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Photochemistry of *N*-benzylideneanilinium cations in concentrated sulphuric acid solutions

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Abstract

The photoreversible $E \rightleftarrows Z$ isomerization of a series of protonated *N*-benzylideneanilines ($X–C_6H_5CH=NC_6H_5–Y$; $X \equiv H, N(CH_3)_2$; $Y \equiv H, NO_2$) was investigated in concentrated sulphuric acid solution. The UV absorption spectra of the *E* isomers are practically independent of substituents on benzene rings and suggest a planar conformation for protonated *N*-benzylideneanilines. The UV spectra of *Z* isomers were obtained from photostationary state conditions at two wavelengths. Also the quantum yields of $E \rightarrow Z$ and $Z \rightarrow E$ photoisomerization are not markedly affected by the ring substituents and are compatible with a photoreversible process occurring through a common excited state.

Keywords: *N*-benzylideneanilinium cations; *E–Z* Photoisomerization; Quantum yields

1. Introduction

Schiff bases are involved in many fields of chemistry and biochemistry. For example, the azomethine group present in rhodopsin both in the neutral and in the protonated form plays a central role in the light-driven proton pump process occurring during the visual cycle [1–3]. Moreover, *trans-N*-benzylideneaniline is a basic constituent of many compounds showing liquid crystal properties [4].

It is well known that there is a marked dissimilarity in the electronic spectrum of *trans-N*-benzylideneaniline (**1**) and the spectra of the π-isoelectronic *trans*-stilbene and *trans*-azobenzene [5,6]. According to experimental [7–12] and theoretical [13–16] studies this is due to the non-planar conformation of **1**, as a consequence of conjugation between the aniline ring and the nitrogen lone pair, in contrast to the nearly planar structure of the other π-isoelectronic molecular systems.

Also, substituted *trans-N*-benzylideneanilines generally are not planar [17,18]. In particular, intramolecular charge transfer effects determine the molecular shape of such compounds when they are *p*- and *p'*-substituted with strong electron acceptor and donor groups ('push–pull' compounds) [18]. Both intramolecular charge transfer between substituents and that from the bridge nitrogen lone pair to the substituent on the aniline ring have been invoked [18,19]. In any case $E \rightarrow Z$ photoisomerization is the main deactivation pathway of excited *E* isomers [20–24] and no emission has been generally observed, apart from in the case of 'push–pull' derivatives [25]. The *Z* isomer is stable only at low temperature and isomerizes thermally to the *E* form, according to an inversion mechanism [26,27].

Little attention has been devoted, however, to the effects induced by protonation of the azomethine nitrogen and to the photochemical behaviour of protonated *N*-benzylideneanilines. A long time ago Brocklehurst noticed that the UV spectrum of protonated **1** differs markedly from that of the unprotonated compound and closely resembles that of stilbene [5]. Evidence of a reversible $E \rightleftarrows Z$ photoisomerization process involving protonated **1** has also been observed [22,28].

In the present work investigations are reported concerning the photochemical behaviour of protonated *trans-N*-benzylideneanilines **1–4** (Scheme 1), including the 'push–pull' compound **4**.

2. Experimental details

2.1. Materials

The four *N*-benzylideneanilines, *N*-(phenylmethylene)-benzenamine (**1**), *N*-[(4-nitrophenyl)methylene]-benzenamine (**2**), *N,N*-dimethyl-4-[(phenylimino)methyl]-benzenamine (**3**) and *N,N*-dimethyl-4-[[(4-nitrophenyl)imino]-methyl]-benzenamine (**4**), were synthesized by condensa-

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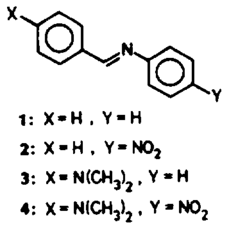

Scheme 1.

tion of the appropriate benzaldehyde and aniline (Fluka products). Equimolar amounts of the two reactants were refluxed in ethanol under stirring for at least 1 h, then anhydrified and cooled to precipitate the product, which was recrystallized at least twice from anhydrous ethanol or *n*-hexane. The melting points were in agreement with literature values [25,29]. Elemental analysis always matched theoretical values, while molar extinction coefficients in cyclohexane solution always coincided with those already reported in the literature [17].

