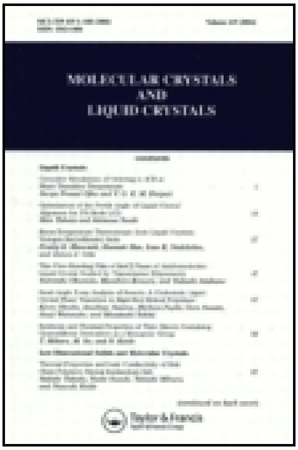


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Molecular-Ionic Tautomerism of 4-Dimethylamino-Benzylidene-4-Chloroaniline: HCL Complex

E. Hadjoudis [a]

[a] Chemistry Department, Nuclear Research Center "Demokritos", Aghia Paraskevi, Attiki, Greece

Version of record first published: 13 Dec 2006.

To cite this article: E. Hadjoudis (1986): Molecular-Ionic Tautomerism of 4-Dimethylamino-Benzylidene-4-Chloroaniline: HCL Complex, Molecular Crystals and Liquid Crystals, 137:1, 17-27

To link to this article: http://dx.doi.org/10.1080/00268948608070908

Mol. Cryst. Liq. Cryst., 1986, Vol. 137, pp. 17-27
0026-8941/86/1374-0017$20.00/0

Printed in the United States of America

MOLECULAR-IONIC TAUTOMERISM OF 4-DIMETHYLAMINO-BENZYLIDENE-4-CHLOROANILINE : HCl COMPLEX.

E. HADJOUDIS
Chemistry Department, Nuclear Research Center "Demokritos", Aghia Paraskevi, Attiki, Greece.

Abstract: When gaseous HCl interacts with yellow crystalline N-(4-dimethylamino-benzylidene)-4-chloroaniline a red-orange charge transfer crystalline complex is formed. When this crystalline complex is disolved in polar solvents an intracomplex proton-transfer takes place leading to a molecular ionic form of the complex. This proton-transfer does not take place or with very small efficiency when non polar solvents are used. In all the cases, after prolonged time, decomposition takes place and only the decomposition products are observed.

INTRODUCTION

The gradual transformation of a molecular complex into an ionic pair continuously and how this is accomplished, is always of particular interest[1]. In general the interaction between a protic acid (AH), and a neutral base (B), in aprotic low-polarity solvents results in the formation of an hydrogen-bonded complex the structure of which, depending upon the acid-base strength of the contributors and the solvent polarity, may vary from molecular (AH...B) to ionic (A^-...HB^+).

The energy of the acid-base interaction is rougly characterized by the usually available ΔpKa[2,3] value which, plotted against spectroscopic values indicating the strength of an H-bond (e.g. the chemical shift of a bridge proton, the frequency and integral intensity of the stretching vibration (v_s) etc.) were shown to pass through their maxima and failed to give unambigous proof of the gradual ionization of a molecular complex upon increase of the interaction energy. However in a number of papers[4-7] the existance of the"molecular-ionic tautomerism" of H-bonded complexes was demonstrated:

$$AH....B \rightleftharpoons A^{-}.....HB^{+} \qquad (1)$$

The tautomerism implies a sharp change in structure and the equilibrium (1) is shifted to the right as the acid-base interaction gets stronger. Using low temperatures one would observe either a molecular or ionic complex depending on the ΔpKa value.

In the present investigation the molecular complex 4-dimethylamino-benzylidene-4-chloroaniline with HCl was prepared independently as a stable coloured solid by a gas--solid reaction. The stable molecular complex then was studied by dissolving it in various solvents and its continuous transformation to the ionic form followed spectrophotometrically.

A number of related compounds were also studied for comparison.

EXPERIMENTAL

The compounds were synthesized by direct condensation of the appropriate benzaldehyde with the appropriate aniline in ethanol, followed by repeated recrystallization from the same solvent. I.R., melting points and elemental analysis were utilized to establish the purity of the compounds.

The quantitative experiments in which HCl uptake was followed were carried out on crystalline samples (average weight 50 mg) sieved to 350 mesh size and placed on a special weight pan. These samples were introduced into a modified washbottle through which gaseous HCl (Matheson, 99%) was admitted via a drying agent. The samples were removed periodically and introduced into a Cahn R.G. Electrobalance and weighed.

