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[Arylazobenzene−BF_3] dyes: Electronic absorption and NMR spectroscopic evidence for a novel class of dyes stable in aprotic solvents

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Dedicated to Professor Marcello Tiecco on the occasion of his 70th birthday

Abstract

Treatment of a number of 4-substituted arylazobenzenes (−H, −Me, −CF_3, −Br, −F and −OMe) with $BF_3 \cdot OEt_2$ in dry chloroform solution afforded chromophores that exhibited significant hyper- (log ε 4.41−4.60) and bathochromic shifts (λ_{max} 416−473) in electronic spectra, together with significant shifts in their ^{1}H NMR and ^{13}C NMR spectra, indicating the formation of novel chemical species. It is proposed that complexes are formed between the azo dyes and the Lewis acid, similarly to what happens for the well-known protic acids. The equilibrium constants (log K) of the proposed complexes have been calculated from the experimental data. Numerical modelling has also been performed to investigate the nature of the new systems, revealing a correlation between the electronic levels of the azo dye and the ones of the $BF_3 \cdot OEt_2$.

Keywords: Absorption spectra; [Arylazobenzene−BF_3] dyes; Lewis acid; Electronic structures; Numerical modelling (B3LYP/6-31G*)

1. Introduction

Azo dyes represent the most popular class of commercial organic colourants [1,2], as exemplified by the overwhelming number of studies on their chemical and physical properties and their application, which also encompass pharmaceuticals [3−6] and technologically advanced fields, such as, for example photonics and optical data storage [7−15]. As a consequence of the notable importance of these compounds, extensive research has been carried out, and is still in progress, into the chemical and physical properties of this class of dye. In particular, it is well known that azo dyes may undergo protonation following treatment with protic acids [16−18], with a consequent strong variation of their physico-chemical properties, especially their electronic charactersitics. In this context, the use of theoretical approaches such as molecular orbital calculations such as PPP, INDO/1 and, more recently, quantum chemical methods [19−21], have been effectively used to calculate the π-electron charge densities of azo dyes [22,23]. In contrast, to our knowledge, no report has ever been issued on the interaction between azo dyes and Lewis acids, while investigations in this area could potentially be useful for a deeper understanding of the electronic characteristics of the azo bond in response to environmental stimuli.

We present herein a preliminary report on the interactions between 1,2-diphenyldiazene (**1**, Scheme 1, R = H) and a series of 5-substituted arylazobenzenes **2**−**6** (Scheme 1,

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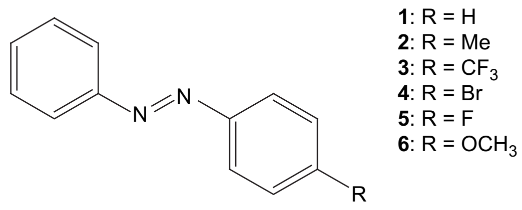

1: R = H
2: R = Me
3: R = CF_3
4: R = Br
5: R = F
6: R = OCH_3

Scheme 1.

R = Me, CF_3, Br, F and OMe, respectively) with $BF_3 \cdot OEt_2$, in dry $CHCl_3$. While the investigation began using gaseous BF_3, as the pure gas proved difficult to handle, its etherated form was preferred for the remainder of the study.

2. Experimental

2.1. Materials

Boron trifluoride etherate, 1,2-diphenyldiazene (**1**) and nitrosobenzene were purchased from Aldrich and were used as received; $CHCl_3$ for UV spectroscopy (Aldrich) was dried and purified as described [24]. Glacial acetic acid was purchased from Carlo Erba Reagents. The (*E*)-arylazobenzenes (**2**–**6**) were prepared in accordance with the Mills reaction [25], according to which, 0.01 M of the appropriate 4-substituted arylamine was combined with 0.01 M of nitrosobenzene in 20 mL glacial acetic acid and the ensuing mixture was refluxed for the required time (until TLC showed the absence of the starting reagents). The resulting (*E*)-arylazobenzenes (**2**, mp = 70–72 °C; **3**, mp = 98–99 °C; **6**, mp = 55–56 °C [26]; **4**, mp = 88–89 °C [27]; **5**, mp = 82–84 °C [28]) were isolated as yellow-orange crystalline products in good yield (85–95%). All isolated compounds were purified by chromatography on a silica column using petroleum ether (distillation range 30–60 °C) and increasing amounts of diethyl ether (up to 20%) as the eluent, and then characterized by IR, NMR and mass spectrometry.