Protonated *N*-benzylideneanilines were obtained in stable form by dissolving the bases in concentrated (approximately 96%, 36 N) sulphuric acid (Fluka). Stable solutions could also be obtained if concentrated sulphuric acid was somewhat diluted, up to ca. 27 N, while hydrolysis of the Schiff bases occurred in more diluted acid solutions. In organic solvents, such as hexane, ether or chloroform, benzylideneanilinium cations decompose rapidly in a normal atmosphere [30].

2.2. *Methods*

Continuous irradiations were carried out at 23 °C in spectrophotometric cuvettes placed on an optical bench, equipped with an Oriel model 7340 xenon lamp (Oriel model 68742 power supply) and an Oriel model 77250 monochromator. The initial concentration of cations **1–4** was in the range $(1–5)\times10^{-5}$ M. Irradiations were performed mainly at 313 and 366 nm, until a photostationary state was reached. The light intensity at these two wavelengths was frequently checked by potassium ferrioxalate actinometry [31] and varied between 6.8 and 4.2×10^{-6} Einstein s^{-1} dm^{-3} at $\lambda=366$ nm and between 3.8 and 2.7×10^{-6} Einstein s^{-1} dm^{-3} at $\lambda=313$ nm during the time period in which quantum yield measurements were carried out.

The kinetics of the photochemical reaction and that of $Z\rightarrow E$ thermal isomerization of protonated **4** were followed spectrophotometrically, as described previously [32,33]. In some of the runs, the spectrophotometric cuvettes containing the acid solutions were thoroughly degassed before irradiation by freeze–pump–thaw cycles and sealed under high vacuum (approximately 10^{-4} Torr).

The absorption spectrum of the Z isomer was obtained from that of the *E* isomer and the absorption spectrum obtained after photostationary states had been reached at 366 and 313 nm. Quantum yields of photoisomerization were calculated according to the model of a photoreversible $E\rightleftarrows Z$ system, irradiated monochromatically at wavelengths which are absorbed by both *E* and *Z* species [34]. The reported values are the mean of the results obtained from at least four different irradiations at the two wavelengths. Reproducibility was better than 15%. The simultaneous thermal $Z\rightarrow E$ isomerization reaction was taken into account in quantum yield calculations of protonated **4**. The rate constant values of this reaction were determined from at least three different runs at each investigated temperature.

Laser flash photolysis measurements were carried out at the University of Perugia, using a Q-switched ruby laser as excitation ($\lambda_{exc}=347$ nm, pulse width approximately 20 ns). Details of the apparatus are given in Ref. [35].

3. Results and discussion

3.1. *Absorption spectra*

Absorption spectra of unprotonated **1–4** differ markedly from each other. The absorption spectra of **1** and **4**, as limiting cases in the examined series, are reported in Fig. 1. In general, the introduction of substituent groups in the aniline and benzaldehyde ring of this class influences the degree of rotation between the two aromatic rings and thus the extent of their π conjugation [17]. Moreover, in the case of unprotonated **4** the intense band at 380 nm clearly reflects a strong charge transfer (CT) interaction between the para-substituted NO_2 and $N(CH_3)_2$ groups in the excited singlet state [18].

In contrast, the absorption spectra of protonated **1–4** do not differ much from each other. A maximum is observed around 340 nm in any case (see Table 1) and the overall spectral shape seems to be scarcely affected by different substituents. In particular, a CT band does not appear in the spectrum of protonated **4**. In concentrated sulphuric acid *N*-benzylideneanilines are completely protonated and exist exclusively as the *trans*-iminium ion, with negligible contribution by the aminocarbocation [36–38]. Moreover, both iminium and ammonium sites of **3** and **4** should be protonated [37,38].