Absorption spectra were recorded on a Cary-17 spectrophotometer, fluorescence spectra on an Aminco and infrared spectra were recorded on a Perking-Elmer Model infrared spectrophotometer over the spectral range 4000-400 cm^{-1}.

X-ray photographs of powdered samples were taken on a Debye-Scherrer camera of radius 5.7 cm with Cukα radiation at about 2.5 hrs exposure.

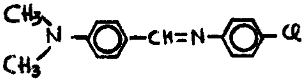
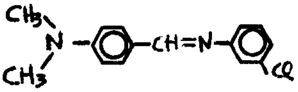
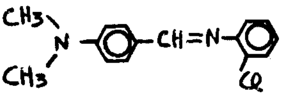
The ^{35}Cl quadrupole resonances were observed using the DECCA NQR spectrometer. Half to one gram samples were sealed in glass tubes of 1 cm diameter and positioned in the spectrometer coil. The nuclear quadrupole resonance (NQR) spectra were obtained at 77 and 298 K.

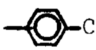
RESULTS AND DISCUSSION

THE SOLID STATE COMPLEX

Table I shows the crystalline benzylideneanilines tested for gaseous-HCl uptake in a gas-solid reaction as described in the experimental part.

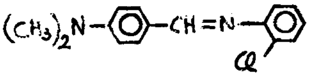
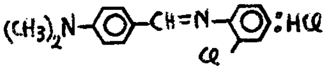
Table I. Solid Benzylideneanilines

Compounds	m.p. (°C)	colour	complex composition	colour of complex	mp of complex
	149	yellow	1 : 1	red-orange	210
	75	yellow	1 : 1	orange	240 (dec)
	-	yellow	1 : 1	orange	185

The stronger colour on complexation is observed with 4-dimethyl-aminobenzylidene-4-chloroaniline. Benzylideneanilines without the dimethylamino-grouping failed to show any HCl-uptake and no colour change is observed. Also, complexes are not formed with the corresponding benzaldehydes and amines from which the compounds of Table 1 were synthesized such as $(CH_3)N$  CHO and H_2N  Cl Therefore not only is the dimethylamino-grouping important for the reaction but also the $\rangle C = N-$ bond of the bridge. These results in connection with the observation that the strongest colouration takes place with 4-dimethylamino-benzylidene-4-chloroaniline seem to be related to the effective π-electron charge on the azomethine nitrogen which is increased by the inclusion of the powerful effects of the direct polar conjugation of the π-electrons of the azomethine bond with the sp^3 electrons of the 4-$N(CH_3)_2$ group.

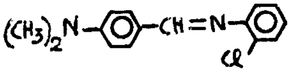
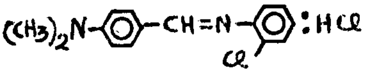
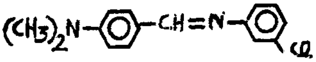
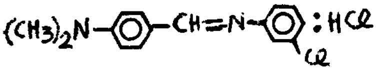
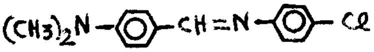
The complexation after the gas-solid reaction was verified by x-ray diffraction of powdered samples taken before and after the exposure of the crystalline compounds to gaseous HCl. We observed changes both in spacing and in intensity of the lines which were estimated as strong (s), moderately strong (ms), medium (m), moderately weak (mw), and weak (w). Table II shows the results with 4-dimethylaminobenzylidene-2-chloroaniline.

Table II. d spacings of 4-dimethylaminobenzylidene-2-chloroaniline before and after the interaction with gaseous-HCl

I_o		I_o	
ms	9.06	w	15.40
s	7.00	w	11.00
s	6.42	w	9.63
s	5.92	vw	7.70
vw	5.50	ms	7.00
mw	5.13	vs	6.42
s	4.81	ms	5.92
vs	4.53	vw	5.13
s	4.40	w	4.81
s	3.85	vs	4.53
s	3.67	s	4.28
vs	3.50	s	4.28

The complexation was also verified by nuclear quadrupole resonance and I.R. measurements. Thus Table III shows the ^{35}Cl NQR frequencies of the pure and "complexed" compounds at room temperature (RT) and liquid nitrogen temperature (LN).

