

Nuclear Quadrupole Resonance Studies of Schiff Bases*

E. Hadjoudis, I. Moustakali-Mavridis, and F. Milia

Nuclear Research Center "Demokritos"
Athens, Greece

J. Seliger, R. Blinc, and V. Zegar

J. "Stefan" Institute
University of Ljubljana
Ljubljana, Yugoslavia

I. INTRODUCTION

Crystalline anils (Schiff bases, I) undergo photochromism or thermochromism by hydrogen transfer and present common features in their structures and reaction mechanisms:

- 1) The intramolecular hydrogen-transfer step occurs via a six-membered ring transition state.
- 2) The hydrogen-transfer produces quinoid structures.
- 3) The thermally stable forms are the *ortho*-OH substituted aromatic structures.
- 4) One or more processes occur to cause some stabilization of the photocolored species formed by the endothermic photolysis step.
- 5) The thermochromic compounds display planar structures while the photochromic ones, non-planar structures.
- 6) Both photochromic and thermochromic compounds show (in their transfer reaction) a high degree of reversibility.

Thus, if we prepare a thin polycrystalline film between two quartz plates, the photochromic phenomenon is illustrated in Figure 1A with the compound having X=H, Y=2-Cl, and thermochromism is illustrated in Figure 1B with the compound having X=5'-Cl, Y=H, i.e. reversible color change in the spectrum as a result of

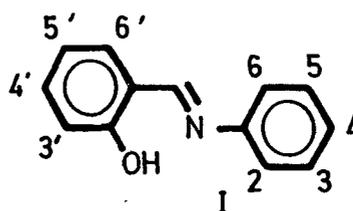


photo-irradiation or of variation in temperature

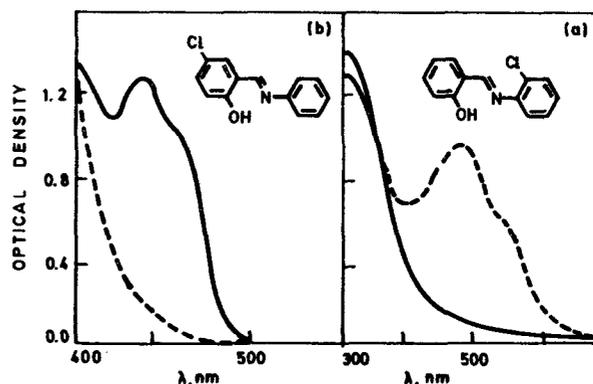


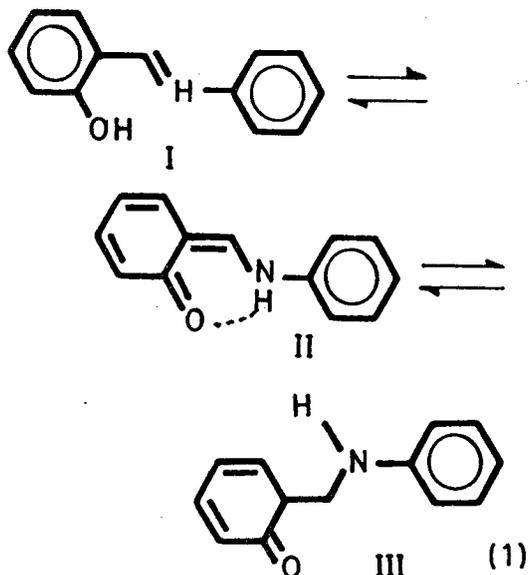
Figure 1(A). Photochromism of salicylidene-2-chloroaniline, before (-) and after (---) illumination, and (B) thermochromism of 5'-chlorosalicylideneaniline at rt (-) and liquid nitrogen temperature (---).

*Presented at the 6th Specialized Colloque Ampere on "Quadrupole Interactions and Spatially Resolved NMR in Solids," Crete, Greece, September, 12-17, 1983.

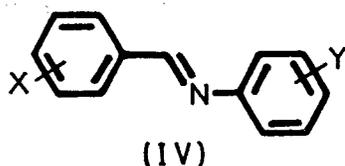
(1,2).