As recently reported [30], protonation brings about many changes also in the vibrational spectrum of **1**, probably owing to a change in hybridization at the nitrogen atom and a dif-

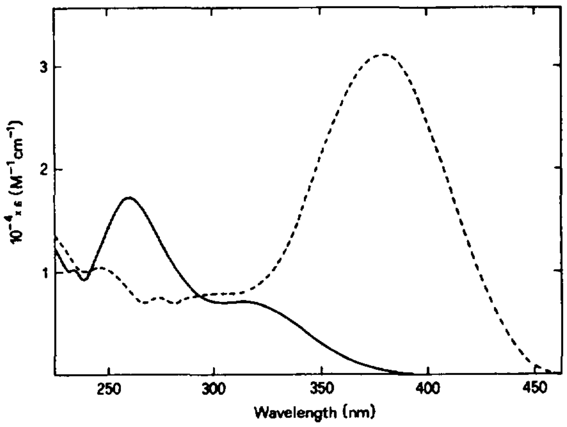

Fig. 1. Absorption spectra of 1 (———) and 4 (– – –) in cyclohexane at room temperature.

Table 1
Extinction coefficients ϵ_{max} at the maximum adsorption wavelength λ_{max} for E and Z protonated isomers in concentrated sulphuric acid

Compound	λ^E_{max} (nm)	ϵ^E_{max} (M^{-1} cm^{-1})	λ^Z_{max} (nm)	ϵ^Z_{max} (M^{-1} cm^{-1})
1	340	21 100	274	12 000
2	350	29 950	296	13 600
3	345	17 800	262	15 000
4	332	28 800	260	16 000

ferent conformation around the imino group. Indeed, a planar conformation can be hypothesized for the investigated cations **1–4** by taking into account the similarity of their UV absorption spectra with that of *trans*-stilbene [5]. This is also in agreement with the results of ^{1}H NMR studies concerning the transmission of electronic effects of substituents on the benzaldehyde and aniline rings in protonated and unprotonated *N*-benzylideanilines [38]. Protonation should prevent delocalization of the nitrogen lone pair, with subsequent coplanarity and π-conjugation between the imine group and the aniline group.

3.2. Photoreactivity

On irradiation, cations **1–4** undergo $E \rightleftarrows Z$ photoisomerization, until a photostationary state is reached. Irradiations were performed always in concentrated sulphuric acid solutions, to achieve better stability of the photoreactive system and to avoid side reactions. Indeed, the very sharp isosbestic points obtained in all cases ensure that no side reaction occurs during irradiation.

The absorption spectra of Z isomers were estimated [21] by extrapolation from the photostationary state absorption spectra obtained by irradiating cations **1–4** at two different wavelengths within the main (π–π^*) absorption band (313 and 366 nm). All investigated systems present similar behaviour. The main absorption band of the Z form is shifted to shorter wavelengths and is less intense than for the E form, as is usual in these systems. Moreover, a second absorption band generally appears around 260 nm.

The Z isomer of protonated compounds **1–3** is fairly stable at room temperature, while in the case of cation **4** a rather slow thermal $Z \rightarrow E$ isomerization reaction occurs, according to a first-order mechanism. The rate constant values of this process measured at different temperatures are reported in Table 2. From these data an activation energy $E_a = (78.3 \pm 0.7)$ kJ mol^{-1} was calculated, with a pre-exponential factor $A = 3 \times 10^{10}$ s^{-1}.

It is well known that Z isomers of unprotonated Schiff bases undergo relatively fast $Z \rightarrow E$ thermal reactions [22–26]. A comparison of the above results with the corresponding results reported recently for the thermal $Z \rightarrow E$ isomerization of unprotonated **4** in methylcyclohexane ($k_{Z\rightarrow E} = 600$ s^{-1} at 25 °C, $E_a = 60.3$ kJ mol^{-1}, $A = 1.6 \times 10^{13}$ s^{-1}) [25] and in benzene ($k_{Z\rightarrow E} = 704$ s^{-1} at 25 °C) [26] clearly reveals that protonation at the nitrogen lone pair of the imino group strongly suppresses the $Z \rightarrow E$ isomerization, blocking the inversion mechanism.

