this indicates the formation of floating aggregates of the type $(\mathbf{1})_n$ in $CDCl_3$ via weak hydrogen bonds, with increasing concentration.

Keywords: ionic liquids · molten salts · NMR spectroscopy · X-ray absorption spectroscopy

Introduction

There is a considerable and increasing interest in various types of weak hydrogen bonds in the fields of molecular recognition, crystal engineering, and supramolecular chemistry.[1] In this respect, it has been repeatedly demonstrated from gas phase experiments, crystal structure analyses, solid state IR measurements, and theoretical calculations, that aromatic rings and other π bonds can interact with X−H bonds (usually X = O, N, and halide), typically with hydrogen-bond properties (π-hydrogen bonds).[1, 2]

It is also well recognized that hydrogen bonds play an important role in the organization and structure of ionic liquids (molten salts), in both the solid and liquid phase, especially those derived from the 1,3-dialkylimidazolium cation. It is assumed that the structure of these ionic liquids should not be considered as statistical aggregates of anions and cations but instead as three-dimensional networks of anions and cations, linked together by hydrogen bonds. Since direct structural information of these materials in the liquid phase or in solution is difficult to obtain, they are usually studied indirectly assuming that the solid state and the liquid phase/solution structures are the same.[3] These compounds have received special attention due to their distinct physicochemical properties and potential applications in electrochemistry,[4] two-phase organometallic catalysis,[5] as solvents for organic synthesis[6] and extraction technology,[7] and as liquid crystals.[8]

[a] J. Dupont, P. A. Z. Suarez, R. F. De Souza
Laboratory of Molecular Catalysis
Instituto de Química, UFGRS, Av. Bento Gonçalves
95000, CEP 91501-970, Porto Alegre, RS (Brazil)
E-mail: dupont@if.ufrgs.br

[b] R. A. Burrow
Departamento de Química
Universidade Federal de Santa Maria, Santa Maria, RS (Brazil)

[c] J.-P. Kintzinger
Laboratoire de RMN et de Modelisation Moléculaire
UMR 7510, ULP-CNRS-BRUKER, 4, rue Blaise Pascal
Strasbourg, 67000 (France)

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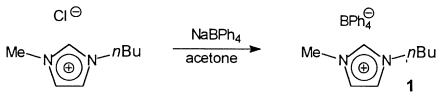
While investigating the synthesis and applications of various ionic liquids based on the 1-*n*-butyl-3-methylimidazolium cation[3f] we have prepared the tetraphenylborate analogue **1** (Scheme 1). This compound displays characteristic



Scheme 1. Synthesis of **1**.

C-H – π hydrogen bonds between the cation and anion, in both the solid state and in solution.

Results and Discussion

The reaction of 1-*n*-butyl-3-methylimidazolium chloride with an excess of sodium tetraphenylborate in acetone at room temperature produces **1** (Scheme 1) in almost quantitative yield. Compound **1** was obtained as large colorless plate-like crystals from acetone solutions at room temperature.