The interpretation of the color formation is as follows (3): there is a temperature sensitive

equilibrium in the crystal between two tautomers of the molecule, one with the chelating hydrogen covalently bonded to the oxygen, the "OH-form" (I), and the "NH-form" (II) with the hydrogen



bonded to the nitrogen (equation 1). The "NH-form" absorbs at longer wavelengths; raising the temperature increases the population of this form and thus causes a deepening of color. The intramolecular hydrogen transfer can occur in either the ground or excited electronic state. In contrast, a high energy is required for hydrogen transfer in the ground electronic state of molecules in photochromic crystals because of the non-planarity and, as a result, no absorption attributable to the NH-forms is observed. Hydrogen transfer can occur, however, in the excited state and the crystal is sufficiently open (non-planar molecules) to permit a subsequent geometric isomerization which leads to the colored photo-product, III. It was further claimed (1) that neither photochromism or thermochromism or the associated "chromo-isomerism" can be observed in the absence of the *ortho*-OH group and, therefore, benzylideneaniline and its derivatives IV should be inactive towards temperature



and light. Therefore, the active compounds have different solid phases with different dynamic states, and the inactive compounds have only one solid phase in which molecular motions are restricted to lattice or torsional oscillations. Thus, we expected that by examining a number of solid Schiff bases with the NQR technique, we could differentiate motions such as *enol-keto* tautomerization or *cis-trans* isomerization in addition to the temperature dependent shifts in the resonance frequency predicted by the Bayer (4) theory. It should be mentioned here that in spite of the continued efforts no clear direct evidence on the nature of the photo-induced colored species II or III have been obtained in the solid state. Thus, the color changes in thermochromic crystals ($X=5\text{-Cl}$, $Y=H$) are not accompanied by an observable change in the crystal structure as determined by X-ray diffraction (5).

To achieve our goal we performed two kinds of measurements: we measured thermochromic compounds at various temperatures and photochromic compounds before and after irradiation. The nuclei measured were ^{35}Cl at various positions of the two rings and ^{14}N at the bridge of the molecules ($\text{C}=\text{N}$) and in the *ortho*-position of the aniline ring, that is in salicylidene-2-aminopyridines.

II. EXPERIMENTAL

The compounds used in this work were synthesized by direct condensation of the appropriate salicylaldehyde with the appropriate aniline or amino pyridine in ethanol, followed by repeated recrystallization from the same solvent. IR spectra, melting points, and elemental analysis were utilized to establish the purity of the compounds. Table 1 contains the compounds used for the NQR measurements together with their properties and the available structural information.

The ^{35}Cl NQR frequencies were measured by means of two spectrometers: one of the type described by Dean and Pollak (6) and another of the DECCA RADAR. These instruments gave a signal-to-noise ratio of about 20, which in most cases, decreased with a decrease in temperature. Thus, in many cases the temperature dependence could not be studied over the whole desired range because of loss of the signal.

The photochromic compounds were measured before and after irradiation with light of $\lambda = 365$ nm, that is in their yellow and red form at liquid nitrogen temperature; this was possible because when these compounds are irradiated at a temperature at which the yield of color is high (rt),

Table 1. Salicylideneanilines and Salicylideneaminopyridines

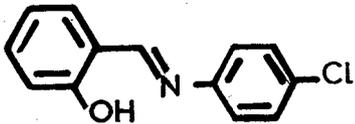
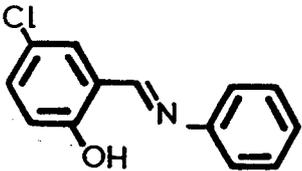
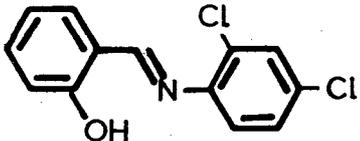
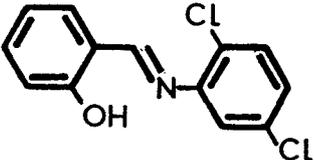
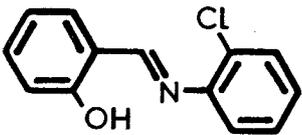
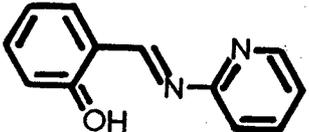
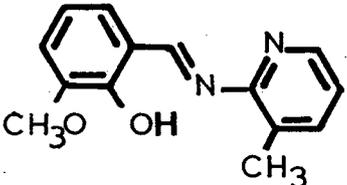
No.	Compound	mp (K)	Structure	Effect of Heat or Light
1		377	Planar ⁵	Thermochromic
2		383	Planar ⁵	Thermochromic
3		348	-	Thermochromic
4		367	-	Thermochromic
5		356	Non-planar ^{1,3}	Photochromic
6		330	Planar ^{1,3}	Thermochromic
7		400	Planar ^{1,3}	Thermochromic