Table 2
First-order rate constants at different temperatures for the $Z \rightarrow E$ thermal isomerization of protonated **4** in concentrated sulphuric acid

T (°C)	$k_{Z\rightarrow E}$ (s^{-1})
18	$(2.70 \pm 0.03) \times 10^{-4}$
23	$(4.58 \pm 0.05) \times 10^{-4}$
28	$(7.92 \pm 0.08) \times 10^{-4}$
33	$(1.31 \pm 0.02) \times 10^{-3}$

Table 3
Percentage of protonated Z-isomer α, at the photostationary states obtained by irradiation at 313 and 366 nm and photoisomerization quantum yields

Compound	λ_{irr} (nm)	α (%)	$\Phi_{E\rightarrow Z}$	$\Phi_{Z\rightarrow E}$
1	366	86	0.39	0.45
1	313	56	0.36	0.42
2	366	88	0.40	0.39
2	313	54	0.38	0.37
3	366	82	0.40	0.49
3	313	61	0.38	0.47
4	366	89	0.40	0.43
4	313	64	0.38	0.39

Moreover, Z isomers photogenerated in acidic medium undergo a slow, dark cyclization reaction. In fact, if photostationary state mixtures, containing a great amount of protonated Z isomer (see Table 3), were left to stand overnight or for even longer, changes in the absorption spectrum were observed, indicating the formation of small amounts of the corresponding phenanthridines. Thus cyclization may occur from long-lived protonated Z isomers [39], while it is not observable from the corresponding unprotonated compounds, which are much more short lived.

Photoisomerization quantum yields $\Phi_{E\rightarrow Z}$ and $\Phi_{Z\rightarrow E}$ were evaluated from maximum absorbance vs. time curves, according to the model of a photoreversible $Z \rightleftarrows E$ system, with no side reactions [34]. The results are shown in Table 3. All quantum yield values are below 0.5, as expected for photoreversible systems, in which a common excited state can be reached from both excited Z and E isomers. Moreover, the fact that very similar quantum yield values are obtained for cations **1–4** confirms that the substituents have a minor influence on their photochemical behaviour.

As to the excited states involved in these phototransformations, the most plausible hypothesis points to a short-lived

(π–π^*) S_1 state, by analogy with similar systems [40], although excited triplet states cannot be excluded [41]. Indeed, runs carried out in the absence of oxygen (under vacuum or under Ar purging) have shown that oxygen has no influence on both $\Phi_{E \rightarrow Z}$ and $\Phi_{Z \rightarrow E}$ photoisomerization quantum yields. Moreover, laser flash photolysis studies (with a pulse width of ca. 20 ns) have not revealed any transient at room temperature in sulphuric acid solutions of **1**–**4**. Unfortunately, such measurements could not be carried out at lower temperature, as the sulphuric acid matrix becomes opaque.

In conclusion, major changes occur in *N*-benzylideneanilines on protonation. Substituents on the aromatic rings, which greatly influence the conformation and the photochemical and photophysical processes in unprotonated Schiff bases, have little or no effect on the absorption spectra and photochemistry of protonated compounds. Calculations are needed for a deeper insight into the observed experimental behaviour.

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References

[1] R. Henderson, J.M. Baldwin, T.A. Ceska, F. Zemlin, E. Beckmann and K. Downing, *J. Mol. Biol., 213* (1990) 899.

[2] M.A. El-Sayed, *Acc. Chem. Res., 25* (1992) 279.

[3] A.K. Singh and N. Majumdar, *Photochem. Photobiol., 60* (1994) 510.

[4] H. Kelker and R. Hatz, *Handbook of Liquid Crystals*, Verlag Chemie, Weinheim, 1980.

[5] P. Brocklehurst, *Tetrahedron, 18* (1962) 299.

[6] E. Haselbach and E. Heilbronner, *Helv. Chim. Acta, 51* (1968) 16.

[7] H.B. Bürgi and J.D. Dunitz, *Helv. Chim. Acta, 53* (1970) 1747.

[8] M.A. El-Bayoumi, M. El-Aasser and F. Adbel-Halim, *J. Am. Chem. Soc., 93* (1971) 586.

[9] T. Bally, E. Haselbach, S. Lanyiova, F. Marschner and M. Rossi, *Helv. Chim. Acta, 59* (1976) 486.

