

## <sup>13</sup>C CPMAS NMR Spectra of Solid Proton-exchanging *p*-Substituted Benzoylacetones: Observation of <sup>13</sup>C, <sup>35,37</sup>Cl Residual Dipolar Coupling in the *p*-Chloro Derivative

Raquel M. Cravero,<sup>a</sup> Manuel González-Sierra,<sup>a</sup> Claudio Fernández<sup>b</sup> and Alejandro C. Olivieri\*<sup>c</sup>

<sup>a</sup> IQUIOS, Facultad de Ciencias Bioquímicas y Farmacéuticas Suipacha 531, Rosario (2000), Argentina

<sup>b</sup> PRIBIOR-CONICET, Catedra de Fitoquímica, Facultad de Farmacia y Bioquímica, Junin 956, Buenos Aires (1113), Argentina

<sup>c</sup> Departamento de Química Analítica, Facultad de Ciencias Bioquímicas y Farmacéuticas, Suipacha 531, Rosario (2000), Argentina

Residual dipolar coupling to spin- $\frac{3}{2}$  <sup>35,37</sup>Cl nuclei appears as a symmetric doublet of 0.69 kHz in the <sup>13</sup>C CPMAS NMR spectrum of *p*-chlorobenzoylacetone at 75.4 MHz, in agreement with theoretical calculations; carbon chemical shifts of a series of *p*-substituted benzoylacetones undergoing solid proton transfer are also reported, which show tautomeric populations similar to the solution ones.

Residual dipolar coupling to quadrupolar nuclei as observed in magic angle spinning (MAS) solid-state NMR spectra of spin- $\frac{1}{2}$  nuclei is receiving increasing attention both from experimental and theoretical perspectives.<sup>1</sup> Interest in this phenomenon has grown due to the interplay of several interesting molecular parameters such as the quadrupole data ( $\chi$  and  $\eta$ ) for the quadrupolar nucleus  $S$ , the Zeeman frequency of  $S$  ( $\nu_S$ ), the distance between both nuclei ( $r_{IS}$ ), and the polar angles ( $\beta^D$  and  $\alpha^D$ ) which locate the vector  $r_{IS}$  in the electric field gradient main frame.<sup>1,2</sup> Some of the most studied pairs include <sup>13</sup>C, <sup>14</sup>N;<sup>3</sup> <sup>119</sup>Sn, <sup>35,37</sup>Cl<sup>4</sup> and <sup>31</sup>P, <sup>63,65</sup>Cu,<sup>5</sup> with several further observations in other pairs of nuclei.<sup>1</sup> As part of a project aimed at characterizing fast proton transfer processes in solid materials, we recorded 75.4 MHz <sup>13</sup>C CPMAS NMR spectra of a series of *p*-substituted benzoylacetones (compounds 1–5). The chemical shifts are reported in Table 1, where they are compared with solution (CDCl<sub>3</sub>) values. The close similarity between the two sets of chemical shifts of the relevant carbons C(1)–C(3) is a strong indication that similar proton exchange phenomena are taking place in both phases. Previous solution work has established that in all compounds 1–5 the equilibrium constants  $K_{eq}$  are only slightly deviated from equipopulation in favour of **b**,<sup>6</sup> a situation that, according to Table 1, is also observed in crystals. Only in the case of **4** a further shift towards tautomer **b** seems to occur on

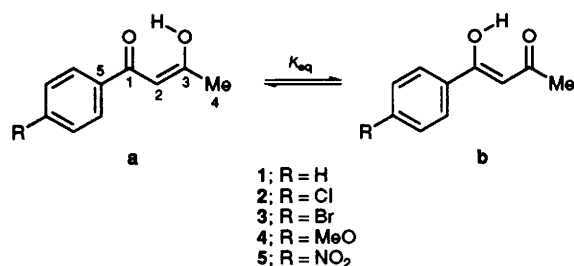


Table 1 <sup>13</sup>C Chemical shifts for compounds 1–5 in solution and in the solid state<sup>a</sup>

Com- pound	Solution			Solid		
	1	2	3	1	2	3
1	183.15	96.53	193.64	182.1	97.5	194.3
2 <sup>b</sup>	182.00	96.32	193.41	182.9	96.0	194.2
3	181.98	96.41	193.66	182.9	96.7	193.7
4 <sup>c</sup>	183.98	95.61	191.42	182.3	96.0	195.7
5	179.03	97.91	196.04	180.5	98.2	196.0