Abstract in Portuguese: *A estrutura cristalina do sal tetrafenilborato de 1-n-butil-3-metilimidazólio **1** mostra interações do tipo C-H – π entre os hidrogênios do cátion imidazólio e os anéis fenila do ânion tetrafluoroborato. O anel imidazólio está cercado por três ânions tetrafenilborato, os quais estão ligados ao mesmo cátion via interações C-H – π. A interação interiônica mais curta é encontrada entre o hidrogênio N-CH-N do cátion e o centróide da fenila do ânion (2,349 Å) com uma geometria aproximadamente do tipo T. A estrutura interiônica de **1** em solução foi estudada pela detecção dos contatos interiônicos em espectro de RMN de ^1H (NOESY) entre os hidrogênios do cátion e do ânion. Quando em solução de [D6]DMSO, os deslocamentos químico de ^1H do composto **1** são praticamente independentes da concentração. Os deslocamentos químicos dos hidrogênios do anel imidazólio estão na região esperada e não há efeitos tipo NOE observáveis entre os hidrogênios do cátion e os do ânion, indicando que **1** comporta-se em [D6]DMSO como um par iônico dissociado. Já em $CDCl_3$ o espectro de RMN ^1H de **1** é dependente da concentração e todos os hidrogênios do anel imidazólio estão em freqüências mais baixas que aquelas observadas em [D6]DMSO. Além disto, o espectro de ^1H RMN (NOESY) mostra todos os deslocamentos afetados por interações entre os hidrogênios do cátion imidazólio e os do ânion, indicando que em $CDCl_3$ **1** possui uma estrutura do tipo par iônico de contato. O hidrogênio N-CH-N do cátion exibe maior desblindagem (de até -4.5 ppm), indicando a existência de interações do tipo C-H – π, mesmo em solução. A distância calculada deste próton até o centróide da fenila é de 2.3 Å para um ângulo C-H – π de 180°. O volume aparente para o cátion e o ânion, calculados a partir dos tempos de relaxação do ^{13}C, aumentam de 38 Å^3 e 140 Å^3 em [D6]DMSO para 360 Å^3 e 600 Å^3 em $CDCl_3$, respectivamente, indicando a formação de agregados do tipo $(\mathbf{1})_n$ em $CDCl_3$ via ligações fracas de hidrogênio, com o incremento da concentração.*

An X-ray diffraction study of **1** shows the expected structural features for the BMI^+ cation and BPh_4 anion; all bond lengths and angles are in normal range. ORTEPs of the BMI^+ cation and BPh_4^- anion, packing diagrams, and tables of atomic coordinates, equivalent isotropic displacement parameters and selected bond lengths and angles are provided as Supporting Information. The molecules pack in alternating stacks of anions and cations with some long-range graphitic interactions between the phenyl rings on BPh_4^-. The distances between the hydrogen atoms of the BMI^+ cation and the phenyl rings of the BPh_4^- anion, however, are very close. Figure 1 shows a BMI^+ cation and its interactions to its nearest neighboring BPh_4^- anions; the distances and angles are summarized in Table 1.

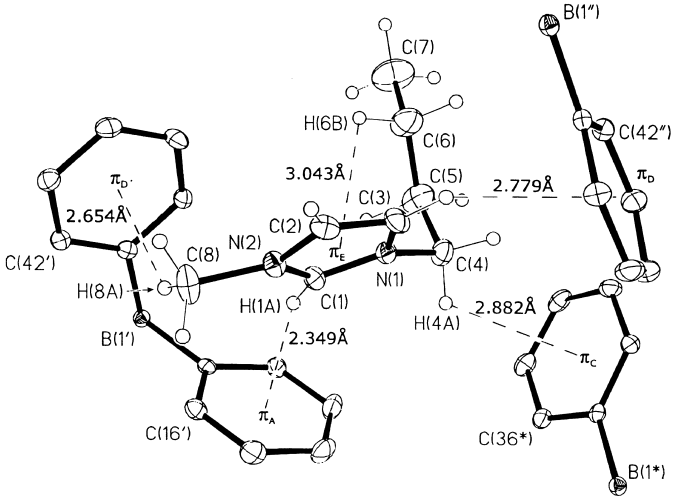


Figure 1. A view of the close contacts between the 1-*n*-butyl-3-methylimidazolium cation and BPh_4^- anion (only relevant parts shown) with hydrogen bonding distances to the phenyl ring centroid indicated. The H atoms on the phenyl rings are omitted and all anisotropic displacement ellipsoids are at the 50% probability level.

Table 1. Nearest hydrogen-π ring interactions in solid state.

C-H – ring centroid[a] interaction	H – π distance (Å)	γ[b] (°)	C-H – π angle (°)
C(1)–H(1A)···π_A	2.349	3.4	148.7
C(3)–H(3A)···π_D	2.779	17.2	155.8
C(4)–H(4A)···π_C	2.882	9.1	122.0
C(6)–H(6B)···π_E	3.043	28.7	116.3
C(8)–H(8A)···π_D	2.654	7.4	134.3

[a] The centroids are of the following atoms with symmetry operators in brackets applied: π_A C(11) to C(16) [$x-½, ½-y, z-2$]; π_C C(31) to C(36) [$2-x, -½+y, 1½+z$]; π_D C(41) to C(46) [$1-x, -½+y, 1½+z$]; $\pi_{D'}$ C(41) to C(46) [$-½+x, ½-y, 2-z$]; π_E N(1), C(1), N(2), C(2), C(3) [x, y, z]. [b] γ is defined as the angle between the normal to the plane of the π ring and the vector of the H – centroid interaction.