[10] R. Akaba, K. Tokumaru, T. Kobayashi and C. Utsunomiya, *Bull. Chem. Soc. Jpn., 53* (1980) 2002.

[11] K. Maeda, K.A. Muszkat and S. Sharafi-Ozeri, *J. Chem. Soc., Perkin Trans. II*, (1980) 1282.

[12] J.W. Lewis and C. Sandorfy, *Can. J. Chem., 60* (1982) 1720.

[13] R. Akaba, K. Tokumaru and T. Kobayashi, *Bull. Chem. Soc. Jpn., 53* (1980) 1993.

[14] J. Bernstein, Y.M. Engel and A.T. Hagler, *J. Chem. Phys., 75* (1981) 2346.

[15] L.N. Patnaik and S. Das, *Int. J. Quantum Chem., 27* (1985) 135.

[16] M. Kontoyianni, A.J. Hoffman and J.P. Bowen, *J. Comput. Chem., 13* (1992) 57.

[17] P. Skrabal, J. Steiger and H. Zollinger, *Helv. Chim. Acta, 58* (1975) 800.

[18] H. Nakai, M. Shiro, K. Ezumi, S. Sakata and T. Kubota, *Acta Crystallogr. B, 32* (1976) 1827.

[19] L.N. Patnaik and S. Das, *Int. J. Quantum Chem., 27* (1985) 135.

[20] E. Fischer and Y. Frei, *J. Chem. Phys., 27* (1957) 808.

[21] E. Fischer, *J. Phys. Chem., 71* (1967) 3704.

[22] K. Geibel, B. Staudinger, K.H. Grellmann and H. Wendt, *Ber. Bunsenges. Phys. Chem., 76* (1972) 1246.

[23] K. Maeda and E. Fischer, *Isr. J. Chem., 16* (1977) 294; K. Maeda and E. Fischer, *Helv. Chim. Acta, 66* (1983) 1961.

[24] D.G. Anderson and G. Wettermark, *J. Am. Chem. Soc., 87* (1965) 1433.

[25] H. Görner and E. Fischer, *J. Photochem. Photobiol. A: Chem., 57* (1991) 235.

[26] T. Asano, H. Furuta, H.-J. Hofmann, R. Cimiraglia, Y. Tsuno and M. Mizue, *J. Org. Chem., 58* (1993) 4418.

[27] T. Asano, H. Furuta and H. Sumi, *J. Am. Chem. Soc., 116* (1994) 5545.

[28] K. Geibel, B. Staudinger, K.H. Grellmann and H. Wendt, *J. Photochem., 3* (1974) 241.

[29] W.F. Smith, *Tetrahedron, 19* (1963) 445.

[30] Z. Meic, G. Baranovic and T. Suste, *J. Mol. Struct., 296* (1993) 1163.

[31] C.G. Hatchard and C.A. Parker, *Proc. R. Soc. London, Ser. A, 235* (1956) 518.

[32] B. Marcandalli, E. Selli, I.R. Bellobono and L. Basini, *J. Photochem., 36* (1987) 297.

[33] E. Selli, I.R. Bellobono, G. Polimeni and B. Marcandalli, *J. Photochem. Photobiol. A: Chem., 58* (1991) 253.

[34] G. Gauglitz, *J. Photochem., 5* (1976) 41.

[35] G. Galiazzo, A. Spalletti, F. Elisei and G. Gennari, *Gazz. Chim. Ital., 119* (1989) 277.

[36] R.L. Reeves and W.F. Smith, *J. Am. Chem. Soc., 85* (1963) 724.

[37] A.A.H. Saeed, *Indian J. Chem., 17A* (1979) 105.

[38] G. Odian, N. Yang and Y. Wei, *Magn. Reson. Chem., 23* (1985) 908.

[39] F.B. Mallory and C.S. Wood, *Tetrahedron Lett., 30* (1965) 2643.

[40] J. Saltiel and J.L. Charlton, in P. de Mayo (ed.), *Rearrangements in Ground and Excited States*, Vol. 3, Academic Press, New York, 1980, p. 25.

[41] H. Gruen and H. Görner, *J. Phys. Chem., 93* (1989) 7144.