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Solution electrochemistry of indolenium squarylium cyanine dyes

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Abstract

The redox potential of a class of donor–acceptor–donor (D–A–D) molecules, bis(5-substituent-2,3,3,-trimethylindolenium-2-ylidene)squaraines (Sq 1–8), were determined. All the dyes exhibit two reversible oxidation potentials in methanol. C-5 substituents at the indolenium moieties exert a small effect on the first oxidation potential, and the substituent effect is attributed to the inductive parameters. The frontier orbital energy levels were calculated by the AM1–SCF method. A good linear relationship between the highest occupied molecular orbital energy level and the first oxidation potential was found. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Squaraine dyes; Squaraines; Squarylium Cyanine Dyes; Electrochemistry; Energy levels; Frontier orbita energy levels

1. Introduction

Squaraine dyes have received much attention because of their potential applications in xerographic photoreceptor [1–4], solar cell [5–7], optical recording media [8,9], photopolymer initiators [10] and gas sensors [11,12]. For their functional application basis on charge or energy transfer, such as in photoreceptor as charge generation agents, the energy level match between the donor and acceptor becomes the basic requirement. So the energy level's relative position, especially for the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO) between the donor and acceptor, is very important. Those values can be estimated directly by quantum chemistry calculation or indirectly by the redox potential determination [13].

In a previous paper, we reported on the synthesis [14] and photophysical properties [15] of the bis(5-substituent-1-sulfonatopropyl-2,3,3-trimethyl indolenium-2–ylidene)squaraine bistriethyl amino salt. In continuation of this work, we report here the redox determination results of those dyes and discuss the C-5 substituent effect on the redox properties. Also, the semi-empirical quantum chemistry calculation (AM1–SCF) is used to directly estimate HOMO and LUMO energy levels and compared to the observed values.

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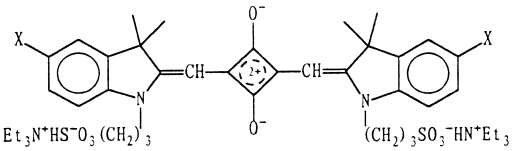


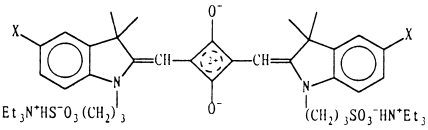
X= H, CH_3, OCH_3, F, Cl, Br, NO_2, CO_2H

2. Results and discussion

2.1. Electrochemistry

The Sq1(X = H) redox spectra in methanol is shown in Fig. 1. All the Sqs exhibit similar redox spectrum. The two revisable oxidation states, with the cation and the ionic peak, are observed in all the Sqs. But the reduction potential of some dyes cannot be determined because the peak is out of the determination window of the methanol. The $E_{1/2}$ values, the potential average value of the cation peak and ionic peak in the same redox state, are calculated and listed in Table 1. The values range from 0.62∼1.06 V for the first oxidation potential($E^1{}_{1/2,ox}$), and 0.8∼1.18 V for the second ($E^2_{1/2,ox}$). The C-5 substituents affect the potential values, but the effect is small.

As the dye molecule is a donor–acceptor–donor (D–A–D) structure, the four-membered carbon ring moiety of the molecule is an electron acceptor, and the two indolenium moieties are electron donors; both the ground and singlet excited states are D–A–D charge transfer states (CT) [16]. The small C-5 substituent effect on the oxidation potential suggests a small involvement of D-A interaction in ground state. Because the oxidized state is associated with the loss of electrons, the increase in electron donating ability is thought to facilitate oxidation. So the oxidation potential value decreases as the substituent electron donating ability increases; the reverse is true. Thus, the oxidation potential is anticipated to be in the order: $NO_2 > CO_2H > F > Cl$, $Br > H > CH_3 > OCH_3$. This order is in accordance with the experimental results except for the $-CO_2H$ and the $-NO_2$ groups, which exhibit slight by lower potential values than –F. So the effect of the C-5 substituention oxidation potential should mainly arise from electrostatic induction.



2.2. AM1 quantum chemistry calculation

The simplified molecular model with the N-sulfonatopropyl group replaced by the methyl group, and the overall **trans**-structure is used to obtain geometry optimization. The molecular ionization potentials (I_p) and electron affinities (E_A) data are obtained and also listed in Table 1. The I_ps

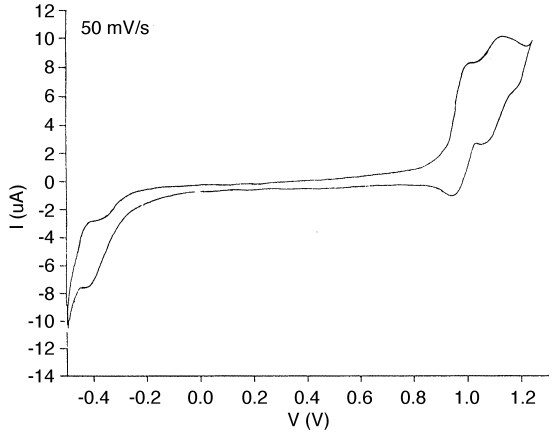


Fig. 1. Redox spectrum of Sq1 in methanol.

