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Electronic Absorption Spectra and Electron Transport Properties of 1-Benzothiopyrylium Ions

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SUMMARY

The electronic absorption spectra of a series of 1-benzothiopyrylium salts have been calculated by the variable β PPP method. The agreement between calculated and experimental data is satisfactory in most cases using a general parameter set. The calculated results show that the bathochromic effect of a methoxy group is essentially due to a HOMO–HOMO interaction, and the bathochromic effect of a benzothiopyran ring in the 2-position is due to raising of a HOMO.

The electron transfer properties of 1-benzothiopyrylium salts were examined by means of cyclic voltammogram and xerographic discharge techniques. It was found that the reduction wave of thioflavylium ions is reversible.

1. INTRODUCTION

2-Phenyl[1]benzopyrylium (flavylium) salts are an important group of naturally occurring colouring matters known as anthocyanins. We have prepared the 1-benzothiopyrylium salts **1–3** which are the interesting thio analogues of anthocyanin and cyanin dyes.[1–3]

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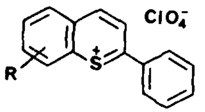

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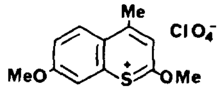
1a: R= H
1b: R= 5-OCH_3
1c: R= 6-OCH_3
1d: R= 7-OCH_3
1e: R= 8-OCH_3



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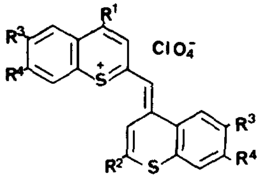

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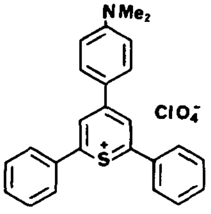
3a: R^1= OCH_3, R^2= CH_3, R^3=R^4= H
3b: R^1= CH_3, R^2=R^3=R^4= H
3c: R^1= R^3= CH_3, R^2=R^4= H
3d: R^1= CH_3, R^2=R^3= H, R^4= OCH_3

However, a systematic approach to the spectroscopic properties of these 1-benzothiopyrylium salts has not been previously reported. PPP molecular orbital theory has been applied to the study of the electronic absorption properties of organic dyes, particularly azo compounds, anthraquinones and naphthoquinones and numerous PPP calculations for other dye systems have been reviewed.[4-6] The relationship between colour and constitution of various sulphur-containing heterocyclic compounds has been well interpreted by the PPP molecular orbital method using a suitable parameter set.[7,8]

In this paper, the 1-benzothiopyrylium dyes were examined by the PPP method, using as far as possible parameters derived for other dye classes, and the substituent effect on the absorption spectra were interpreted. Their voltamperometric curves were also measured to examine electrochemical properties, and some thiocyanin dyes were applied as electrophotographic sensitizers.

2. THE COMPUTATIONAL METHOD

The PPP method was used with the variable β approximation. Electronic excitation energies were similarly refined by a CI treatment as described in a previous paper.[9] The ionization potential (I_p) and one-centre electron repulsion integral (γ_{rr}) for all atoms were as used elsewhere.[9,10] The I_p and γ_{rr} for the cationic sulphur and oxygen were taken from values calculated by Hinze and Jaffe,[11] and were the same as those for sulphur and oxygen of the



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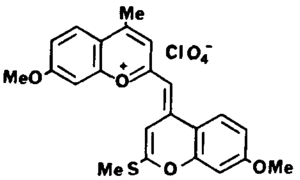

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thiocarbonyl and carbonyl groups (—$\overset{+}{\text{S}}$=: $I_p = 12{\cdot}7$ eV; $\gamma_{rr} = 9{\cdot}94$ eV; $\beta = -1{\cdot}0$ eV (fixed). —$\overset{+}{\text{O}}$=: $I_p = 17{\cdot}7$ eV; $\gamma_{rr} = 15{\cdot}23$ eV). The identical I_p, γ_{rr} and core charge values were taken as values for the two seemingly different heteroatoms (sulphur and oxygen in **3** and **5**, respectively). A similar treatment has been applied in the calculation of the spectra of diarylmethane and triarylmethane dyes.[12] As the methyl substituent effect on the absorption maximum of the 1-benzothiopyran derivatives is very small,[9] the methyl group of **2** and **3** was ignored for calculations. The simplest possible geometries and planar structures were assumed for the various molecules studied. The bond lengths and valence angles were taken from values used for the thiochromone compounds.

