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The origin of the splitting of ^{13}C and ^{15}N NMR signals of 3(5)-phenyl-5(3)-methylpyrazolium chloride and bromide in the solid state: Quantum Espresso calculations

Ibon Alkorta [a,*], Rosa M. Claramunt [b], José Elguero [a], Marta B. Ferraro [c], Julio C. Facelli [d], Patricio F. Provasi [e], Felipe Reviriego [a]

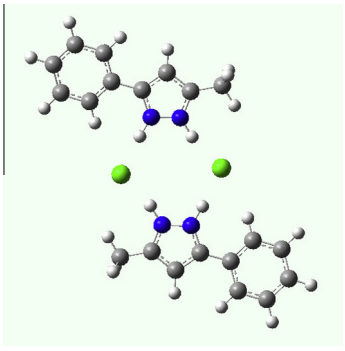
[a] Instituto de Química Médica, Centro de Química Orgánica "Manuel Lora-Tamayo", CSIC, Juan de la Cierva, 3, E-28006 Madrid, Spain
[b] Departamento de Química Orgánica y Bio-Orgánica, Facultad de Ciencias, Universidad Nacional de Educación a Distancia (UNED), Senda del Rey 9, E-28040 Madrid, Spain
[c] Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires and IFIBA, CONICET, Ciudad Universitaria, Pabellón 1, 1428 Buenos Aires, Argentina
[d] Department of Biomedical Informatics, The University of Utah, 421 Wakara Way, Suite 140, Salt Lake City, UT 84108, United States
[e] Department of Physics, Northeastern University of Argentina, Avenida Libertad 5500, W 3404 AAS Corrientes, Argentina

HIGHLIGHTS

- The ^{13}C and ^{15}N CPMAS NMR spectra of two pyrazolium salts have been recorded.
- DFT-D and Quantum Espresso calculations have been performed on the chloride.
- Only Quantum Espresso calculations are able to reproduce the experimental splittings.
- There is a biunivocal relationship between X-ray geometries and SSNMR chemical shifts.

GRAPHICAL ABSTRACT

The origin of the very clear splittings observed for the title compound has been ascertained through Quantum Espresso calculations.



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ABSTRACT

A combination of ^{13}C and ^{15}N CPMAS NMR spectroscopy and theoretical methods (DFT and DFT-D) was used to discuss the observation of large splittings affecting some atoms in 3(5)-phenyl-5(3)-methylpyrazolium chloride and bromide. Conventional calculations using fully optimized structures with C_2 symmetry reproduce solution spectra, but the large splitting observed for the signals of several pyrazolium carbon and nitrogen atoms in the solid-state can only be explained by calculations employing the experimental $P2_1/n$ geometry and periodic boundary calculations.

* Corresponding author. Tel.: +34 91 562 29 00; fax: +34 91 564 48 53.
E-mail address: ibon@iqm.csic.es (I. Alkorta).
URL: http://www.iqm.csic.es/are (I. Alkorta).

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Introduction

There are at least four main causes to explain additional splittings observed in solid-state NMR (SSNMR) when compared with solution spectra [1]: (i) the existence of two or more independent molecules in the unit cell that in solution are dynamically averaged into a unique structure; (ii) crystal-field effects that reduce the effective symmetry of the molecules in the solid; (iii) the presence of restricted rotations and conformations that become free in solution because of low barriers; (iv) the effect of quadrupolar nuclei like ^{14}N, $^{35(37)}$Cl and $^{79(81)}$Br. Obviously these factors can coexist and in many cases only computational methods can be used to determine their relative importance. In previous work, we have found that the pyrazolium salts 3(5)-phenyl-5(3)-methylpyrazolium chloride (**1**) and 3(5)-phenyl-5(3)-methylpyrazolium bromide (**2**) show some signals that appear as doublets [2]. In this paper we present results of a number of different DFT and DFT-D calculations performed to elucidate the origin of the observed splittings. Calculations are based on the known X-ray structures of both salts (SEGNIB and SEGNOH, respectively) [3] These structures show a dimer structure with two cations and two anions; the non-hydrogen atoms of the central pseudo-ring form a sort of cyclohexane, chair for the chloride **1** and boat for the bromide **2** both close to the planarity (Fig. 1 bottom). Additionally we present calculations with periodic boundary conditions of chemical shifts using optimized crystal structures, in order to explore the possibility that SSNMR could correspond to a less symmetric structure than the one observed by X-ray, like it was reported by Facelli and Grant for naphthalene [4]. These calculations are limited to the chloride **1** because there are no potentials available for bromine in Quantum Espresso calculations (see ***Periodic Boundary Calculations***).