2.2. Physico-chemical measurements

IR spectra were carried out using a Perkin–Elmer 1750 spectrophotometer equipped with an Epson Endeavor II data station on samples prepared as KBr pellets. ^1H NMR and ^{13}C NMR spectra were obtained at room temperature, in 1% w/w $CDCl_3$ solutions, using a Varian NMR Gemini 300 spectrometer. Chemical shifts are given in ppm using tetramethylsilane (TMS) as the internal reference. ^1H NMR spectra were secured at 300 MHz using the following experimental conditions: 24,000 data points, 4.5-kHz spectral width, 2.6-s acquisition time, 128 transients. ^{13}C NMR spectra were recorded at 75.5 MHz, under full proton decoupling, using the following experimental conditions: 24,000 data points, 20-kHz spectral width, 0.6-s acquisition time, 32,000 transients.

UV–vis absorption spectra of compounds **1**–**6** (about 5×10^{-4} M) in dry $CHCl_3$ were recorded at 25 °C on a Perkin–Elmer Lambda 19 spectrophotometer, using cells of path lengths 1.0 and 0.1 cm for the 550–400 and 400–230 nm spectral regions, respectively. Data for the maximum absorption and absorption coefficient (ε) are reported in Table 1. Reactions between $BF_3 \cdot OEt_2$ and **1**–**6** in dry $CHCl_3$ at 25 °C were monitored in the 700–230 nm spectral region, using a cell with a path length of 0.1 cm. Calculations were performed using the program Spartan '04 Windows* running on an AMD K7 processor at 1333 MHz [29,30].

Table 1
UV–vis spectral data and some properties of azobenzenes **1**–**6** and **1a**–**6a**

	R	λ_{max} ($\log \varepsilon_{max}$)[a]	λ_{max} ($\log \varepsilon_{max}$)[b]	λ_{max} ($\log \varepsilon_{max}$)[c]	Dipole[d]	log *K*[e]
1	H	320 (4.42)	442 (2.79)		0.000	
1a				425 (4.56)		0.949
2	Me	327 (4.36)	444 (2.89)		0.656	
2a				441 (4.54)		0.819
3	CF_3	318 (4.32)	448 (2.75)		3.265	
3a				416 (4.41)		0.740
4	Br	327 (4.40)	442 (2.88)		2.183	
4a				445 (4.56)		0.722
5	F	321 (4.31)	443 (2.82)		1.299	
5a				430 (4.48)		0.556
6	OMe	346 (4.39)	434 (2.99)		2.030	
6a				473 (4.60)		1.427

[a] Measured in $CHCl_3$, λ_{max} $\pi \rightarrow \pi^*$ in nm, ($\log \varepsilon_{max}$) in L mol cm^{-1}.
[b] λ_{max} $n \rightarrow \pi^*$ in nm, ($\log \varepsilon_{max}$) in L mol cm^{-1}.
[c] λ_{max} $\pi \rightarrow \pi^*$ in nm, ($\log \varepsilon_{max}$) in L mol cm^{-1} relative to the complex.
[d] In Debye, calculated by B3LYP (6-31G* level) density functional method using Spartan '04 software.
[e] Calculated using the procedure in Refs. [39,40].

3. Results and discussion

The UV–vis spectra of the arylazobenzene dyes in dry $CHCl_3$ were recorded in the range 230–700 nm and are reported in Table 1. The λ_{max} values for the lowest energy $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions for the azobenzenic chromophores, together with the positive solvatochromic aspects [31–33], correspond well with predicted values drawn from similar results obtained in ethanol and other solvents [34]. The bands at 230–240 nm, corresponding to $\Phi \rightarrow \Phi^*$ transition, however, are only fractionally visible, due to their partial overlap with the solvent cut-off point [35]. The absorption maxima of those phenylazobenzenes comprising chromogenic substituents (**2**–**4**) occur at higher wavelengths with respect to the simplest phenylazobenzene chromophore (**1**), in contrast with the absorption maximum obtained for **3**, which can be ascribed to the anti-auxochromic effects associated with the trifluoromethyl substituent [2,36,37].

