

Solid-state electronic absorption, fluorescence and ^{13}C CPMAS NMR spectroscopic study of thermo- and photo-chromic aromatic Schiff bases



Sergio H. Alarcón,^a Alejandro C. Olivieri,^{*a} Alison Nordon^b and Robin K. Harris^{*b}

^a Departamento de Química Analítica, Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Suipacha 531, Rosario (2000), Argentina

^b Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE

Solid-state electronic absorption, fluorescence emission and ^{13}C CPMAS spectroscopies have been applied to a series of aromatic Schiff bases displaying both ground and excited state intramolecular proton transfer phenomena. All the results can be explained on the basis of a thermal equilibrium between enol-imine and keto-enamine tautomeric forms in the crystalline state. Most of the studied compounds are thermochromic. However, a few are photochromic. The carbon-13 NMR data in the solid state show, in general, residual (^{13}C , ^{14}N) dipolar coupling effects. In certain cases, however, where fast proton transfer occurs in the ground state, these effects are shown to be self-decoupled.

Introduction

Reversible solid-state thermal and photochemical reactions are of interest due to their potential use as a basis for optical data storage devices.^{1,2} We have previously studied the solution-state proton transfer tautomerism both in the ground and excited states of the aromatic Schiff bases 1–15 (Scheme 1) using a variety of spectroscopic techniques together with semi-empirical molecular orbital and chemical ionisation calculations.^{3–5} Excited-state intramolecular proton transfer (ESIPT) takes place upon irradiation of one of the tautomers according to a so-called Förster cycle (Scheme 2). In certain cases, however, it has been reported that excitation of tautomer **a** in the solid state gives the excited state **b*** which does not fluoresce, but undergoes a *cis*–*trans* isomerization to give a dark coloured photoproduct **c**, which then reverts to **a** or **b** (depending on their relative stabilities, see Scheme 2).^{6,7} This latter process is slow in the dark, but is accelerated by irradiation of **c** with visible light.⁶ In this report we assess the possibility that these processes also operate in the solid state for the materials 1–15. Electronic absorption and fluorescence spectral data help to characterize whether the studied materials are photo- or thermo-chromic in the solid state. Carbon-13 CPMAS NMR results on the series 1–10 indicate the absence of the well-known (^{13}C , ^{14}N) residual dipolar coupling effects due to proton transfer induced self-decoupling in certain cases. In others, the effects are present as the expected 2:1 ^{13}C doublets. This allows us to distinguish between compounds significantly displaced towards one of the tautomeric forms in the solid state on the one hand, and proton energy profiles of a double-well type on the other.

Experimental

All compounds were synthesized following known methods. In particular, compounds 11–15 were synthesized according to a recently described procedure.^{4,5}

Electronic absorption spectra were recorded on a Beckman DU 640 spectrophotometer on thin solid films deposited on one of the internal walls of a quartz cuvette. Fluorescence emission spectra were obtained with a JASCO FP 770 spectrofluorimeter, following irradiation of a thin film of solid deposited on a black surface covered with a polymethylmethacrylate film.