<sup>a</sup> In ppm downfield from SiMe<sub>4</sub>. <sup>b</sup>  $\delta$  C(8) 138.24 in solution;  $\delta$  133.6 and 142.8 in the solid. <sup>c</sup>  $\delta$  C(7) 113.78 in solution;  $\delta$  110.0 and 116.9 in the solid.

crystallization, as monitored by a downfield shift in  $\delta$  C(3) accompanied by a similar upfield shift in  $\delta$  C(1) [in **4** in the solid C(7) is split due to the rigid conformation about the C(7)–OMe bond, see Table 1]. The overall results are in agreement with the X-ray diffraction data,<sup>7</sup> since **1**, **3** and **5** display dynamically averaged C–O bond lengths [*i.e.* C(1)–O, C(3)–O are 1.282, 1.279 Å in **1**;<sup>8</sup> 1.306, 1.290 Å in **3**;<sup>9</sup> and 1.297, 1.289 Å in **5**<sup>10</sup>]. A noteworthy difference between solution and solid-state data corresponds to  $\delta$  C(8) in **2** ( $\delta$  138.24 in solution and  $\delta$  133.6, 142.8 in the solid, see Fig. 1). The appearance of the carbon bonded to Cl as a doublet split by 0.69 kHz ( $\delta$  9.2 ppm at 75.4 MHz) and centred at the solution value is not expected as a consequence of  $J$  coupling to spin- $\frac{3}{2}$  <sup>35,37</sup>Cl nuclei, but can be ascribed to residual dipolar <sup>13</sup>C, <sup>35,37</sup>Cl coupling. According to a well-known first-order perturbative approach,<sup>2</sup> MAS spectra of spin- $\frac{1}{2}$  nuclei which are dipolar coupled to a spin- $\frac{3}{2}$  quadrupolar nucleus should appear as a symmetric doublet when  $\chi/\nu_S \ll 1$ , with a partition given by  $6D\chi/10\nu_S$  [ $D = (\mu_0/4\pi)\gamma_I\gamma_S h/4\pi^2 r_{IS}^3$ ] under the assumption that the inter-

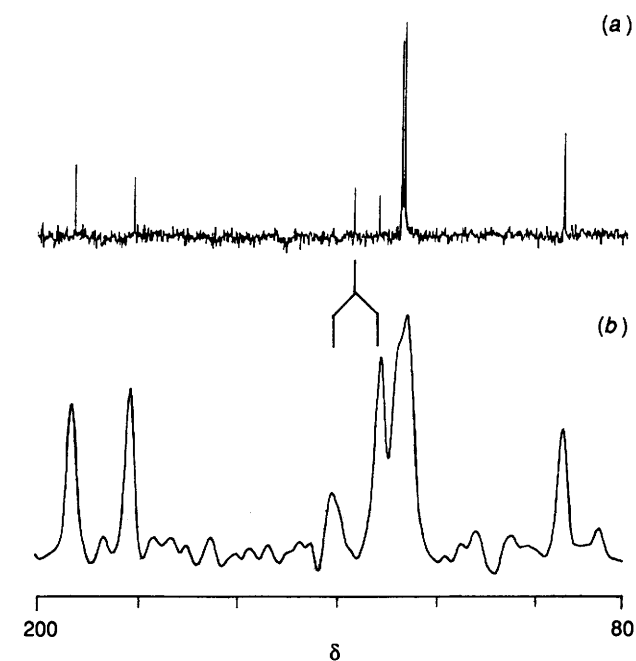
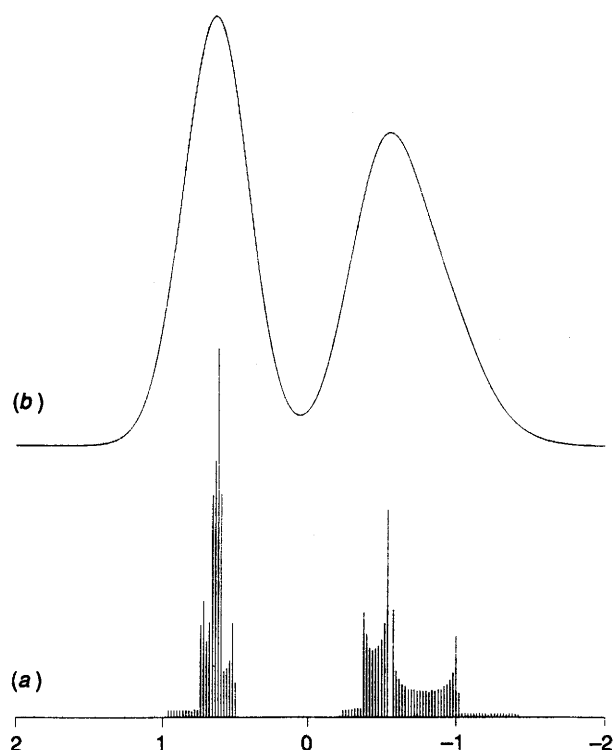