The distance of 2.349 Å is closer than those found for C-H – π interactions in a recent survey.[2c] The angle γ (defined in Table 1) at 3.4° is likewise very small; this indicates a nearly T-shaped geometry which, although ideal, is rarely found in the solid state.[2i] The other inter-ionic interactions are around the average, 2.79(2) Å, found in the study. An intra-ionic interaction between a hydrogen atom of the butyl group and

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the imidazolium ring also exists, although this is somewhat long.

The ^{1}H-NMR spectrum of **1** in [D$_6$]DMSO is almost independent of the concentration and the spectrum shows the expected chemical shifts for all protons. However, the ^{1}H-NMR spectra in $CDCl_3$ show significant concentration dependence. Moreover, all the chemical shifts of the imidiazolium ring protons are shielded compared with the chemical shifts observed in [D$_6$]DMSO (Figure 2).

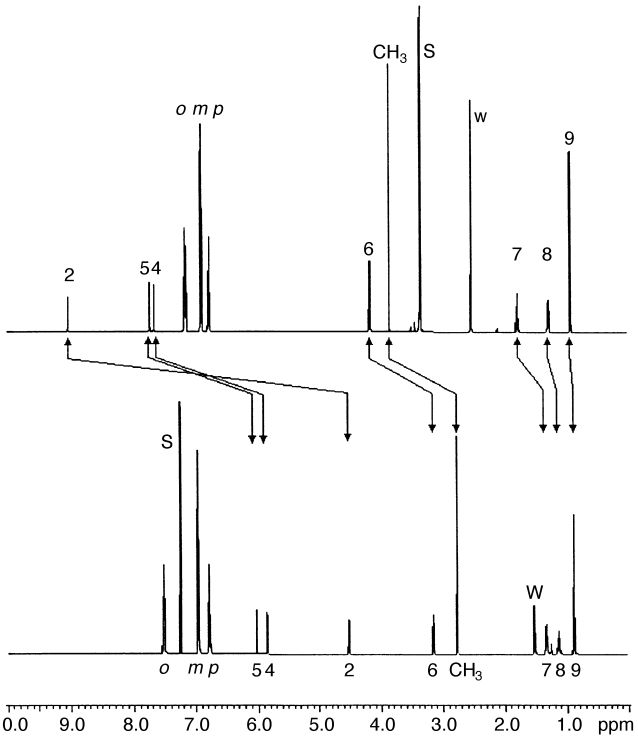
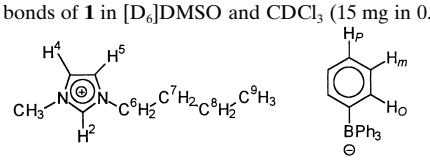


Figure 2. ^{1}H-NMR spectra of **1** in [D$_6$]DMSO (top) and $CDCl_3$ (bottom) at 500 MHz (RT, concentration: 5 mg of **1** in 0.5 mL solvent). Signals marked by S and W are for solvent and water.

In particular, the spectra displays an unexpected relative high field position for the aromatic H^2 ($\delta = 4.58$) in contrast with the low field position in [D$_6$]DMSO ($\delta = 9.12$). Figure 3 shows the chemical shift dependence of the imidazolium protons on the concentration in $CDCl_3$ solutions.

The ^{13}C-NMR spectrum of **1** (15 mg in 0.5 mL) displays almost the same chemical shifts in [D$_6$]DMSO as in $CDCl_3$; the most important shielding were observed for the carbons of the imidazolium cation from -1.9 to -1.2 ppm. Although $CDCl_3$ is less viscous than [D$_6$]DMSO (0.537 Cp for the $CDCl_3$ and 1.987 Cp for the [D$_6$]DMSO at 25 °C) the relaxation times are shorter in $CDCl_3$ than in [D$_6$]DMSO. The most important reductions (factor of 0.4) were observed for the imidazolium carbons (Table 2).