3. RESULTS AND DISCUSSION

3.1. Absorption spectra and PPP–MO calculations for 1-benzothiopyrylium salts

As shown in Tables 1 and 2, the absorption wavelengths of 1-benzothiopyrylium salts are well reproduced by PPP calculations. The correlation coefficient between the calculated longest wavelength λ_1 and the experimental data of **1**–**4** is 0·968. MO calculations suggest that the first and second absorption maxima of 1-benzothiopyrylium salts are π–π^* transitions. Similar spectral data were obtained when a parameter set was used which had been optimized for thiopyrylium compounds.[7]

The absorption maxima of **1a** which was observed at 399 nm consisted of two close transitions. Adapting the standard parameter set, the substituent effect on absorption spectra of 2-phenyl[1]benzothiopyrylium salts (**1**) was predicted extremely well. The calculated bathochromic shift of λ_1 caused by the methoxy substituent in the benzene ring gave the following order: **1d** < **1c** < **1b** < **1e**. This is in good agreement with the shifts of 46 nm, 79 nm and 86 nm found experimentally. Results of SCF–CI calculation showed that the first two electronic excitations are approximated by HOMO–LUMO and NHOMO–LUMO transitions. A good linear correlation existed

TABLE 1
Theoretical and Experimental Absorption Wavelengths of Thioflavylium Ions

Compound	λ_{max}(*calc.*)[a] (*nm*)	*f*(*calc.*)[a]	λ_{max}(*calc.*)[b] (*nm*)	*f*(*calc.*)[b]	λ_{max}(*exp.*) (*nm*)	$\varepsilon \times 10^{-4}$ *in MeOH*
1a	402	0·320	433	0·853	399	0·762
	389	0·247	394	0·149		
1b	439	0·177	472	0·284	478	0·237
	394	0·361	424	0·739	393	1·16
1c	426	0·296	473	0·358	445	0·667
	386	0·211	408	0·667	392	1·27
1d	423	0·319	453	0·995	445	0·861
	397	0·316	391	0·017	385	0·538
1e	462	0·085	531	0·038	485s	0·042
	396	0·374	429	0·881	397	0·850

[a] This work; *f*, oscillator strength.

[b] Parameters collected from ref. 7 were used for sulphur atom ($I_p = 20$ eV; $\gamma_{rr} = -10·84$ eV; $\beta = -1·623$ eV).

TABLE 2
Theoretical and Experimental Absorption Wavelengths of 1-Benzothiopyrylium Salts and Related Compounds

Compound	λ_{max}(*calc.*) (*nm*)	*f*(*calc.*)	λ_{max}(*exp.*) (*nm*)	$\varepsilon \times 10^{-4}$ *in acetone*	*Ref.*
2	398	0·252	386	1·10	1
	375	0·162			
3a	603	0·774	590	6·24	1
3b	601	0·746	616	6·14	1
3c	601	0·746	624	4·30	1
3d	602	0·803	625	6·20	1
4	510	1·21	580	14·7[a]	13
5	513	0·998	562	5·98	1

[a] In CH_2Cl_2.

TABLE 3
Orbital Energies of the MO in 1-Benzothiopyrylium Salts

Compound	*HOMO* (*eV*)	*LUMO* (*eV*)	$-E_{HO-LU}$ (*eV*)
1a	−8·923	−3·470	5·453
1b	−8·653	−3·347	5·306
1c	−8·717	−3·348	5·369
1d	−8·708	−3·299	5·409
1e	−8·673	−3·419	5·254
2	−8·615	−2·844	5·771
3d	−6·445	−2·448	3·997

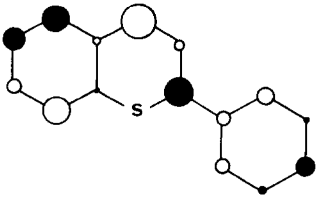

Fig. 1. Pictorial representation of the expansion coefficients of the HOMO of **1a**.

between the calculated first-excited energies and the singly excited configuration energies ($E_{\mathrm{HO-LU}}$). Thus, the bathochromic shift of a methoxy substituent was caused to a large extent by an increase in the HOMO energy, as shown in Table 3.