To investigate the effect of a Lewis acid-like species on azo dyes, direct bubbling, in a dry environment, of gaseous BF_3 into the solutions of the chosen azobenzenes was at first attempted. Evident colour variations were seen in the so-treated solutions, but the difficulties in handling and dosing the BF_3 as a gas induced us to test the utilization of $BF_3 \cdot OEt_2$, which was found to give the same effect of pure BF_3, and to be much easier to be dosed and manipulated. In fact, by using the

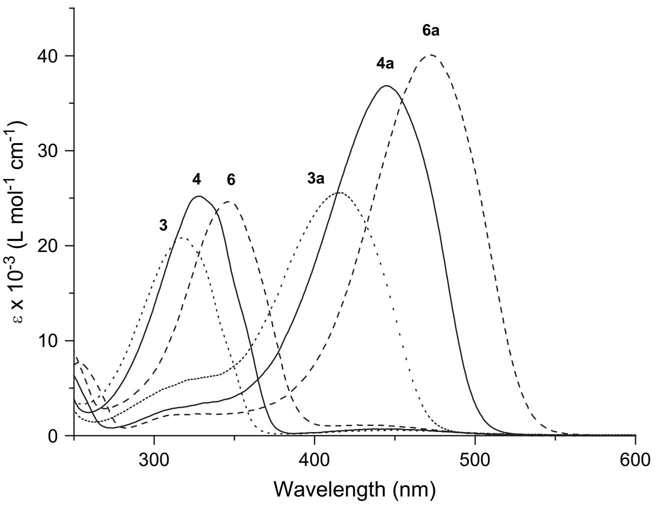

Fig. 1. UV–vis spectra of azoaromatic derivatives in dry $CHCl_3$ solution before (**3**, **4** and **6**) and after (**3a**, **4a** and **6a**) the additions of equal amounts of $BF_3 \cdot OEt_2$

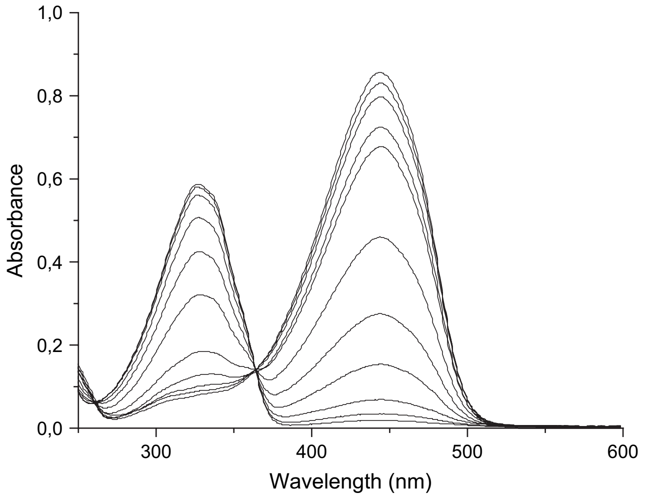

Fig. 2. A UV–vis spectrum depicting the gradual absorption changes as successive increments of neat $BF_3 \cdot OEt_2$ (100, 125, 150, 175, 200, 225, 250, 300, 400, 500 μL) were added to a 10 mL of dry chloroform solution (4.62×10^{-4} mol L^{-1}) of **4** (left), resulting in the formation of [arylazobenzene-$BF_3 \cdot OEt_2$] **4a** (right).

etherated form of BF_3 it was possible to add well controlled amounts of the Lewis acid to dry $CHCl_3$ solutions of the **1–6** azobenzenes (see Section 2), and to reduce substantially the hazards connected with the use of pure BF_3.

Upon addition of the Lewis acid, each of the derived systems **1a–6a** evidenced a very intense colour change with respect to the corresponding starting azo dyes **1–6**. The spectra of some of the dyes, and of the corresponding $BF_3 \cdot OEt_2$-added systems, are shown in Fig. 1 (the remaining dyes and the relative $BF_3 \cdot OEt_2$-added systems have been left out in the figure only for the sake of clarity). For all the considered species the absorption coefficient of the final systems **1a–6a** was found to be higher than that of the starting azo dyes **1–6** (Table 1).

Moreover, $BF_3 \cdot OEt_2$ addition to the $CHCl_3$ solution of the dyes produced not only electronic behaviour that was common to all of the examined moieties, but also remarkable stability of the obtained systems (which persisted over several months when left in aprotic solvents and inert atmosphere at room temperature).