Table 2. ^{13}C-NMR chemical shifts, relaxation times and correlation times for the C–H bonds of **1** in [D$_6$]DMSO and $CDCl_3$ (15 mg in 0.5 mL).



Carbon	[D$_6$]DMSO			$CDCl_3$		
	δ ^{13}C	T_1 (s)	τ (ps)	δ ^{13}C	T_1 (s)	τ (ps)
o	135.46	0.77	36.2	135.71	0.42	66.3
m	125.24	0.77	36.2	125.94	0.43	64.8
p	121.45	0.42	66.3	122.01	0.35	79.6
C^2	136.36	1.65	16.9	134.68	0.65	42.8
C^4	123.52	1.39	20.0	122.36	0.59	47.2
C^5	122.17	1.42	19.6	120.29	0.55	50.6
CH_3	35.65	2.50	6.10	35.41	1.44	10.5
C^6	48.42	1.07	21.2	48.96	0.63	36.1
C^7	31.27	1.24	18.3	31.64	0.95	23.9
C^8	18.70	1.86	12.2	19.40	1.68	13.5
C^9	13.20	2.55	5.90	13.42	2.67	5.70

The ^{1}H NMR NOESY spectrum of **1** in [D$_6$]DMSO (5 mg in 0.5 mL) shows all the expected peaks due to the atoms in close proximity within the same ion fragment. However, in $CDCl_3$ at the same concentration, the spectrum shows additional peaks arising from cation–anion interactions (Figure 4).

The *N*-methyl protons, the N-CH^2 protons and H^2, H^4, and H^5 of the imidazolium cation produce a nuclear Overhauser effect with the H$_o$, H$_m$, and H$_p$ of the anion. These effects persist when the concentration is decreased to 0.5 mg in 0.5 mL or increased to 15 mg in 0.5 mL. The most intense NOE effects are detected between H^2 of the cation and H$_o$ of the anion (Figure 4).

The ^{1}H-NMR chemical shifts and the absence of effects between the protons of the anion and cation observed in the ^{1}H NMR NOESY spectrum in [D$_6$]DMSO indicate that **1** possesses a solvent-separated ion-pair structure. In contrast, in $CDCl_3$ the observed shielding for all imidazolium proton chemical shifts as well as the NOE effects observed between the protons of the cation and anion are strong indications that **1** behaves as a contact ion pair. The greater shielding observed for H^2 (-4.5 ppm) compared with that for H^4 and H^5 (-1.6 ppm) of the imidazolium cation might result from a C-H–π interaction between H^2 and one of the phenyl rings of the anion. For an arrangement similar to that observed in the crystal structure (Figure 5) the contribution to the chemical shift of H^2 due to the ring

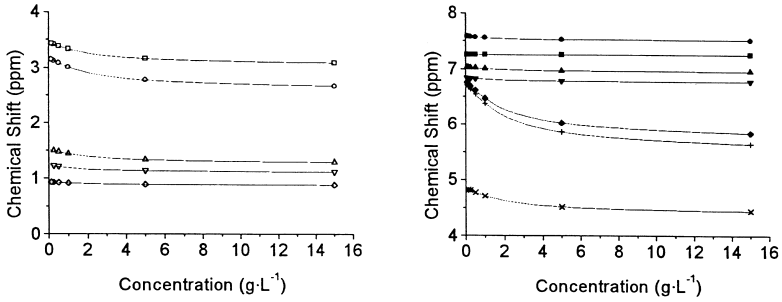


Figure 3. Variation of ^{1}H-NMR chemical shifts of the imidazolium cation with the concentration in $CDCl_3$. (◇) H^9; (▽) H^8; (△) H^7; (○) H^{10}; (□) H^6; (×) H^2; (+) H^4; (◆) H^5; (▼) H$_p$; (▲) H$_m$; (●) H$_o$; (■) $CDCl_3$.