This bathochromic shift can be also interpreted by considering the position of the most effective HOMO–HOMO interaction occurring between a methoxy substituent orbital and the orbital of **1a**. According to the expansion coefficients of the HOMO, illustrated in Fig. 1, introduction of a methoxy group in the 5- or 8-position is more effective in producing a bathochromic shift than in the 6- or 7-position.

Whereas the lowest excited states of **1c** and **1d** as well as that of **1a** are described by the locally excited state, the charge-transfer configurations from the benzothiopyran containing a methoxy group on the hetero ring and the 2-phenyl group contribute strongly to the lowest excited state of **1b** and **1e**, as shown in Fig. 2.

The second absorption maxima (λ_2) of **1** was not changed by the methoxy substituent. This prediction was well reproduced.

Comparison of **1d** and **2** shows that replacement of a phenyl group in the 2-position of **1d** by a methoxy group causes raising of the LUMO rather than the HOMO, and results in a hypsochromic shift of λ_1. On the other hand, replacement of a phenyl group in the 2-position with a benzothiopyran ring causes predominantly a raising of the HOMO rather than the LUMO, and results in a pronounced bathochromic shift. Thus, λ_1 in **3** was shifted to 625 nm. Adapting a similar standard parameter set for the oxa

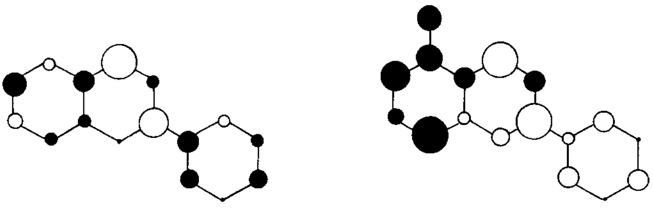

Fig. 2. Change of electron density of one-electron transitions responsible for the first absorption maxima of **1a** and **1b**. The magnitude of positive or negative change is indicated by the size of the open or filled circles, respectively.

analogue **5** and the thiopyrlium dye **4**, which is a component of an aggregate photoconductor for electrophotographic application,[13] the first absorption maxima were calculated to be 398 nm and 510 nm, respectively. This is in reasonable agreement with 386 nm and 580 nm found experimentally.

3.2. Cyclic voltammetry of 1-benzothiopyrylium salts

Voltamperometric curves of **1** and **3** show at least one reduction wave and one oxidation wave. The reduction wave of **1** was reversible, and that of **3** was irreversible. Figure 3 depicts the typical cyclic voltammogram of **1a**. This cyclic voltammogram showed a reversible electron transfer between +1·0 eV and −0·5 eV, and a simple kinetically diffusion-controlled reduction of the molecule to the corresponding radical which was stable within the time scale of measurement. Reduction of various flavylium ions also leads to formation of the corresponding radical, which has been studied by polarography.[14] The reduction potential of **1a**–**1e** increased in the sequence **1a** < **1e** < **1b** < **1c** < **1d** (Table 4). This is in agreement with the calculated sequence of the energy levels of the LUMOs. Replacement of a phenyl group in **1a** with a benzothiopyran ring led to the higher reduction potential (**3a**: −0·44 eV).

TABLE 4
Reduction Potential of **1** Measured by Cyclic Voltammetry

Compound	*R*	*Reduction potential (V)*
1a	H	+0·045
1b	5-OCH_3	+0·035
1c	6-OCH_3	−0·005
1d	7-OCH_3	−0·055
1e	8-OCH_3	+0·040

3.3. Application of 1-benzothiopyrylium salts as sensitizers for electrophotographic materials

A type of bis(benzothiopyrylium) salt **3** is useful for the spectral sensitization of electrophotographic layers composed of organic photoconductors as described in the patent literature.[15–17] The sensitizer properties of the three substituted 1-benzothiopyrylium salts **3a**–**3c** were investigated by the xerographic discharge technique.