Table 2. Pure Quadrupole Resonance (^{35}Cl and ^{14}N) of Salicylidineanilines and Salicylideneaminopyridines

Compound	Observed Frequencies			
	290 K	^{35}Cl (MHz) 77 K	^{14}N (KHz)	
			298 K	170 K
1	34.024(296) ^a	34.520		
2	34.559(300)	34.900	$\nu_+ = 2890$ $\nu_- = 2590$ $\nu_+ = 3260$ $\nu_- = 2780$	$\nu_+ = 3740$ $\nu_- = 2960$
3	34.720(270)	35.132		
4	34.275	34.650		
5	34.410	35.040	$\nu_+ = 2715^b$ $\nu_- = 2625$	$\nu_+ = 2735^c$ $\nu_- = 2630$ $\nu_+ = 2915$ $\nu_- = 2830$
6			$\nu_+ = 2800$ $\nu_- = 2680$ $\nu_+ = 3535$ $\nu_- = 2968$	$\nu_+ = 3594(153)$ $\nu_- = 3000$
7			$\nu_+ = 2840$ $\nu_- = 2700$ $\nu_+ = 3600$ $\nu_- = 3000$	$\nu_+ = 3628(188)$ $\nu_- = 3024$

a) In parantheses is shown the temperature when different from 290 K and 170 K.

b) Before irradiation and c) after irradiation.

III. RESULTS AND DISCUSSION

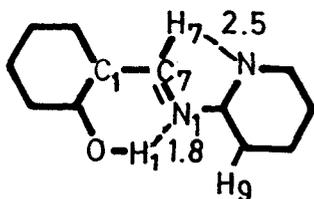


Figure 2. Bond angles (O) and distance (Å) for salicylidene-2-aminopyridine.

and are subsequently cooled to liquid nitrogen temperature, the photo-color is found to persist without loss of intensity.

The rather low ^{14}N NQR frequencies were measured with the help of a proton-nitrogen double resonance technique based on the solid effect (7). The method is based on rf-induced coupling between the dipolar frame of the protons and the rotating frame of the ^{14}N nuclei.

The NQR spectrum of ^{35}Cl in the chlorine substituted compounds listed in Table 1 has been studied over the temperature range 77 to 298 K (8). Although four of these compounds, 1-4, display thermochromic phenomena, i.e. a serious change of color with temperature, there was no evidence of a phase transition or discontinuity in the plot of NQR frequency vs temperature. We therefore give in Table 2 only the observed ^{35}Cl frequencies at 290 and 77 K. The inability to observe differences in the above measurements, which could be attributed to the proton transfer from the *ortho*-OH group to the nitrogen of the C=N bond (equation 1), is attributed to the fact that the charge distribution of the nitrogen atoms is outside the radius of the chlorine atom. Therefore, the contribution to the electric field gradient is less than 1% of that due to a typical p-valence electron in the case of the halogens (9). In order to gain information about the proton transfer we studied the changes in the ^{14}N spectra of photochromic salicylidene-2-chloroaniline induced by UV light to compare with the changes induced by temperature variations in the ^{14}N NQR spectra