Table III. ^{35}Cl nuclear quadrupole resonance frequencies (in MHz)

Compound	ν_{RT}	ν_{LN}
	34.016	34.653
	34.982	35.863
	33.747	34.280
	not observed	35.140
	33.757	34.400
	not observed	not observed

The results of Table 3 show that, in all the cases where we succeeded in measuring the ^{35}Cl frequencies before and after complexation, the frequency of the pure compounds are shifted to higher frequencies when complexed with HCl.

We were unable to detect shifted signals in the case of 4-dimethylaminobenzylidene-4- chloroaniline. This may be due to the crystal structure of the resulting complex.

The I.R. spectra (in KBr pellets) also show characteristic structural changes due to the complex formation. Fig. 1 shows for example the I.R. spectra of uncomplexed and complexed 4-dimethylaminobenzylidene-4-chroroaniline.

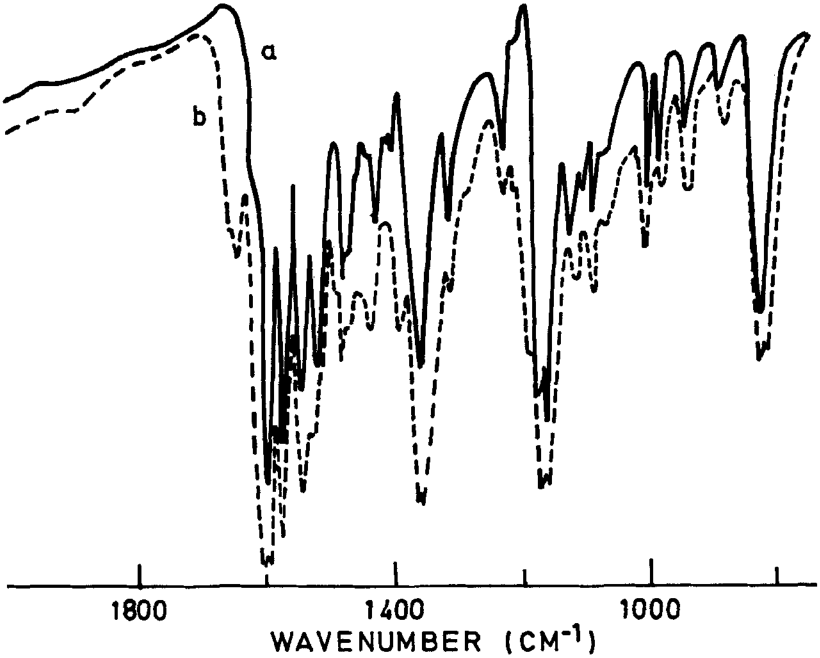


FIGURE 1. I.R. spectrum of 4-dimethylaminobenzylidene-4-chloroaniline (a) and of 4-dimethylaminobenzylideneaniline-4-chloroaniline : HCl complex (b).

Two broad continua between 2500 cm^{-1} and 3500 cm^{-1} and other spectral changes, mainly the one around

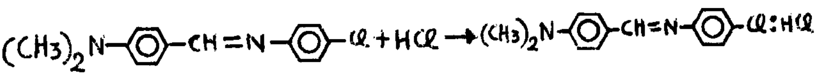
1640 cm^{-1}, constitute additional evidence for the complex formation.

MOLECULAR-IONIC TAUTOMERISM

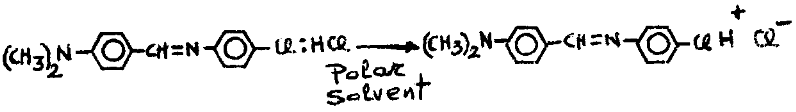
When the solid coloured complex, e.g. 4-dimethylaminobenzylidene-4-chloroaniline which was studied in detail, is dissolved in polar solvents (e.g. $CHCl_3$), a new strong band appears in the visible region (max. 442 nm) and the band of the pure compounds (max. 360 nm) is shifted to shorter wavelengths (max. 336 nm) as it is seen in Fig. 2.

This new band (max. ≈442 nm) is not stable but changes with time following second order kinetics with $k = 9.73$ lit sec^{-1} mol^{-1}. Thus the band at 442 nm decreases and the band at 336 nm increases with two distinct isosbestic points at 285 and 365 nm respectively. Finally an equilibrium is attained in which the intensities of the two bands have practically interchanged.