The λ_{max} of the systems **1a–6a** exhibited good collinearity ($r = 0.987$) with those of the $\pi \rightarrow \pi^*$ electronic transitions of the corresponding starting materials **1–6**. Together with the aforementioned common behaviour of the **1a–6a** systems, this finding suggests that the structures of the arylazobenzenes before and after the addition of $BF_3 \cdot OEt_2$ are strongly related.

The gradual and controlled addition of $BF_3 \cdot OEt_2$ to the azo dyes revealed that the observed spectral modifications imparted a decrease in the starting absorption maximum and an increase of a new, strong band, rather than a shift in the maximum absorption of the band ascribable to the $\pi \rightarrow \pi^*$ transition of the chromophore. For example, in Fig. 2 is reported the case of the azo dye **4** and its related system **4a**. In addition to the new band, two isosbestic points are evident around 250 and 350 nm, an evidence pointing to the presence of two different absorbing species.

A possible interpretation of the observed behaviour of the $BF_3 \cdot OEt_2$-added systems may be given considering that the Lewis acid, $BF_3 \cdot OEt_2$, has the ability to accept electron couples from nitrogen atoms, and that protic acids are likely to form adducts with azobenzenes [38]. Hence we propose that $BF_3 \cdot OEt_2$ forms a complex with the considered azobenzenic moieties to give the following equilibrium:

$$\mathbf{\mathit{1–6}} + BF_3 \cdot OEt_2 = \mathbf{\mathit{1a–6a}}$$

Accordingly, the equilibrium constants of the proposed complexes **1a–6a** were calculated from the UV–vis spectra in accordance with the Scatchard procedure [39,40]. The concentrations of **1–6** and **1a–6a** were continually monitored through measurement of the corresponding absorbance values at 310 and 420 or 450 nm (see Fig. 1) as each aliquot of $BF_3 \cdot OEt_2$ was added. All measurements were found to be consistent for each of the selected wavelengths, and the corresponding $\log K$ values are listed in Table 1.

In order to deepen the view on the proposed equilibrium, we performed numerical modelling (B3LYP/6-31G*) on the starting azobenzenes, calculating the HOMO and LUMO levels for any considered compound in the gaseous phase and for the etherated form of the Lewis acid also. A very tight linear correlation ($R = 0.9977$) between the Hammett constant and the energy gap between the LUMO level of the $BF_3 \cdot OEt_2$ and the HOMO level of the azobenzenic moieties (hetero-HOMO/LUMO gap) was found for each of the compounds, except for **6**, which appeared to be definitely out of the linear correlation (Fig. 3). Such a differentiation of the methoxy-substituted azobenzene (Hammett constant of −0.27 and LUMO($BF_3 \cdot OEt_2$)/HOMO(dye **6**) of 7.38 eV) from the other moieties can be attributed to the methoxylic oxygen lone pairs, which may compete with the nitrogen lone pairs for the electrophilic attack of $BF_3 \cdot OEt_2$ or may affect, by mesomeric

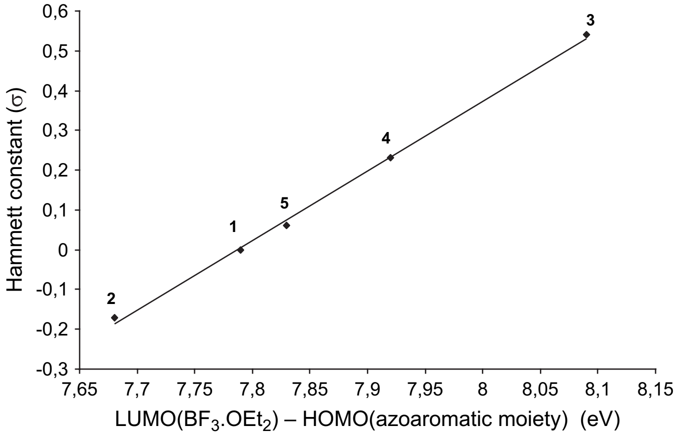

Fig. 3. Linear plot of Hammett constant vs. the relative energy difference in eV between LUMO($BF_3 \cdot OEt_2$) and HOMO(azoaromatic moieties **1**–**5**).