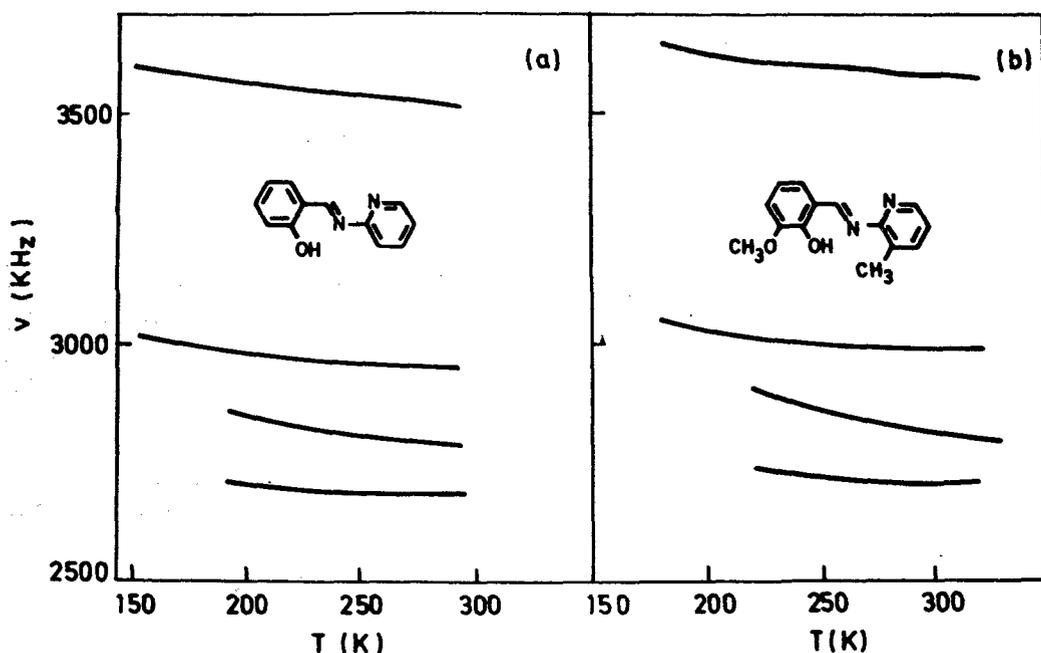
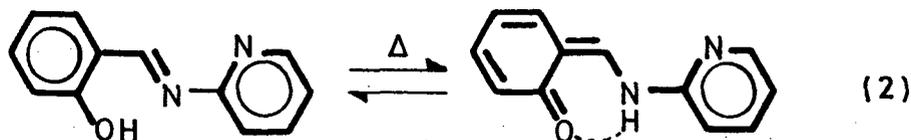


Figure 3. Frequency vs. temperature curves for (A) salicylidene-2-aminopyridine and (B) 3'-methoxysalicylidene-2-amino-3-methylpyridine.



of thermochromic 5'-chlorosalicylideneaniline (10). Table 2 shows the effect of temperature on the pure ^{14}N NQR spectra at 170 and 310 K. At low temperatures we observed two spectral lines in the NQR spectrum of ^{14}N (spin, 1) and therefore, one chemically non-equivalent ^{14}N sites per unit cell. The results obtained at high temperatures are evidently a superposition of the low and high temperature spectra, thus demonstrating the presence of a keto-enol equilibrium in solid 5'-chlorosalicylideneaniline (equation 1). Table 2 shows also the effect of irradiation on the pure ^{14}N NQR spectra of salicylidene-2-chloroaniline before and after irradiation. The results obtained in this case are also a superposition of the spectra before and after irradiation, demonstrating again the presence of the keto and enol forms (equation 1). It should be emphasized here that we succeeded in observing (11) in the case of 5'-chlorosalicylideneaniline at 295 all three resonances (V_+ , V_- , and V_0), and this allowed us an unambiguous pairing of the observed lines in the two distinct crystalline sites present.

The results with the salicylideneaminopyridines are not conclusive and are more complicated. These compounds contain one type of nitrogen atom (two-fold coordination) in their enol form and two types of nitrogen atoms (two-fold and three-fold coordination) in their keto form (equation 2). Therefore, one expects four frequency signals in the enol form and eight in the case of the equilibrium of equation 2. It should be pointed out that all the examined molecules of the salicylidene-2-aminopyridines are thermochromic in the solid state (12). This generality can be explained by examining the crystal and molecular structure of this class of compounds. Thus, salicylidene-2-aminopyridine, 5'-bromosalicylidene-2-aminopyridine, 5'-methoxysalicylidene-2-amino-5-chloropyridine and 3'-methoxysalicylidene-2-amino-methoxy-pyridine, investigated by X-ray diffraction, show that the molecules are essentially planar (13). In the planar molecular structure the lone pair of the imino nitrogen atom does not overlap with the electrons of the pyridine ring, and consequently the basicity of the bridge N atom and hence the strength of the hydrogen bond between the H atom of the OH group and the imino N atom should be higher. Therefore the proton transfer postulated in equation 2 (quinoid *cis* form) is favored in the planar as against a non-planar conformation. The molecular structures of all salicylidene-2-aminopyridines investigated so far show a strong intramolecular hydrogen bond

with a mean H(1)---N((1) distance of 1.8 Å, and and also show the appropriate geometry for the hydrogen atom to point towards the lone pair of the N(1) atom as it is shown in Figure 2 for the case of salicylidene-2-aminopyridine.