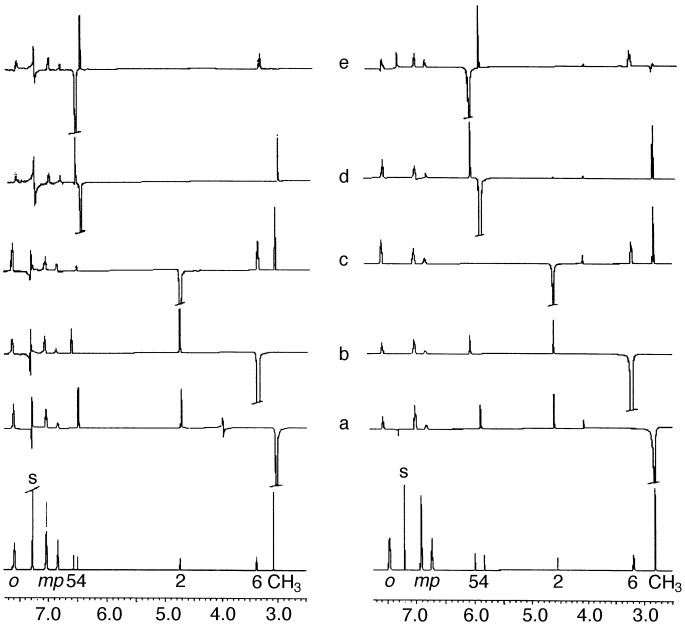


Figure 4. F_2 sections through the NOESY spectrum (500 MHz), at the chemical shifts of H^{10} a), H^6 b), H^2 c), H^4 d), and H^5 e) at two different concentrations in $CDCl_3$ (left: 0.5 mg of **1** in 0.5 mL; right: 5 mg of **1** in 0.5 mL).

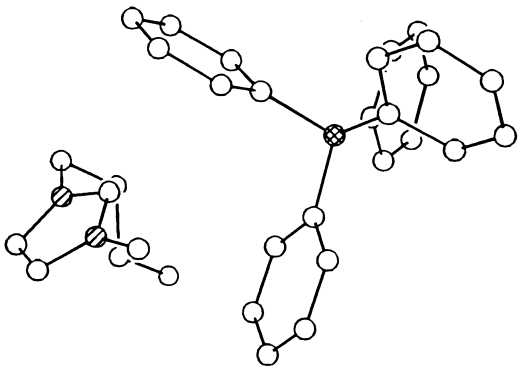


Figure 5. Proposed structure for the contact ion pair of **1** diluted in $CDCl_3$.

current of the phenyl group is calculated from Equation (1), where r and θ are the polar coordinates of H^2 relative to the phenyl centroid. With $r = 2.3$ Å and $\theta = 0^\circ$, one calculates an induced chemical shift of -4.5 ppm.

$$\Delta\delta = 27.6\,\frac{1 - 3\cos^2\theta}{r^3} \qquad (1)$$

Noteworthy in conjunction with the formation of the contact ion pair, which is seen for all concentrations investigated, there is a second phenomenon that increases the shielding of the cation protons when the concentration rises from 0.5 mg to 15 mg. The shielding observed for H^4 and H^5 (-1.2 ppm) is greater than that for H^2 (-0.4 ppm). This observation can be attributed to the formation of contact ion pair aggregates of the type $(\mathbf{1})_n$ (Scheme 2). The structure of these aggregates is probably floating since, despite the new inter-ion proximity, there are no new observable NOE effects.

The measurement of ^{13}C-NMR relaxation times allows to investigate the species involved in this dynamic process. The relaxation time for the CH group is the sum of the dipolar contribution (T_{1d}) and of the chemical shift anisotropic contribution (T_{1an}) following Equation (2).