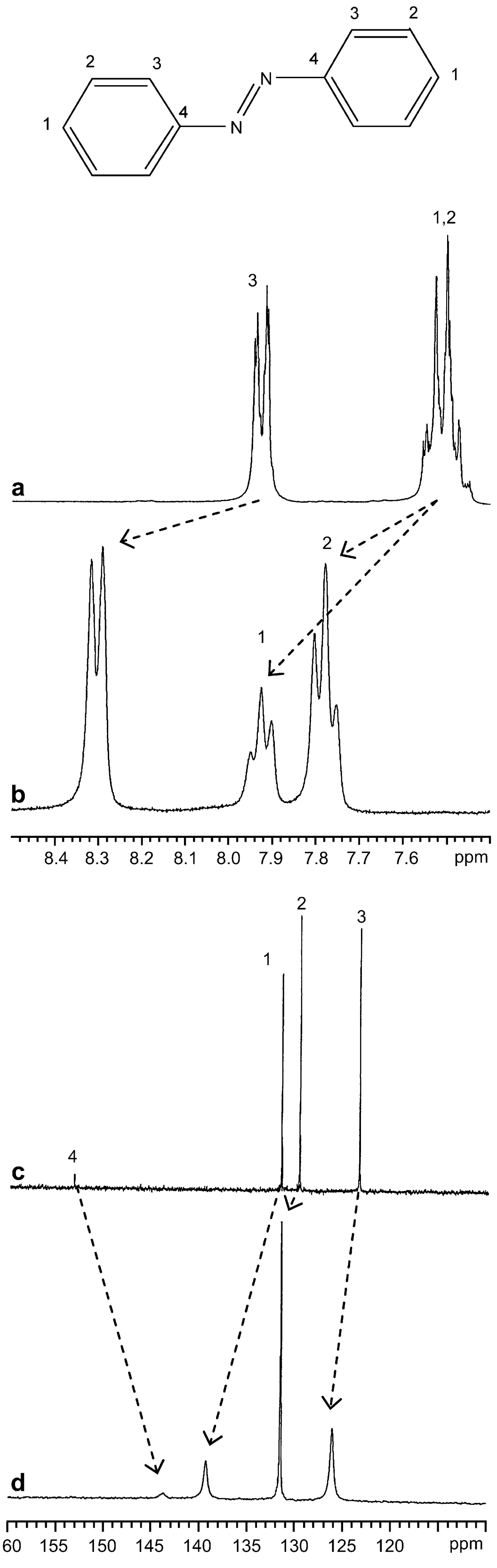

Fig. 4. ^{1}H NMR and ^{13}C NMR spectra of azobenzene (**1**) before (a and c, respectively) and after (b and d, respectively) the addition of a stoichiometric excess of $BF_3 \cdot OEt_2$. In the inset: structural formula of the starting azobenzene, with a reference numbering of the carbons and of the relative protons.

effect, the molecular orbitals of the azobenzene leading to the observed markedly different behaviour [29].

While the proposed formation of the azobenzene–BF_3 complex appears to gain support from the preliminary computational calculations, no correlation was found between the experimental equilibrium constants and the calculated hetero-HOMO(azoaromatic moiety)/LUMO($BF_3 \cdot OEt_2$) gaps. This finding can be explained by considering that numerical modelling gives information only on the possible interactions between a single $BF_3 \cdot OEt_2$ molecule and a "naked" azobenzenic chromophore, while the experimentally determined constants are calculated on the basis of optical measurements of solutions of the azobenzenic compounds, which are known to be influenced by factors such as the solvent used, the chromophore concentration, tautomerization constants, etc. The observed mismatch between the computational data and the experimental results may thus indicate that the complex formation follows a mechanism that differs from the simple interaction between the Lewis acid and the azo bond [41].

In order to acquire more information on the interactions occurring between $BF_3 \cdot OEt_2$ and the species **1**–**6**, NMR measurements were performed on both the starting azobenzenes and the Lewis acid-added systems.

