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Infrared and NMR study of some 2-styrylindolium dyes

S. Metsov, T. Dudev*, V. Koleva

Department of Chemistry, University of Sofia, 1126 Sofia, Bulgaria

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Abstract

A series of 18 molecules of the 2-styrylindolium dyes group is examined by means of infrared and ^{1}H NMR spectroscopy. The effect of electron-withdrawing and electron-releasing substituents on the spectral behavior of the compounds is assessed and the most appropriate structure for these molecules is suggested.

1. Introduction

Combined application of infrared and ^{1}H NMR spectroscopic techniques has proved successful in investigating the structure of organic molecules and in analyzing the influence of specific structural factors, such as the nature of substituents, steric effects, and various intramolecular and intermolecular interactions on the electron-density distribution. These methods are especially important in examining the structure of different classes of dyes whose coloristic properties strongly depend on the way the molecule has been built. Thus, by studying the correlation between chemical shifts produced by different substituents and the respective Hammett σ constants, the transmission mechanisms of the substituent effects have been established for a number of molecules belonging to various groups of dyes: triarylmethin dyes [1], azo-dyes [2], quinolinium dyes [3], unsymmetrical [4] and symmetrical [4,5] cyanine dyes.

The 2-styrylindolium dyes belong to the class of unsymmetrical polymethine dyes [6]. No systematic investigation of their IR and NMR spectral properties has been reported so far, though the spectral characteristics of some representatives of this group have been published [7,8].

2. Experimental

The synthesis of most of the compounds included in the present study has been published [8] but products **1b**, **2b–d**, **2h**, **3a–b** and **4a–b** are synthesized for the first time. Compound **4b** from the newly obtained series is expected to be the most interesting from a coloristic point of view. The products were obtained by condensation of 1,2,3,3-tetramethyl-3*H*-indolium iodide (**1a** in Fig. 1) with the respective carbonyl components in acetic acid as a reaction medium under reflux for 3–10 h with yields of about 80%. The compounds were verified by elemental analysis and spectroscopic methods.

Infrared spectra were obtained on a Perkin–Elmer 983G ratio recording spectrometer equipped with a PE 3600 data station. Spectra were measured with spectral resolution of about

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* Corresponding author.

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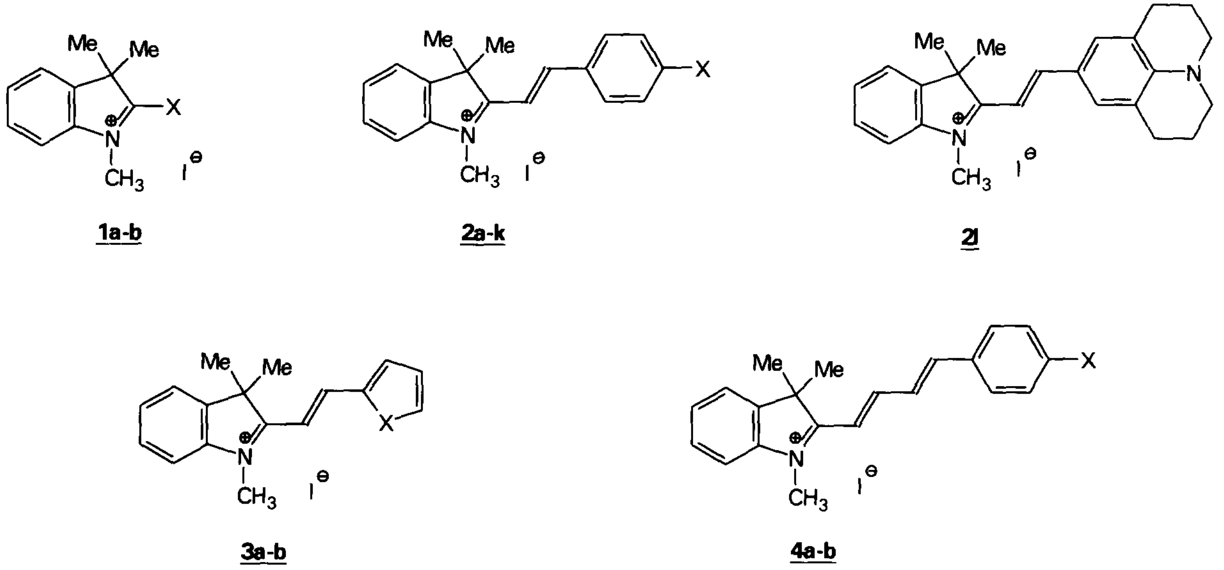