The composition of the device and the exposure required to reduce the

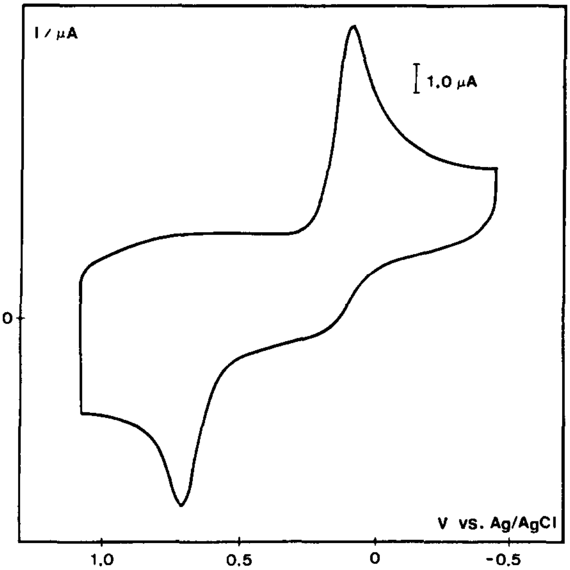

Fig. 3. Typical cyclic voltammogram of **1a**.

surface charge to half the initial charge ($E_{1/2}$) are summarized in Table 5. Both in the homogeneous device (runs 1–3) and the composite device (runs 4–6), dye **3b** had the greatest photosensitivity. The minimum value of $E_{1/2}$ for the device using dye **3b** is 50 lux s, which is higher than that of the reference dye (7 lux s).[17] Comparison of runs 5 and 7 shows that replacement of the sulphur atom in **3** by an oxygen atom resulted in an

TABLE 5

Characterization of Sensitizers of **3** for Electrophotographic Materials

Run	*Device*	*Exposure required to reduce the surface charge to half the initial value*[c] *(lux s)*
1	Dye **3a**–PVK[a]	140
2	Dye **3b**–PVK[a]	95
3	Dye **3c**–PVK[a]	205
4	CGL of dye **3a**–CTL[b]	86
5	CGL of dye **3b**–CTL[b]	50
6	CGL of dye **3c**–CTL[b]	96
7	CGL of dye **5**–CTL[b]	240

[a] A homogeneous layer of poly(*N*-vinylcarbazole) and a dye, 100:1 by wt.

[b] Composite device consisting of the following CGL and CTL. CGL: charge carrier generation layer composed of a polyester resin 100 (Byron 200; Thoyobo Co. Ltd) and a dye, 100:1 by wt. CTL: charge carrier transport layer composed of a poly(*N*-vinylcarbazole).

[c] The device was charged in a 6 kV corona discharge and exposed to a white lamp for 2 s.

approximately five-fold decrease in sensitivity. Thus, the devices studied herein were not sensitive enough for practical application.

The maximum photoresponse of a composite device containing dye **3b** is 650 nm and is shifted to longer wavelength than the absorption maximum of **3b** in acetone. The other devices containing dye **3a** or **3c** showed a similar photoresponse. Thus, these devices are expected to be useful organic photoconductors for lasers with emitting wavelengths of 600–650 nm.

4. EXPERIMENTAL

4.1. Materials

All 1-benzothiopyrylium salts used were prepared as previously described by us.[1,2] All compounds were recrystallized from acetic acid. Absorption spectra were recorded at a concentration of 10^{-4} M using a Shimazu UV-240 spectrophotometer.

4.2. Reduction potential measurement

The reduction potentials of **1** were obtained by cyclic voltammetry using a Yanagimoto VMA-010 potentiostat analyzer with a model WX-1000 X–Y recorder. The cyclic voltammetric measurements were carried out in acetonitrile at room temperature using a platinum wire auxiliary electrode, a glassy carbon working electrode, an Ag/AgCl reference electrode, and tetrabutylammonium perchlorate as supporting electrolyte. Sample concentration was 5×10^{-4} M.

4.3. Characterization of sensitizers

The characterization of the sensitizer of thiocyanin dyes for electrophotographic material was performed using the xerographic discharge technique. The photoconductive layered device used for measurement was prepared as follows. A homogeneous layer (10–20 μm) comprising a dye in PVK was solvent-cast onto an aluminium substrate using a Bird film applicator. A thin layer of CTL (charge carrier transport layer) was solvent-cast on top of the CGL (charge carrier generation layer) to serve as the composite device. The device was corona-charged to a negative surface potential and was discharged by exposing it to a light flash from a white lamp. The resulting photo-induced discharge of the device was monitored by an electronic paper analyzer.

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