^{1}H NMR ($CDCl_3$) spectra showed that the addition of $BF_3 \cdot OEt_2$ to the azo dyes resulted in a marked deshielding of the phenylazobenzenic protons. As an example, the ^{1}H NMR spectrum of **1** before and after the addition of the Lewis acid is shown in Fig. 4a and b, respectively. A remarkable variation of the chemical shift of all the aromatic protons is visible; in particular, the protons H-1 H-2, H-3 (see Fig. 4 for the numbering references of the H and C atoms) are subjected to a downfield variation of 0.41, 0.27 and 0.37 ppm, respectively. It is interesting to note that the multiplet signal due to H-1 and H-2 in the pure azobenzene (centered at 7.52 ppm) is splitted into two new different peaks (at 7.86 and 7.68 ppm) upon addition of $BF_3 \cdot OEt_2$. On the basis of the integration of the peaks and of the ^{13}C analysis (vide infra) we attribute the most downfield signal (centered at 7.86 ppm) to the protons in *para* to the azo bond (H-1), and the signal centered around

7.68 ppm to the ones in *meta* (H-2). The remaining of the spectrum showed only the signal due to the etheric protons (at 1.41 and 4.20 ppm), and no evidence of further signals was found.

The ^{13}C NMR permitted to confirm that the addition of $BF_3 \cdot OEt_2$ definitely changed the nature of the azobenzenic dye, and to elucidate the results obtained from the ^1H experiment. In Fig. 4c and d is shown the ^{13}C NMR spectra of **1** before and after the addition of the Lewis acid to the azobenzene. The absence of peaks supplementary to the four related to the benzenic rings testifies for the absence of symmetry breakage with respect to the starting azobenzene, and permits hence to confirm that the new peak emerged from the ^1H NMR experiment at 7.86 ppm is actually due to the *para* protons. Definite and consistent variations of the shift of the signals due to the benzenic carbons were found also in this case upon the addition of $BF_3 \cdot OEt_2$ to the azo dye (2.70, 1.83 and 7.67 ppm downfield for C-3, -2 and -1 respectively; 9.59 ppm upfield for C-4). The discussed behaviour is in line with previously reported data on 4-aminoazobenzene in presence of protic acid [18], and adds more support for the hypothesis of the formation of an actual complex between the azobenzenes and the Lewis acid. In order to rule out any role of the Et_2O molecule in causing the observed behaviour, tests adding pure, gaseous BF_3 to deuterated chloroform solutions of azobenzene, carried out in an inert atmosphere, showed for both ^1H and ^{13}C experiments the same above mentioned behaviour.

4. Conclusions

Variously substituted arylazobenzenes **1–6** were treated in dry $CHCl_3$ solution with controlled amounts of the Lewis acid, $BF_3 \cdot OEt_2$. UV–vis analysis of compounds **1a–6a** showed notable changes in electronic spectra with respect to the starting azobenzenes, namely, the rise of a strong absorption band due to $n \rightarrow \pi^*$ transition of the chromophore, with a concurrent decrease of the band associated with $\pi \rightarrow \pi^*$ transition of the aromatic molecular cloud. The net manifestation of this electronic behaviour change is a very marked red-shift of the maximum absorption of the azobenzenic moiety. In addition, two isosbestic points were found in the spectra of the systems **1–6** when converted to the corresponding **1a–6a** compounds, indicating the formation of new chemical species that differ from the starting material. The formation of BF_3–azobenzenic complexes were proposed to explain these findings and the relative complex formation constants were calculated from the experimental data for all of the compounds under investigation.

Numerical modelling revealed that the observed phenomena are likely to be due to molecular interactions between the Lewis acid and the whole chromophore, rather than with the azo bond alone. NMR analysis of both the starting compounds and of the resulting BF_3-added systems confirmed the view of the formation of new chemical species, evidencing appreciable variations of chemical shifts in both ^1H NMR and ^{13}C NMR experiments. The hypothesized complexes could be similar to the well-known protonated azo dyes, where the Lewis acid plays the part of the proton. More work is underway in order to clarify the nature of these compounds.

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References

[1] Colour index international. 4th ed. Society of Dyers and Colourists and American Association of Textile Chemists and Colorists. Online, <http://www.colour-index.org/>; 2002.

[2] Zollinger H. Color chemistry. 2nd ed. Weinheim: VCH; 1991.

[3] Nagasaki T, Wada K, Tamagaki S. Chem Lett 2003;32:88–9.

[4] Ajoula HS, Clarke DJ. PCT Int Appl; 2002. WO 059147, CAN 137:129850.

[5] Luengo JI, Duffy KJ. PCT Int. Appl; 2001. WO 017349, CAN 134:231869.