Fig. 1. General formulae of compounds **1–4**.

2 cm^{-1} (mode 5 filter 1) in KBr cells and using spectroscopic grade chloroform as a solvent. Some compounds with low solubility in $CHCl_3$ were probed by the Nujol suspension technique as well.

^1H NMR spectra were recorded on a Tesla BS 487C (80 MHz) spectrometer and a Bruker 100 MHz instrument with deuterochloroform as a solvent. Chemical shifts were measured in parts per million with respect to internal standard TMS. The infinite dilution method and a double resonance technique were applied for the accurate measurements of signal positions. The accuracy achieved was of the order of ±0.003 ppm (Tesla spectrometer) and ±0.001 ppm (Bruker spectrometer).

3. Results and discussion

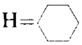
3.1. Infrared spectra

The molecules of series **1–4** (Fig. 1) contain several infrared-active chromophores, such as $C{=}N^+$, $C{=}C$ and the benzene ring. The respective characteristic frequencies lie in the medium part of the IR spectrum [9,10]. Our attention was therefore focused on the 1800–1400 cm^{-1} spectral range, where the spectra of all molecules were carefully examined. Semiempirical quantum-mechanical calculations [8] reveal that the strong conjugation between π electron containing units in some of these molecules results in a significant change in the respective bond orders. The latter appear to be quite sensitive to the chemical character of the para substituent introduced in the second benzene ring. This is expected to affect infrared band positions of stretching modes of the chromophores. The analysis of the spectral curve in this region is however not trivial since all chromophores mentioned above absorb in this narrow interval. That is why, before proceeding further, we had to assign, though tentatively, the spectral bands in this region. Some considerations are given below.

Compound **1a**, which contains a $C{=}N^+$ bond and one benzene ring, has four absorption bands in the 1800–1400 cm^{-1} spectral region positioned at 1628, 1606, 1593 and 1476 cm^{-1} (Table 1). The first band is attributed to the stretching of the $C{=}N^+$ double bond and the next two to vibrations of the ortho-substituted benzene ring [10,11]. The last band at 1476 cm^{-1} is due to asymmetric deformational modes of the methyl groups present in the molecule.

Product **1b** contains one more chromophore with respect to **1a** — the double $C{=}C$ bond. It

Table 1
IR and NMR spectral parameters for the molecules of series 1–4

No.	X	$\bar{\nu}_{\text{aromatic}}$ (cm^{-1})	$\bar{\nu}_{\text{C=N}^+}$ (cm^{-1})	δ (ppm)	$\Delta\delta$ (ppm)
1a	CH_3	1606, 1593	1628	4.182	
1b	CH= 	1605, 1596	1630	4.253	
2a	H	1606, 1592, 1572, 1535	–	4.532	0
2b	CF_3	1605, 1573, 1539	–	4.497	−0.035
2c	CHO	1607, 1590, 1574^a, 1539	–	4.432	−0.100
2d	CN	1609, 1601, 1560, 1540	–	4.506	−0.026
2e	NO_2	1612^a, 1598^a, 1549^a	–	4.591	+0.059
2f	CH_3	1611, 1590, 1564, 1535	–	4.470	−0.062
2g	Cl	1606, 1586, 1561, 1534	–	4.502	−0.030
2h	F	1609, 1593, 1582, 1535	–	4.521	−0.011
2i	OCH_3	1581, 1564, 1529	–	4.461	−0.071
2j	NMe_2	1598, 1569, 1525	–	4.238	−0.294
2k	NEt_2	1567, 1517	–	4.251	−0.281
2l	–	1568, 1515	–	4.146	−0.386
3a	O	1604	–	4.295	−0.237
3b	S	1596, 1584	–	4.319	−0.213
4a	H	1598, 1573, 1522	–	4.226	−0.306
4b	NEt_2	1610, 1590, 1546, 1498	–	4.264	−0.268