Fig. 1 <sup>13</sup>C NMR spectra of compound **2**. (a) solution (CDCl<sub>3</sub>) spectrum recorded on a Bruker AC 200 Spectrometer at 50.3 MHz; (b) CPMAS spectrum run on a Bruker MSI 300 spectrometer at 75.4 MHz; spectral conditions were: 90° <sup>1</sup>H pulse, 6  $\mu$ s; contact time, 5 ms; recycle time, 2 s; SW, 30 kHz; no. of scans, 500; spinning speed (Zr rotors), 8 kHz; memory, 4 K. Chemical shifts were externally referenced against the glycine signal at  $\delta$  176.1 and then converted to the SiMe<sub>4</sub> scale. Partitioning in the signal of the C–Cl carbon on going from solution to the solid state is indicated.



**Fig. 2** (a) Stick spectrum obtained by exact computer diagonalization of the  $^{35}\text{Cl}$  Hamiltonian, followed by calculation of the  $^{13}\text{C}$ ,  $^{35}\text{Cl}$  dipolar coupling, using  $\nu_s = 29.4$  MHz,  $\chi = -70$  MHz, and assuming coincidence between the  $r_{\text{C-Cl}}$  vector and the unique axis of the  $^{35}\text{Cl}$  EFG tensor. The horizontal scale is in units of the dipolar coupling constant  $D$ . (b) Gaussian convolution of the spectrum (a) with a Gaussian width of 0.5 units of  $D$ . Vertical scale is in arbitrary units.

nuclear vector is coincident with the unique axis of the quadrupole tensor at S atoms. Restricting the discussion to the major  $^{35}\text{Cl}$  isotope, and introducing  $D = 0.57$  kHz (for  $r_{\text{C-Cl}} = 1.73$  Å),  $\nu_s = 29.4$  MHz (the  $^{35}\text{Cl}$  resonance frequency at 7.05 T),  $\chi = 70$  MHz (the approximate  $^{35}\text{Cl}$  quadrupole coupling constant in  $p\text{-ClC}_6\text{H}_4\text{CO}_2\text{H}$ ),<sup>11</sup> the  $^{13}\text{C}$  splitting is computed as 1.43 units of  $D$ , or 0.81 kHz ( $\delta$  10.8), which is larger than the observed value by *ca.* 20%. The discrepancy can be traced to the fact that the first-order condition is not strictly met (*i.e.*  $\chi/\nu_s > 1$ ). Accurate calculations involving full computer diagonalization of the  $^{35}\text{Cl}$  Hamiltonian<sup>12</sup> gives a  $^{13}\text{C}$  line shape as in Fig. 2. Although still a doublet, the calculated partition is 1.20 units of  $D$ , or 0.68 kHz ( $\delta$  9.1 at

75.4 MHz), in excellent agreement with experimental results. To confirm that this partition is due to the presently discussed phenomenon,  $^{13}\text{C}$  CPMAS spectra of **2** and other chlorine-containing materials were recorded at 50.3 MHz. The lines of carbons bonded to Cl are apparently very broad at 4.7 T, and very low *S/N* ratios result. This is expected from the exact calculations of the  $^{13}\text{C}$ ,  $^{35}\text{Cl}$  coupling, which predict a carbon line spread within *ca.* 2.5 units of  $D$ , 1.42 kHz (*ca.*  $\delta$  30 at 50.3 MHz, see Fig. 3 of ref. 12). This emphasizes the need of high-field spectrometers to observe  $^{13}\text{C}$  resonances bonded to Cl. The presently discussed case appears to be one of the first observations of  $^{13}\text{C}$ ,  $^{35,37}\text{Cl}$  residual dipolar coupling in carbon CPMAS spectra.†

Financial support from Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, Argentina) and University of Rosario is gratefully acknowledged. We also thank PRIBIOR-CONICET (Facultad de Farmacia y Bioquímica, Buenos Aires) for access to the solid-state NMR facility. A. C. O. thanks Fundacion Antorchas (RG. No. A-12576/1) for financial support.

Received, 5th April 1993; Com. 3/01938A

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† Note added in proof: After this paper was submitted for publication, we became aware of related work on residual  $^{13}\text{C}$ ,  $^{35,37}\text{Cl}$  effects: R. K. Harris, M. Sunnetcioglu, K. S. Cameron and F. G. Riddell, *Magn. Reson. Chem.*, submitted for publication.