$$\frac{1}{T_1} = \frac{1}{T_{1d}} + \frac{1}{T_{1an}} \qquad (2)$$

$$\text{with} \quad \frac{1}{T_{1d}} = \frac{\gamma_H^2 \cdot \gamma_C^2 \cdot \hbar^2}{r^6}\,\tau_C \quad \text{and} \quad \frac{1}{T_{1an}} = \frac{2}{15}\,(\chi_B B_0 \Delta\delta)^2\,\tau_C$$

where γ_H, γ_C, and $\hbar$ are the usual constants and r is C–H distance (1.0 Å), $\Delta\sigma$ is the anisotropy of a sp^2 carbon chemical shift ($\delta = 180$), B_0 the magnetic field (11.75 Tesla) and τ_c the correlation time from the particular C–H bond. In the case of the BMI^+ cation, the correlation time can be calculated from CH^2, CH^4, and CH^5 which are good indications for the cation reorientation. The average correlation times of 19 ps (in $[D_6]$DMSO) and 47 ps (in $CDCl_3$) were determined from T_1 according to Equation (2). From these T_1 values, the apparent volumes can be calculated by the Debye BPP formula:

$$\tau_C = \frac{4\pi\eta a^3}{3kT} \qquad (3)$$

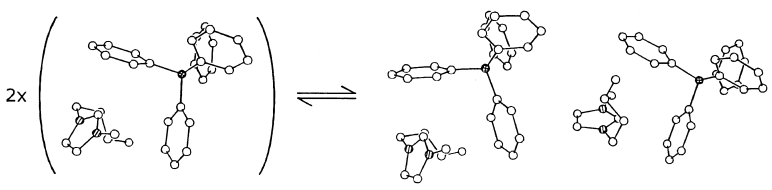
where η is the solvent viscosity, k the Botzmann constant and T the temperature. The calculated apparent volumes ($4\pi a^3/3$) for the cation in $[D_6]$DMSO and $CDCl_3$ are 38 Å^3 and 360 Å^3, respectively. This volume increase observed in $CDCl_3$ might be attributed to the contact ion pair formation and its aggregation process at higher concentrations.

The CH_p bond correlation time of the tetrafluoroborate anion is the best indicator for the modifications of the anion reorientation, in the absence or in the presence of the contact ion pair. The calculated correlation time increases from 66 ps in $[D_6]$DMSO to 80 ps in $CDCl_3$ corresponding an apparent volume increase from 140 Å^3 to 600 Å^3.

The observed apparent volume increase, when of ion pair formation, for each ion is greater than the sum of the apparent volumes of the separated ions. These excess volumes are related to the aggregation process depicted in Scheme 2.

Conclusion

In summary this study shows the following: i) clear evidence of C-H–π hydrogen bonds in the solid state and in the solution structure of the molten salt **1**; ii) a weak hydrogen bond, in the solid state, is directed towards the phenyl centroid with a γ angle of 3.4° (T-shaped geometry); iii) the formation of a solvent-separated ion pair in $[D_6]$DMSO and a contact ion pair in $CDCl_3$; iv) the C-H–π distance in solution



Scheme 2. Proposed path for the formation of contact ion pair aggregates of the type $(\mathbf{1})_n$.

0947-6539/00/0613-2380 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 13

(2.3 Å) is very close to that found in the solid state (2.319 Å); v) the formation of floating aggregate solution structures in $CDCl_3$, through weak C-H – π bonds, with the increasing of concentration; vi) this pattern of weak hydrogen bonds occurs, in both solid and solution structures, as a cooperative network of C-H – π bonds that are probably necessary for the stabilization of networks constituted of weak hydrogen bonds.

Experimental Section

General information: All synthetic procedures were carried out under dry argon using standard Schlenk tube techniques. The solvents were distilled from appropriate drying agents under argon. The $NaBPh_4$ salts were used as purchased from Aldrich Chemical Company. The 1-*n*-butyl-3-methylimidazolium chloride salt was prepared as described earlier.[4b] Infrared (nujol mulls or KBr pellets) spectra were recorded in the 4000 – 400 cm^{-1} region using a Mattson 3020 FTIR spectrophotometer. Elemental analyses were carried out by the "Central Analítica IQ/UFRGS" (Porto Alegre, Brazil). The ^{1}H- and ^{13}C-NMR spectra were recorded at 500.13 and 125.75 MHz on a Bruker ARX 500 instrument. Carbon relaxation times were measured by inversion recovery. The mixing time for the NOESY experiments (2048 F_2 joints, 512 t_1 increments) was set to 1 s.[9]