[a] In Nujol.

may therefore be expected that the two double bonds are conjugated. Surprisingly, the band corresponding to the $C{=}N^+$ stretching vibration remains unshifted (1630 cm^{-1}). At the same time, a broad band with a complex structure covers the 1620–1580 cm^{-1} region. The spectral data obtained imply that no effective conjugation between the two double bonds occurs in this case. This is evidently not the case with the compounds of the series **2**, **3** and **4** where the planar structure [8] favors long-chain conjugation in these molecules. This results in the disappearance of the band near 1630 cm^{-1}. This fact is attributed to the significant decrease in the bond orders of the $C{=}N^+$ and C=C bonds. Our attempts to identify the bands corresponding to the two double bond stretching vibrations in the lower part of the spectrum were unfortunately unsuccessful. Most probably they are strongly overlapped with the benzene ring bands present.

Molecules belonging to series **2** and **4** contain one more benzene ring with respect to compounds **1a** and **b**. That is why we ascribed the two new bands appearing in their infrared spectra near 1570 and 1530 cm^{-1} to vibrations of the second benzene ring [10–12]. Here it should be pointed out that the second of these bands is quite sensitive, in both position and intensity, to the type of para substituent in the benzene ring as well as to the length of the conjugated system. Its properties will be discussed below. As can be seen from Table 1, the frequency changes from 1549 (**2e**) to 1515 cm^{-1} (**2l**) in series **2** and from 1522 to 1498 cm^{-1} in series **4**. Two possible mechanisms could be incorporated in explaining this observation: (1) coupling between the double bond vibrations, which are expected to be sensitive to the nature of substituent, and the deformations of the benzene ring, and (2) a change in the structure of the benzene ring with conjugation (structure **B** in Fig. 2). Data collected in Table 1 reveal that the frequency deviations are in accord with the chemical properties of the substituent. The band located at 1549 cm^{-1} is for the strongest electron-withdrawing nitro group and those at 1540, 1539 and 1539 cm^{-1} for the other strong electron acceptors such as CN, CF_3 and CHO, respectively. This band is quite weak. Derivatives **2f**, **2g** and **2h** containing relatively weak electron-withdrawing and electron-releasing substituents do not exhibit fluctuations

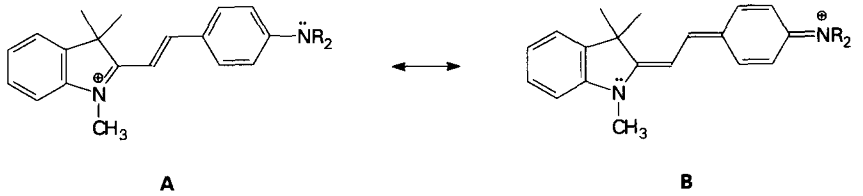


Fig. 2. Extreme resonance structures **A** and **B** for *p*-dialkylamino-2-styrylindolium dyes.

in frequency with respect to the unsubstituted molecule (**2a**) where the transition appears at 1535 cm^{-1}.

Substituents characterized by strong electron-releasing properties, such as dialkylamino groups (**2j–l**), show significant downward shifts of 10, 18 and 20 cm^{-1}, respectively. The bands are quite prominent which is a typical feature of these substituents [10]. It is interesting to note that the overall shape of these spectra is rather different compared with the spectrum of unsubstituted compound **2a** and with those of the molecules containing electron-withdrawing groups.