[6] Fujiwara T, Ichimura K. J Mater Chem 2002;12:3387–91.

[7] Angiolini L, Bozio R, Giorgini L, Pedron D, Turco G, Daurù A. Chem Eur J 2002;8:4241–7.

[8] Angiolini L, Benelli T, Bozio R, Daurù A, Giorgini L, Pedron D, et al. Macromolecules 2006;39:489.

[9] Chigrinov V, Prudnikova E, Kozenkov V, Kwok H, Akiyama H, Kawara T, et al. Liq Cryst 2002;29:1321–7.

[10] Natansohn A. editors. In: Proceedings of the symposium on azobenzene-containing materials. Boston, MA; 1998; Macromolecular symposia 1999;137:1–165.

[11] Wang G, Hou L, Gan F. Proc SPIE Int Soc Opt Eng 1998;3562:51–5.

[12] Gregory P. High-technology applications of organic colorants. London: Plenum Press; 1991.

[13] Prasad PN, Williams DJ. Introduction to nonlinear optical effects in molecules and polymers. New York: Wiley; 1991.

[14] Matsuoka M. Absorption spectra of dyes for diode lasers. Tokyo: Bunshin Co; 1990.

[15] Matsuoka M. Infrared absorbing dyes. New York: Plenum; 1990.

[16] Hesse M, Meier H, Zeeh B. Spectroscopic methods in organic chemistry. Stuttgart: Thieme; 1997.

[17] Sawicki EJ. Org Chem 1957;22:365–7.

[18] Kuroda Y, Lee H, Kuwae A. J Phys Chem 1980;84:3417–23.

[19] Tait KM, Parkinson JA, Jones AC, Ebenezer WJ, Bates SP. Chem Phys Lett 2003;374:372–80.

[20] Tamulis A, Tamuliene J, Balevicius ML, Nunzi JM. Mol Cryst Liq Cryst 2000;354:475–84.

[21] Forber CL, Kelusky EC, Bunce NJ, Zerner MC. J Am Chem Soc 1985;107:5884–90 and references therein.

[22] Fabian J, Hartmann H. Light absorption of organic colorants: theoretical treatment and empirical rules. New York: Springer-Verlag; 1980.

[23] Griffiths J. Colour and constitution of organic molecules. London: Academic Press; 1976.

[24] Riddick JA, Bunger WB. In: Weissberger A, editor. Organic solvent. 3rd ed. New York: Wiley-Interscience; 1970. p. 771.

[25] For a review, see Boyer JH. In: The chemistry of the nitro and nitroso groups. New York: Wiley; 1969. p. 278.

[26] Otruba JP, Weiss RG. J Org Chem 1983;48:3448–53.

[27] Krageloh K, Anderson GH, Stang PJ. J Am Chem Soc 1984;106:6015–21.

[28] Ayyangar NR, Naik SN, Srinivasan KV. Tetrahedron Lett 1989;30:7253–6.

[29] Spartan ’04, tutorial and user’s guide. Irvine, CA: Wavefunction, Inc.; 2004.
[30] Hehre WJ. A guide to molecular mechanisms and quantum chemical calculations. Irvine, CA: Wavefunction, Inc.; 2003.
[31] Swain CG. J Org Chem 1984;49:2005−10.
[32] Taft RW, Abboud JL, Kamlet MJ. J Org Chem 1984;49:2001−4.
[33] Buncel E, Rajagopal S. Acc Chem Res 1990;23:226−31.
[34] Gore PH, Wheeler OH. J Org Chem 1961;26:3295−8 and references therein.
[35] Birnbaum PP, Linford J, Style DWG. Trans Faraday Soc 1953;49:735−44.
[36] Jaffe HH, Orchin M. In: Jaffe HH, editor. Theory and application of ultraviolet spectroscopy. New York: Wiley; 1962.
[37] Brode WR, Seldin IL, Spoerri PE, Wyman GM. J Am Chem Soc 1955;77:2762−5.
[38] Dominique P, Carpentier JM. Bull Soc Chim Fr 1977;1049.
[39] Harris DC. Quantitative chemical analysis. 2nd ed. In: Freeman WH, editor. New York; 1987.
[40] Scatchard G. Ann NY Acad Sci 1949;51:660−72.
[41] Zenhäusern A, Zollinger H. Helv Chim Acta 1962;45:1890−8.