The molecular packing of the four compounds studied is characteristic of that of flat molecules arranged in stacks along the shortest crystal axis with mean interplanar distance of 3.54 Å. Based on their identical behavior it may well be justified to suppose that all the salicylidene-2-aminopyridine compounds will have a similar packing arrangement. We suggest that the planarity is achieved because of the hetero-nitrogen of the pyridine ring. In the case of salicylideneanilines there is steric hindrance due to the short distance of ~ 2 Å between the *ortho*-hydrogen H(9) and the exocyclic hydrogen H(7) when the molecule is planar (5). This repulsion is relieved in the case of salicylidene-2-aminopyridines because the hetero-nitrogen atom is always at the *cis*-position with respect to the H(7) hydrogen atom (Figure 2). The distance of about 2.5 Å between these atoms corresponds to normal van der Waals contact.

The NQR results (see Table 2) show that we observe at rt (where enol and quinoid forms are expected to coexist) four signals in each case and therefore two chemically non-equivalent ^{14}N sites per unit cell. Since, however, the low intensity of the NQR lines (low frequency) and the large spin lattice relaxation time (integer spin $I=1$) complicate the search for NQR signals (14), we decided to follow a number of them with temperature in order to differentiate if possible between enol and quinoid structures. Thus, Figure 3 shows the frequency vs. temperature curves for (a) salicylidene-2-aminopyridine and (b) 3'-methoxysalicylidene-2-amino-3-methylpyridine. The frequency vs. temperature results may be explained in at least two ways:

(a) The two sets of lines belong to the bridge nitrogen in two different configurations (enol and keto forms) and we do not observe the ring nitrogen. This is in agreement with the fact that at low temperatures we observe only two lines (the enol form).

(b) The observed signals, at least at rt, belong to both the bridge and ring nitrogen but not all are observable. The situation could be clarified by measuring the proton-nitrogen cross-relaxation time at different temperatures, since it depends on the population of states.

Such measurements are in progress.

REFERENCES

- ¹M. D. Cohen and G. M. J. Schmidt, *J. Phys. Chem.* **66**, 2442 (1962).
- ²E. Hadjoudis, *J. Mol. Cryst. Liq. Cryst.* **13**, 233 (1971).
- ³M. D. Cohen and E. Hadjoudis, *Mol. Cryst.* **2**, 267 (1967).
- ⁴H. Bayer, *Z. Physik.*, **130**, 227 (1951).
- ⁵J. Bregman, L. Leiserowitz, and G. M. J. Schmidt, *J. Chem. Soc.* 2068 (1964); J. Bregman, L. Leiserowitz, and K. Osaki, *J. Chem. Soc.*, 2086 (1964).
- ⁶C. Dean and M. Pollack, *Rev. Sci. Instr.* **29**, 630 (1958).
- ⁷J. Seliger, R. Blinc, M. Mali, R. Osredkar, and A. Preslesnic, *Phys. Rev., B* **11**, 27 (1975); *Phys. Stat. Sol., A* **25**, K121 (1974).
- ⁸E. Hadjoudis and F. Milia, *Advances in Nuclear Quadrupole Resonance*, Vol.1, J. A. S. Smith, Ed., Heyden, London, 1974, p. 133.
- ⁹C. H. Townes and B. P. Dailey, *J. Chem. Phys.* **20**, 35 (1952).
- ¹⁰E. Hadjoudis, F. Milia, J. Seliger, R. Blinc, and V. Zagar, *Chem. Phys.* **47**, 105 (1980).
- ¹¹E. Hadjoudis, F. Milia, J. Seliger, R. Blinc, and V. Zagar, *Chem. Phys. Letters* **56**, 382 (1978).
- ¹²E. Hadjoudis, I. Moustakali-Mavridis, and J. Xexakis, *Israel J. Chem.* **18**, 202 (1979).
- ¹³I. Moustakali-Mavridis, E. Hadjoudis, and A. Mavridis, *Acta Crystal.* **B34**, 3709 (1978).
- ¹⁴G. K. Semin, T. A. Brushkina, and G. G. Yakobson, *Nuclear Quadrupole Resonance in Chemistry*, John Wiley and Sons, New York, N.Y., 1975, p. 181.