An attempt to correlate the respective frequency shifts $\Delta\bar{\nu}$ ($\Delta\bar{\nu} = \Delta\bar{\nu}_{\text{substituted}} - \Delta\bar{\nu}_{\text{unsubstituted}}$) with the values of the ordinary Hammett constants, σ_p, [13], is shown in Fig. 3. In view of the complex nature suggested for this vibrational transition, the dependence obtained seems quite reasonable (correlation coefficient $R = 0.920$). It should be emphasized that the frequency shifts caused by electron-releasing substituents are larger than those of the electron-withdrawing groups. Moreover, the frequency downward shift changes smoothly in the succession **2f** (CH_3), **2i** (OCH_3), **2j** ($N(CH_3)_2$), **2k** ($N(C_2H_5)_2$) and **2l** following the changes in electron-releasing properties of these substituents. This implies that the polymethine-type structure is more likely in compounds containing strong electron-releasing substituents. The results obtained are in full accord with the expectations that electron-releasing groups will favor long-distance conjugation with the $C{=}N^+$ unit. As far as the influence of the electron-withdrawing groups is concerned, it could be concluded from the experimental data that the polyene-type structure is dominant in these molecules owing to the presence of two electron-withdrawing domains at the two ends of the unsaturated system.

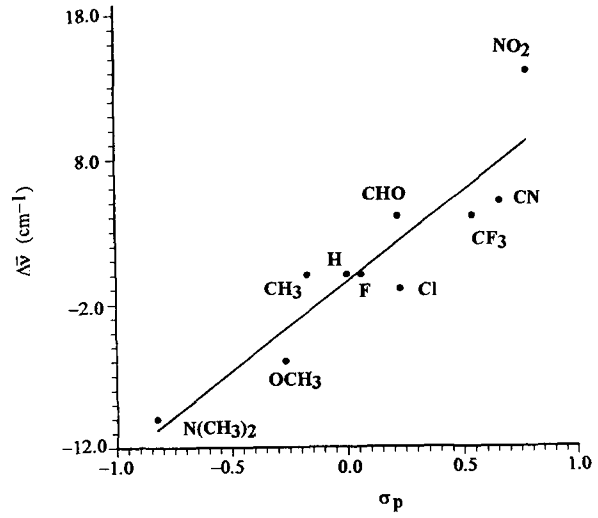


Fig. 3. Plot of the dependence $\Delta\bar{\nu}/\sigma_p$ for molecules of the series **2**.

3.2. NMR spectra

It has been found that the chemical shifts in several series of molecules, having certain similarities with the series studied here, depend linearly on the chemical nature of the respective substituents [2,3]. In our investigation, the signal for the methyl group directly bonded to the positively charged nitrogen atom ($CH_3{-}N^+$) was chosen as a marker and its deviation in the series **1–4** was followed. It is expected that the proximity of a charged atom to the CH_3 group can affect the mechanism of transferring the substituent effect.

It could be seen from the data in Table 1 that the chemical shift differences $\Delta\delta$ ($\Delta\delta = \delta_{\text{substituted}} - \delta_{\text{unsubstituted}}$) for the molecules of the series **2** vary over a large interval (from −0.386 to +0.059 ppm) which suggests the presence of quite flexible

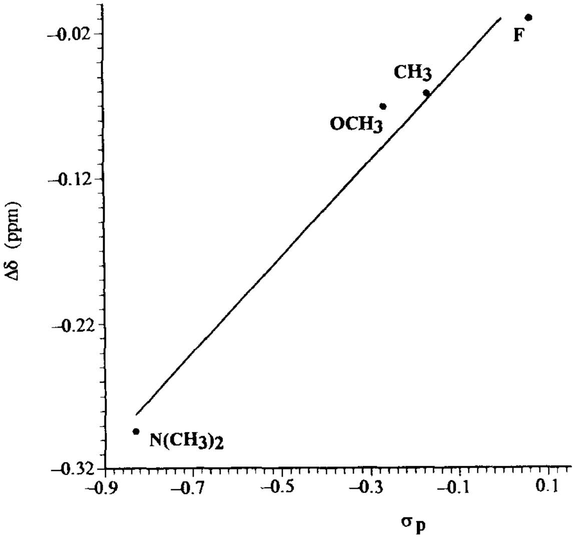


Fig. 4. Plot of the dependence $\Delta\delta/\sigma_p$ for compounds **2h**, **2f**, **2i** and **2j**.