It is important to be aware that the geometries of each pyrazolium salt are different. For instance in the 3(5)-phenyl-5(3)-methylpyrazolium chloride (SEGNIB, **1**) there are some very significant differences between molecules **A** and **B** (Table 1 and Supplementary material) mainly in what concerns the atoms C4 and C12.

Experimental

Compounds **1** and **2** were prepared following the procedure described in Ref. [2]. Crystals were obtained and their identity with previous ones checked (same unit cells).

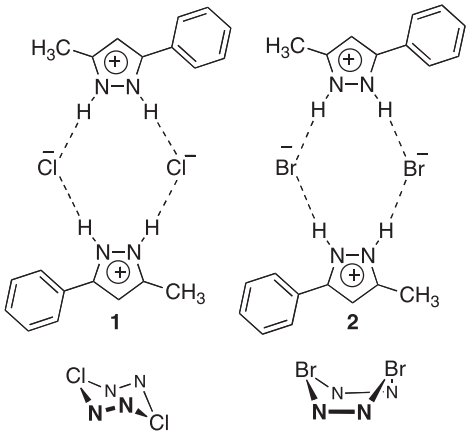
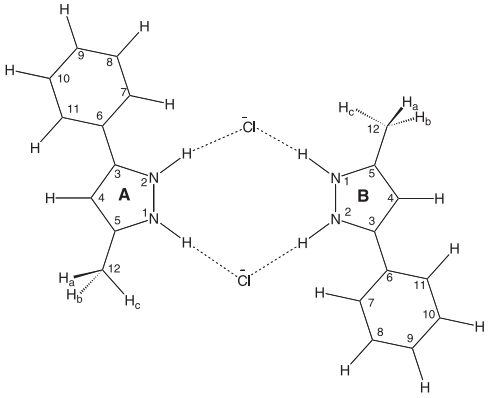


Fig. 1. Scheme of the crystal structures [2]. Distances of the anions to the mean plane of the ten atoms of both pyrazolium rings: SEGNIB (**1**): 0.20 and 0.05 Å (one in each side) and SEGNOH (**2**): 0.22 and 0.31 Å (both in the same side).

Table 1
Some relevant geometrical parameters of SEGNIB excluding H atoms (see numbering below).



Geometry	Molecule **A**	Molecule **B**	Difference
Distances (Å)			
C3–C4	1.395	1.389	0.006
C4–C5	1.377	1.374	0.003
C5–C12	1.482	1.494	−0.012
Angles (°)			
N2–C3–C4	106.22	106.84	−0.62
C3–C4–C5	107.78	107.08	0.70
C4–C5–N1	107.04	107.53	−0.49
N1–C5–C12	121.29	120.97	0.32
C4–C5–C12	131.67	131.50	0.17

NMR

^{13}C (100.73 MHz) and ^{15}N (40.60 MHz, natural abundance) CPMAS NMR spectra have been obtained on a Bruker WB 400 spectrometer at 300 K using a 4 mm DVT probehead. Samples were carefully packed in a 4-mm diameter cylindrical zirconia rotor with Kel-F end-caps. Operating conditions involved 2.9 μs 90° ^{1}H pulses and decoupling field strength of 86.2 kHz by TPPM sequence. ^{13}C spectra were originally referenced to a glycine sample and then the chemical shifts were referred to Me_4Si using the carbonyl atom δ(glycine) at 176.1 ppm as a secondary Ref. [5] and ^{15}N spectra to $^{15}NH_4Cl$ and then converted to nitromethane scale using the following relationship: δ^{15}N(nitromethane) = δ^{15}N(ammonium chloride) – 338.1 ppm [6].

The typical acquisition parameters for ^{13}C CPMAS were: spectral width, 40 kHz; recycle delay, 5 s; acquisition time, 30 ms; contact time, 2 ms; and spin rate, 12 kHz. In order to distinguish protonated and unprotonated carbon atoms, the NQS (Non-Quaternary Suppression) experiment by conventional cross-polarization was recorded; before the acquisition the decoupler is switched off for a very short time of 25 μs [7,8]. And for ^{15}N CPMAS were: spectral width, 40 kHz; recycle delay, 5 s; acquisition time, 35 ms; contact time, 6 ms; and spin rate, 6 kHz. Typical acquisition parameters for ^{15}N CPMAS were as follows: spectral width, 40 kHz; recycle delay, 90–180 s; contact time, 7 ms; and spin rate, 6 kHz.

Computational details

Molecular calculations

Geometries of the different structures of compound **1** were fully optimized at the B3LYP theoretical level [9,10], with the 6-311++G(d,p) basis set [11] as implemented in the Gaussian 09 program [12]. Harmonic frequency calculations [13] verified the nature of the stationary points as minima (all real frequencies).