The above results may be explained as follows :
When gaseous HCl (HA) interacts with the solid compound (B) a red-orange complex (B:HA) is formed. When this solid co-



loured complex is disolved in a polar solvent, an intracomplex proton transfer takes place leading to an ionic form ($\overset{+}{BH}$ $\bar{A}$)



B:HA $\qquad$ $BH^+ A^-$

which absorbs at lower wavelengths. This proton transfer does not take place or does with very low efficiency when a

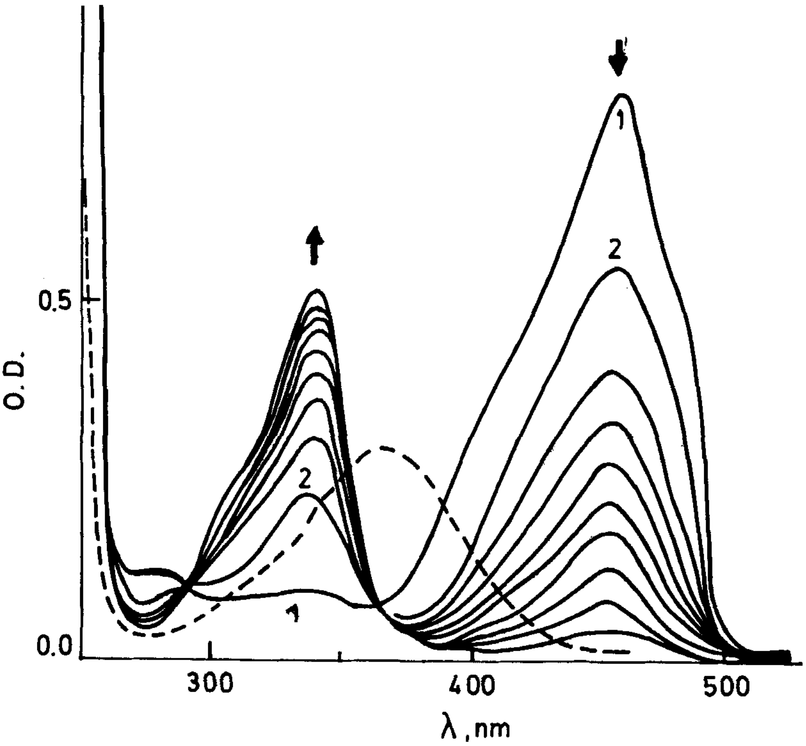


FIGURE 2. Spectral changes observed upon dissolution of the solid complex of 4-dimethylaminobenzylidene-4-chloroaniline, HCl in $CHCl_3$ ($C=10^{-4}M$), with time (10 min. between runs). The spectrum of the uncomplexed compound (dotted line) is displayed for reasons of comparison.

non polar solvent is used. Therefore what we observe during the disappearance of the long-wavelength band and the appearance of the short-wavelength band is nothing else but the flow of change during this transformation.

In all the cases, after a prolonged time, hydrolysis takes place and only the hydrolysis products are observed.

The overall procedure can be described as follows :

$$\underset{\text{gas}}{HA} + \underset{\text{(solid yellow)}}{\{B\}} \longrightarrow \underset{\text{(solid red-orange)}}{\{B.HA\}} \xrightarrow{\text{Polar Solvent}} B.H....A \rightleftharpoons BH^{+}....A^{-}$$

where $\{\ \}$ denotes that the compound is in a particular crystalline structure.

ACKNOWLEDGMENT

I would like to thank Mrs. Chr. Mallerou for her skilful technical assistance.

REFERENCES

1. N.S. Golubev, S.F. Bureiko and G.S. Denisov, Adv. Mol. Relax. and Interat. Processes, 24, 225 (1982).
2. D. Hadzi, J. Chem. Soc., A,3, 418 (1970).
3. B.S. Ault, E. Steiback, G.C. Pimentel, J. Phys. Chem., 79, 615 (1975).
4. G.M. Barrow, J. Amer. Chem. Soc., 78, 5802 (1956).
5. R. Scott, D. de Palma, S. Vinogradov, J. Phys. Chem., 72, 3192 (1968).

6. R.A. Hudson, R.M. Scott, S. Vinogradov, J. Phys. Chem., 76, 1989 (1972).
7. R. Lindemann, G. Zundel, J. Chem. Soc. Faraday Trans. II, 73, 788 (1977).