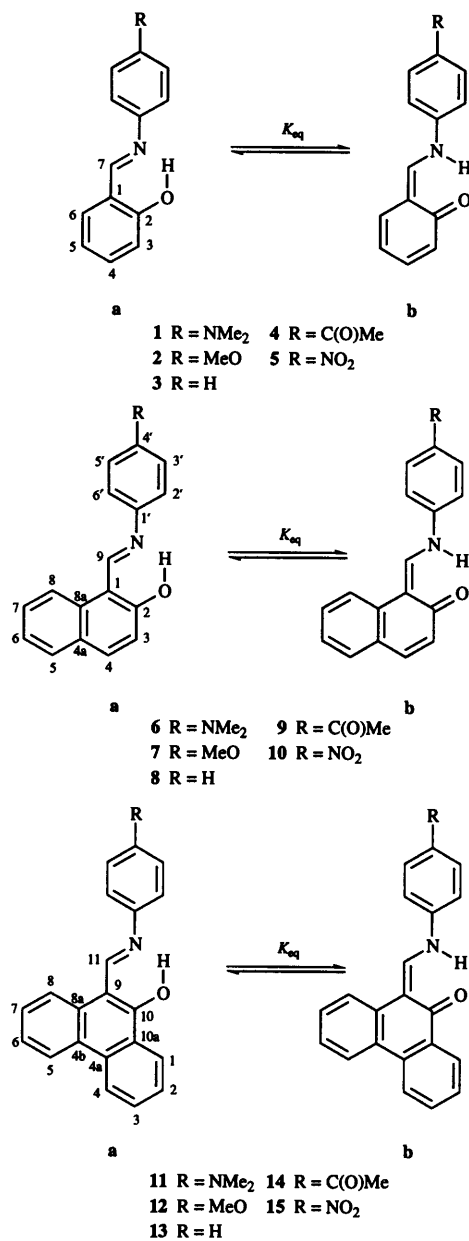
Solid-state ^{13}C CPMAS NMR spectra were recorded on a Chemagnetics CMX 200 NMR spectrometer operating at 50.33 MHz for ^{13}C . Spectral conditions were: pulse duration, 4 μs ; contact time, 1–5 ms; spectral width, 20 kHz; pulse delay, 3.5–100 s; acquisition time, 102.4 ms; spin rates, 4–5 kHz. Interrupted decoupling spectra were obtained by inserting a delay of 50 μs with no ^1H decoupling prior to acquisition. Variable temperature spectra were obtained for compound 7 by cooling with N_2 gas. The temperatures were measured at the inlet gas and are uncalibrated. Chemical shifts are referenced through the use of the high frequency adamantane peak ($\delta_{\text{C}} = 38.4$ ppm with respect to tetramethylsilane) by replacement.

Results and discussion

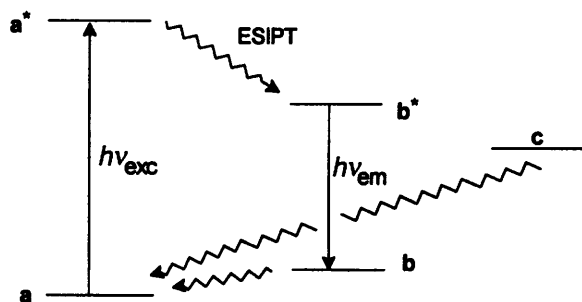
Electronic absorption and fluorescence spectroscopy

Table 1 summarizes the UV–VIS absorption and fluorescence emission data, along with the calculated Stokes shifts (ΔE) for compounds 1–15 in the solid state. The absorption maxima, at approximately 330–370 and 450–480 nm, are similar to those registered in solution.^{4,5} These two bands are assigned to tautomers **a** and **b**, respectively. The relative intensities of these bands help to characterize the position of the tautomeric equilibrium $\text{a} \rightleftharpoons \text{b}$ in the solid state, as previously described for solutions.^{3–5} The results show that compounds 1–5 exist primarily in form **a**, compounds 11–15 in form **b** and compounds 6–10 as equilibrium mixtures of tautomers **a** and **b**. Fig. 1 illustrates representative results of solid-state electronic absorption spectra for the parent compounds 3, 8 and 13. However, the information on the relative populations of tautomers which can be gathered from absorption spectra is only qualitative, since the intrinsic extinction coefficients for each pure tautomer are not known.