Synthesis of 1: Sodium tetraphenylborate (17.11 g, 50.0 mmol) was added at room temperature to a solution of 1-*n*-butyl-3-methylimidazolium chloride (8.28 g, 50.0 mmol) in acetone (50 mL). After 24 h stirring the reaction mixture was filtered through a plug of Celite ($l = 3$ cm) and the volatiles were removed under reduced pressure. Compound **1** was obtained as colorless crystals by slow evaporation of the acetone (20.6 g, 90 %). M.p.: 134 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.54$ (br s, 8H, H_o), 6.99 (t, $^3J_{HH} = 7.3$ Hz, 8H, H_m), 6.80 (t, $^3J_{HH} = 6.9$ Hz, 4H, H_p), 6.12 (s, 1H, H^4), 5.96 (s, 1H, H^5), 4.58 (s, 1H, H^2), 3.21 (t, $^3J_{HH} = 7.1$ Hz, 2H, H^6), 2.84 (s, 3H, H^{10}), 1.29 (m, 2H, H^7), 1.19 (m, 2H, H^8), 0.93 (t, $^3J_{HH} = 6.9$ Hz, 3H, H^9); ^{13}C{^{1}H} NMR ($CDCl_3$,): $\delta = 135.8$ (C_o), 135.2 (C^2), 126 (C_m), 122.4 (C^4), 122.0 (C_p), 120.4 (C^5), 49.1 (C^6), 35.5 (C^{10}), 31.7 (C^7), 19.4 (C^8), 13.5 (C^9); IR: (KBr pellets): $\tilde{\nu} = 3165 – 2866$ cm^{-1} ($\tilde{\nu}$C-H aromatic and aliphatic), 1563, 1477 cm^{-1} ($\tilde{\nu}$C = C); $C_{32}H_{35}BN_2$ (458.43): calcd C 83.84, H 7.69, N 6.11; found: C 83.45, H 8.10 N 5.77.

X-ray measurements: A crystal of approximate dimensions $0.2 \times 0.4 \times 0.4$ mm, suitable for X-ray determination, was fractured from a large colorless plate-like crystal of **1**, crystallized from acetone. The data were collected with the crystal under a cold stream ($T = 173$ K) of nitrogen on a Siemens P4 diffractometer using graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.710\ 73$ Å). The cell parameters were determined from 29 centered reflections with a theta range of 21.3° to 23°. The crystal data and data collection parameters are: $C_{32}H_{35}BN_2$, $M = 458.43$ g mol^{-1}, orthorhombic, $P2_12_12_1$, $a = 8.833(1)$ Å, $b = 17.001(2)$ Å, $c = 17.860(2)$ Å, $V = 2682.0(5)$ Å^3, $Z = 4$, $\mu = 0.056$ mm, $D_c = 1.135$ Mg m^{-3}, $F(000) = 934.3995$ reflections (all unique) were collected using ω scans of a θ range of 2.6° to 29.0°, $0 \le h \le 12$, $0 \le k \le 23$, $0 \le l \le 24$. A 9.1 % decrease in intensity, as measured by three check reflections every 97 reflections over the course of collection, was corrected. No absorption correction was made. SHELXTL/PC version 5.0 and SHELXL97[10] were used to solve and refine the structure. The final cycles used full-matrix least squares on F^2 of all the date with all non-hydrogen atoms treated anisotropically, extinction coefficient = 0.0037(5), $wR^2 = 0.1008$ for 337 parameters, g.o.f. = 0.870, $\Delta/\sigma = 0.00$, $\Delta\rho_{max} = 0.308$ e$^-$ Å^3, $\Delta\rho_{min} = -0.238$ e$^-$ Å^3; the conventional $R_1[F] = 0.0502$ for those reflections with $I > 2\sigma(I)$. The absolute structure could not be determined (and the structural results, atomic positions, *R* factors etc, showed no dependence on the hand chosen for solution). The weight expression and *R* factors are as defined in ref. [10]. The fractional atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are given in Table 1.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-130254. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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