Table 1
The redox potential data in methanol and frontier orbital energy of Sqs

Sqs	X	λ_{max} (nm)	$E^1_{1/2OX}$ (V)	$E^2_{1/2OX}$ (V)	I_P (ev)	E_A	E'_A (ev)
Sq1	H	628	0.94	1.10	7.12671	2.235	5.16320
Sq2	CH_3	636	0.90	1.11	7.11563	2.163	5.15023
Sq3	OCH_3	650	0.62	0.80	6.99710	2.148	5.08940
Sq4	F	628	1.06	–	7.19528	2.293	5.21806
Sq5	Cl	634	0.84	1.18	7.11014	2.233	5.26381
Sq6	Br	634	0.94	1.18	7.13855	2.260	5.27157
Sq7	NO_2	652	0.99	–	7.20609	2.373	5.22155
Sq8	CO_2H	640	0.94	1.18	7.13801	2.281	5.15245

range from −6.99 to −7.20 eV, and the E_As range from −2.1 to −2.4 eV. The C-5 substituent exerts a small effect on the frontier orbital energy level. This is in accordance with determined results for the oxidation potential.

Because the I_p means the energy required by losing an electron from the molecule, the substituent effect on I_p should be related to the first oxdiation potential. So a relationship between $E^1_{1/2,ox}$s and I_{ps} was evaluated and the result is shown in Fig. 2. As expected, a good linearship between $E^1_{1/2,ox}$ and I_p is obtained, which implies the feasibility and validity of the theoretical estimation and the experimental determination. The correlation between the $E^1_{1/2ox}$ and the E_{HOMO}, or the I_p, can be obtained as in formula (1).

$$E_{HOMO} = -I_P = -(6.3978 + 0.7879E_{1/2ox}) \quad (1)$$

From the absorption maxmum we can estimate the transition energy (E_T), and the value is used to correct the lowest unoccupied orbital level energy (LUMO) or electron affinity energy E'_A using formula (2). The corrected E'_As are also listed in Table 1.

$$E'_{LUMO} = -E'_A = -I_P + E_T \quad (2)$$

When comparing the E'_{LUMO}s with the AM1 calculation values, a good linear relationship with slope closed to unity (0.9877) is obtained, as shown in Fig. 3. E'_{LUMO} is higher than E_{LUMO} by ~ 3.0 ev, which can be attributed to the lack of configuration interaction in the AM1 calculation.

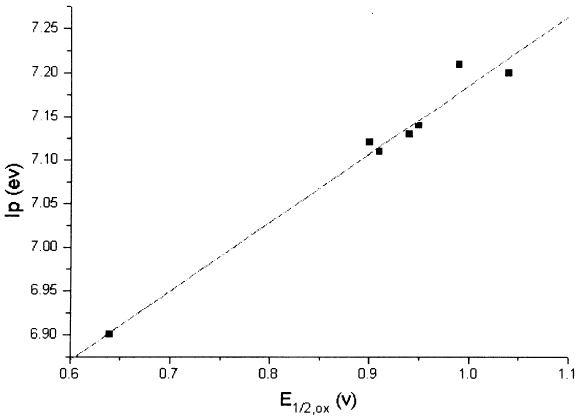


Fig. 2. Relationship between the I_p and $E^1_{1/2ox}$.

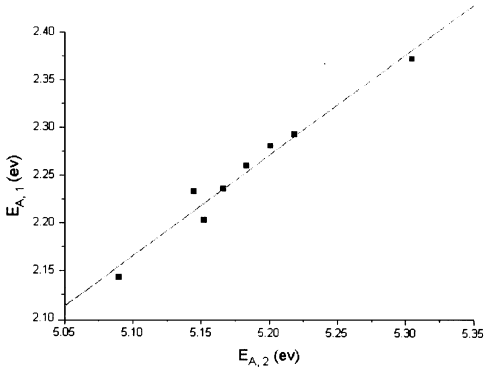


Fig. 3. Relationship between the E'_{LUMO} and E_{LUMO}.

3. Experimental

3.1. Materials

The squaraine dyes were synthesized by condensing the 5-substituted-1-(3–sulfonatopropyl)-2,3,3-trimethylindolenium with squaric acid in the solvent mixture pyridine/n-butanol 1:5, details have been reported in our early previous paper [7]; the dyes were purified by column chromatography before use. All the reagents used in this work were analytically pure.

3.2. Computational

The dye energy levels were calculated in the closed shell spin-restricted AM1 method as contained in the MOPAC6 programs. The default SCF conditions and parameters inherent in MOPAC6 used throughout the calculation and the solvent effect is simulated by introducing the +,−sparkles pairs with the + sparkles opposite to the O-atom.

3.3. Determination

The redox potentials of Sqs were determined by cyclic voltammetry, using an EG&G PAR Model 174 polarographic analyzer and a Model 175 universal programmer. Typically, electrochemical measurements were carried out in methanol (dehydrated before use) containing a supporting electrolyte LiCl (dehydrated before use), in a small three electrode cell (ca. 20 ml). The working electrode was a platinum disk electrode with 3 mm diameter and the counter electrode is a platinum plate. A silver wire was used as a reference electrode, which is 0.4 v negative with respect to the saturated KCl-calomel electrode. The concentration of Sqs and supporting electrolyte were $\sim 10^{-3}$ and 0.1 mol litre^{-1} respectively.

4. Conclusion

Through indirect determination and direct calculation, the frontier orbital energy levels of Sq were obtained. The results are in accordance with each other, which implies the AM1 calculation can simulate practical results. That is very useful in predicting the first oxidation or frontier orbital energy level of other Sq dyes by using the AM1 quantum chemistry calculation. Absolute energy values are being evaluated in continuing studies.

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