Fluorescence measurements revealed that only compounds 3 and 4 are photochromic, *i.e.* they do not fluoresce upon irradiation but transform into dark red photoproducts which revert to the normal yellow form after a few minutes, even in the dark. The structure of the photoproducts is still under some debate, but it has been suggested that they are produced by a *cis*–*trans* rearrangement around the C1–C(N) double bond in the excited state of tautomer **b**. This gives a product which is no longer able to transfer the proton, and reverts thermally and very slowly to the normal state (tautomer **a**). The existence of these photo-transformations in the solid state has been related to the avail-



Scheme 1



able space in the crystal for the *cis*–*trans* reaction (refs. 6 and 7). The rest of the compounds studied are strongly fluorescent upon irradiation at both absorption maxima, as shown in Table 1. The emission wavelength is approximately independent of the irradiated band, implying that the emitting species is tautomer **b** in all cases. The results are consistent with the existence of a Förster cycle (Scheme 2), and are both qualitatively and quantitatively similar to those previously found for solutions,^{4,5} except for the photochromic materials which display a phenomenon typical of the solid phase. In particular, for the thermochromic compounds, the Stokes shift is of the order of 10 000 cm⁻¹ when the band corresponding to tautomer **a** is irradiated.

Table 1 Electronic absorption and fluorescence data for the compounds studied

Compound	$\lambda_{\text{max}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\Delta E/\text{cm}^{-1}$
1	331	580	12 970
	453	580	4 833
2	325	570	13 225
	450	570	4 195
3	347	<i>a</i>	—
	450	<i>a</i>	—
4	322	<i>a</i>	—
	460	<i>a</i>	1 645
5	374	575	9 346
	450	<i>b</i>	—
6	374	600	10 071
	450	600	5 457
7	380	540	5 991
	490	540	2 185
8	375	540	8 148
	455	540	3 459
9	322	565	13 648
	448	565	4 622
10	374	570	9 122
	480	570	3 289
11	350	<i>b</i>	—
	457	<i>b</i>	—
12	<i>b</i>	<i>b</i>	—
	457	540	—
13	340	530	10 540
	435	530	4 120
14	<i>b</i>	<i>b</i>	—
	450	<i>b</i>	—
15	<i>b</i>	<i>b</i>	—
	460	<i>b</i>	—

^a Photochromic materials (see text). ^b Not observed.

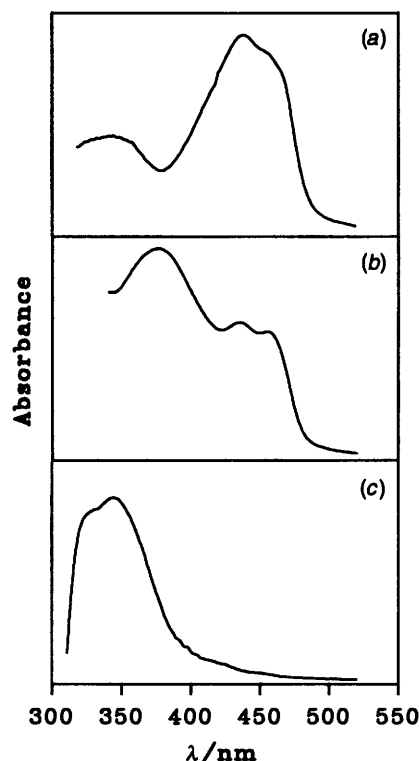


Fig. 1 Electronic absorption spectra of solid films of: (a) compound **3**, (b) compound **8** and (c) compound **13**

¹³C CPMAS NMR spectroscopy

Table 2 summarizes the high resolution ¹³C CPMAS NMR results. To assist in spectral assignment, spectra were obtained for the normal cross polarization (CP) mode and also using the interrupted decoupling method, which selectively detects quaternary and mobile methyl carbons. The results for compounds

Table 2 Carbon-13 NMR results for quaternary carbons in compounds 1–10 in the solid state