π-electronic system. Several attempts to correlate the observed $\Delta\delta$ values with different types of Hammett constants were undertaken but no satisfactory results were obtained. The best correlation was found when σ_p^+ constants were employed (correlation coefficient $R = 0.883$). This implies that complex intramolecular interactions are in force. When the regression analysis was performed for molecules with substituents F (**2h**), CH_3 (**2f**), OCH_3 (**2i**) and $N(CH_3)_2$ (**2j**), a very good linear dependence was found ($R = 0.986$). This is shown in Fig. 4. At the same time, however, no such dependence exists for the series of molecules containing electron-withdrawing substituents (**2b–e**) where $R = 0.546$ was obtained.

These results reveal that, for molecules with electron-releasing substituents, the possibility of effective charge transfer increases. It is especially well expressed in the case of molecules containing dialkylamino groups (**2j–l**). This consideration is in accord with the assumption that the polyene-like structure is dominating in the case of **2a–e**, while the polymethine-like structure with progressive bond equalization is preferred in dialkylamino compounds (**2j–l**). It should be mentioned that the chemical shift value observed for the marker CH_3–N^+ group in **2l** is very close to that reported for the structurally similar symmetrical cyanines [14]. In contrast to symmetrical cyanine dyes, however, the two extreme resonance structures **A** and **B** (Fig. 2) of the unsymmetrical polymethines are not equivalent.

When comparing structural homologue couples **2a**/**4a** and **2k**/**4b**, it can be seen that the difference in δ for the first couple is quite large but is negligible for the second one. Hence, it could be concluded that in the absence of electron-releasing substituents the increase in length of the conjugated system by one double C=C bond (product **4a**) results in a dominant polyene-type molecular structure. When an NR_2 group is introduced, however, its mesomeric effect prevails over the effect of elongation of the polyene chain and the polymethine-like structure appears more likely.

It was of interest to determine $\delta(CH_3N^+)$ values for some structural analogs of molecule **2a** where the second benzene ring was replaced by a five-membered heterocycle (**3a**, **b**). The data obtained show that quite a strong shielding of the marker group is present which shows that the polyenic structure is stabilized in **3a**, **b**. This is probably due to the weakened aromatic character of furane and thiophene residues compared with the benzene ring.

In contrast with **3a** and **b**, the shielding of CH_3–N^+ in compounds **1a** and **b** is due to other reasons. It is related to the inductive effect of the CH_3 group directly attached to the reaction center in **1a** ($X = CH_3$) and to the field effect of the cyclohexylidene residue in **1b**.

The chemical shift analysis of geminal methyl groups in position 3 in the 3*H*-indolium ring in some derivatives of 2-styrylindolium dyes (so-called spyropyranes) has provided valuable information about the molecular stereochemistry [15]. We measured the respective chemical shifts in series **2**. The signal for the $C(CH_3)_2$ groups appears at 1.888 ppm for the unsubstituted derivative **2a** and slightly varies for the other compounds. It deviates over a range of 0.125 ppm while the interval of variation for the CH_3–N^+ methyl group is much larger (0.353 ppm). Evidently the geminal methyl groups, being structurally outside of the main chromophore system, are less influenced by the substituent X.

4. Conclusions

Combined application of both infrared and ^{1}H NMR spectral analyses reveals that the mechanisms of electron density distribution in the molecules studied are quite complex. They strongly depend on the nature of the substituent and on the length of the conjugated system, on the one hand, and on steric factors, on the other. The results obtained imply that the polyene-like structure dominates in molecules containing electron-withdrawing groups while in the case of compounds with electron-releasing substituents, the polymethine-like structure is preferred. In this respect, the 2-styrylindolium dyes investigated, being unsymmetrical polymethines, behave intermediately between cyanines and polyenes.

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