Carbon	Compound									
	1	2	3	4	5	6	7	8	9	10
1	120.7	120.3	120.0	118.4	119.7	109.5	107.4	107.9	108.1	108.7
2	161.5	161.5	162.3	161.2	160.9	168.7	170.2	180.0	179.5	175.3
4a	—	—	—	—	—	127.3	127.9	126.4	127.0	127.9
8a	—	—	—	—	—	131.7	135.1	133.3	133.9	133.2
1'	132.0 ^a	143.6 ^a	149.1 ^a	151.1 ^a	151.3 ^a	133.6	135.1	139.0	143.6 ^a	144.2
4'	150.7	157.7	<i>d</i>	133.1	145.8 ^a	152.2	159.4	<i>d</i>	133.9	144.2
	148.3 ^b					149.6 ^b				
7/9 ^c	151.5 ^a	164.8 ^a	164.2 ^a	163.8 ^a	164.8 ^a	149.1	148.9	145.9	149.1 ^a	150.9
								144.8 ^b		

^a Broad signal. ^b Splitting produced by residual (¹³C,¹⁴N) dipolar coupling. ^c The CH=N carbon. ^d These are C–H carbons (shifts not assigned).

1–5 are consistent with a structure dominated by tautomer **a**, as in solution.³ The carbon chemical shifts are closely similar to those registered in solution, particularly the one assigned for carbon C2 (e.g. for **3** 162.3 ppm in the solid state, Table 1, and 160.9 ppm in CDCl₃, ref. 3), which is the signal most sensitive to the position of the tautomeric equilibrium. However, the resonance attributed to carbon C1' appears significantly broadened with respect to other quaternary carbons in the molecule. This distinctive broadening can be ascribed to the presence of the bonded ¹⁴N atom, and is due to incompletely averaged (¹³C,¹⁴N) dipolar coupling.⁸ This residual coupling is normally manifested as an asymmetric splitting in the carbon signal, which in this case is not large enough to be distinguished in the spectrum but does produce a signal with a full width at half height of *ca.* 150 Hz. Similar broadening effects in nitrogen containing compounds where the carbon is double bonded to ¹⁴N have been reported previously.⁹ The results for compounds **1**, **2**, **4** and **5** show similar features to those for **3** (see Table 2), confirming that they all exist as enolic tautomers in the solid state (as in solution).

The results for compounds **6**–**10** are illustrative of the sensitivity of the NMR measurements towards the position of the tautomeric equilibrium and to the presence of a double-well energy profile for the motion of the labile proton. Compound **8** (Fig. 2) shows a chemical shift for C2 (180.0 ppm), which is characteristic of the keto–enamine form **b**, and is similar to that registered in solution for compound **13** (C10, 181.0 ppm).⁴ The signal ascribed to C1' clearly appears as a 1:2 doublet with a splitting of +70 Hz, due to (¹³C,¹⁴N) residual dipolar coupling. The well-known first-order perturbation equation can be used for the calculation of this effect¹⁰ [eqn. (1)], where *s* is the doublet

$$s = (9/20)(D\chi/\nu_s)(3 \cos^2 \beta^D - 1 + \eta \sin^2 \beta^D \cos 2\alpha^D) \quad (1)$$

splitting, *D* is the dipolar ¹³C,¹⁴N coupling constant [*D* = ($\mu_0/4\pi$)($\gamma_1\gamma_2\hbar/4\pi r^3$)], χ is the ¹⁴N quadrupole coupling constant, ν_s is the ¹⁴N resonance frequency at the applied magnetic field, η is the asymmetry parameter of the ¹⁴N electric field gradient (EFG) and β^D and α^D are the polar angles defining the orientation of the internuclear vector *r* in the EFG principal axis system. Analysis of model hydrazone compounds¹¹ allows us to estimate χ as *ca.* –4 MHz and η as 0.2, while the angles β^D and α^D can be taken as 90° and 30°, respectively, as was the case for a series of solid hydrazone structures previously studied.¹¹ The C–N distance can be set at 1.41 Å, by comparison with X-ray structures of related compounds.^{12–17} Insertion of these values in eqn. (1), together with $\nu_s = 14.5$ MHz, gives the calculated splitting *s* as +85 Hz, in good agreement with that observed experimentally. The CH carbon C9 also appears as a doublet (*s* = +55 Hz) affected by the bonded ¹⁴N atom (see Table 2).

Similar results were obtained for compound **9**, *i.e.* C2 appears at 179.5 ppm, while C1' is significantly broadened with respect to other quaternary carbons. In the case of compound

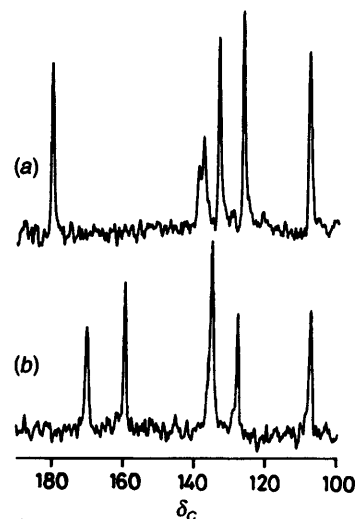


Fig. 2 Carbon-13 CPMAS spectra at ambient temperature obtained using the interrupted decoupling (dipolar dephasing) pulse sequence for (a) compound **8** and (b) compound **7**. Spectral parameters: contact time 1.5 and 2 ms, recycle delay 2.5 s and 20 s, number of transients 7000 and 320, spin rate 4.0 and 4.5 kHz.

7, on the other hand, C2 appears at 170.2 ppm. This value suggests the presence of significant amounts of both tautomeric forms **a** and **b** in rapid equilibrium, and is similar to that observed in solution (169.3 ppm).³ Following our hypothesis about the effect of proton transfer on the ¹³C,¹⁴N interaction, the signal assigned to C1' (135.1 ppm) is a sharp singlet (Fig. 2). This latter signal remains as a singlet when the temperature is decreased to *ca.* 180 K, though all carbon resonances broaden on lowering the temperature. This means, in turn, that the solid-state proton transfer reaction induces a self-decoupling phenomenon of the residual (¹³C,¹⁴N) coupling of the type already described theoretically¹⁸ and experimentally verified on arylazonaphthols.¹⁹ In the case of compound **6**, the signal ascribed to the C–O carbon C2 appears at 168.7 ppm (Table 2), close to that observed in solution (169.8 ppm).³ It may be noticed that the carbon bonded to the NMe₂ group (C4', 151.3 ppm, compared with a solution value³ of 149.2 ppm) does appear as a 1:2 doublet with a splitting of +130 Hz. This latter result is in good agreement with the calculations based on eqn. (1). Using the following values, taken from aromatic compounds substituted with NMe₂ groups,¹⁴ $\chi = -4.3$ MHz, $\eta = 0$, $\beta^D = 90^\circ$, $r = 1.37$ Å, $\nu_s = 14.5$ MHz, the calculated splitting is +113 Hz. The pseudo motion induced by the proton transfer reaction only affects the carbons bonded to the NH nitrogen. This evidence confirms that the self-decoupling phenomenon observed for compound **7** (and also for **6**, though here the situation is complicated by an overlap of resonances) is not due to an overall molecular motion. The latter would collapse all residual dipolar effects.

X-Ray diffraction analyses have been extensively carried out on Schiff bases obtained from salicylaldehyde derivatives.^{12-17,20} The results show that these compounds exist in the crystalline state in the enol-imine form **a**, in agreement with the spectroscopic evidence discussed in the present report. Recently, the structures of three derivatives of 2-hydroxynaphthalene-1-carbaldehyde (including compound **6**) have been reported.¹⁷ The bond lengths around the ring supporting the labile hydrogen are averages between those expected for formally single and double bonds, suggesting the presence of a fast proton transfer equilibrium. Thus the X-ray structure of compound **6**, in agreement with our NMR results, shows bond lengths around the O-C-C-N moiety as follows:²⁰ C-O, 1.309 Å and C-N, 1.297 Å, which are shorter and longer, respectively, than analogous lengths in salicylaldehyde derivatives (C-O, 1.33-1.34 Å and C-N, 1.28 Å). Furthermore, in the case of *N*-(2-hydroxy-1-naphthylmethylene)pyren-1-amine, the C-O bond lengths change on lowering the temperature (1.336 Å at 295 K and 1.319 Å at 120 K).¹⁷ This implies that the solid-state structure is best represented by a fast equilibrium between tautomers **a** and **b**, both present in significant amounts.

In conclusion, spectroscopic evidence is presented which shows that, for most of the Schiff bases investigated, the solid-state behaviour is closely similar to that observed in solution. There are, however, a few exceptions which show photochromic behaviour. Furthermore, the study of (¹³C,¹⁴N) residual coupling effects allows a distinction to be made between dynamic proton transfer systems on the one hand, and structures which are significantly shifted towards one of the tautomers on the other.

Acknowledgements

We thank the UK Engineering and Physical Sciences Research Council for a studentship to one of us (A. N.) and for research grant GR/H96096, which provided finances for the purchase of the Chemagnetics spectrometer. We also thank CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas), the University of Rosario and Fundación Antorchas for financial support. S. H. A. thanks CONICET for a fellowship.

References

- 1 B. L. Feringa, W. F. Jager and B. De Lange, *Tetrahedron*, 1993, **49**, 5525.
- 2 (a) L. G. Arnaut and S. J. Formosinho, *J. Photochem. Photobiol. A*, 1993, **75**, 1; (b) S. J. Formosinho and L. G. Arnaut, *J. Photochem. Photobiol. A*, 1993, **75**, 21.
- 3 S. H. Alarcón, A. C. Olivieri and M. González-Sierra, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1067.
- 4 S. H. Alarcón, A. C. Olivieri, G. R. Labadie, R. M. Cravero and M. González-Sierra, *Tetrahedron*, 1995, **51**, 4619.
- 5 S. H. Alarcón, A. C. Olivieri, G. R. Labadie, R. M. Cravero and M. González-Sierra, *J. Phys. Org. Chem.*, 1995, **8**, 713.
- 6 M. D. Cohen and G. M. J. Schmidt, *J. Phys. Chem.*, 1962, **66**, 2442.
- 7 E. Hadjoudis, M. Vittorakis and I. Moustakali-Mavridis, *Tetrahedron*, 1987, **43**, 1345.
- 8 R. K. Harris and A. C. Olivieri, *Progr. Nucl. Magn. Reson. Spectrosc.*, 1992, **24**, 435.
- 9 A. M. Chippendale, A. Mathias, R. K. Harris, K. J. Packer and B. J. Say, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1031.
- 10 A. C. Olivieri, L. Frydman and L. E. Díaz, *J. Magn. Reson.*, 1987, **75**, 50.
- 11 A. C. Olivieri, R. B. Wilson, I. C. Paul and D. Y. Curtin, *J. Am. Chem. Soc.*, 1989, **111**, 5525.
- 12 T. Inabe, N. Hoshino, T. Mitani and Y. Maruyama, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2245.
- 13 T. Inabe, *New J. Chem.*, 1991, **15**, 129.
- 14 N. Hoshino, T. Inabe, T. Mitani and Y. Maruyama, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 4207.
- 15 T. Inabe, I. Gautier-Luneau, N. Hoshino, K. Okaniwa, H. Okamoto, T. Mitani, U. Nagashima and Y. Maruyama, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 801.
- 16 T. Inabe, I. Luneau, T. Mitani, Y. Maruyama and S. Takeda, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 612.
- 17 T. Inabe, N. Hoshino-Miyajima, I. Luneau, T. Mitani and Y. Maruyama, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 622.
- 18 A. C. Olivieri, *J. Chem. Soc., Perkin Trans. 2*, 1990, 85.
- 19 S. H. Alarcón, A. C. Olivieri and P. Jonsen, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1783.
- 20 K. Wozniak, H. He, J. Klinowski, W. Jones, T. Dzienbowska and E. Grech, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 77.

Paper 6/03573F

Received 22nd May 1996

Accepted 17th June 1996