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The structure and ^{13}C-NMR of an indolenium squaraine dye

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Abstract

Six conformational isomers of bis(1-isopropyl-2,3,3-trimethylindolen-2-ylidene)squaraine were studied using MM + molecular mechanical and AM1 quantum chemical methods. The calculated energies and structures indicate that the planarity of the π system is of great importance. These results were confirmed by NMR spectroscopy. The structure of the aforementioned dye was shown to be the trans-planar isomer. The ^{13}C-NMR spectrum of this isomer was assigned with the aid of C-atom charge density data derived from AM1 calculations.

Keywords: Isomers; Squaraine; Squarylium Indolenium; Structure; ^{13}C-NMR

1. Introduction

Squaraine dyes have attracted much attention because of their potential utility in photoconductive photoreceptors [1], optical recording media [2], gas sensitive devices [3] and fluorescent probes for biological systems [4]. Strong intermolecular interactions in this chromophoric system result in low solubility, limiting fundamental and practical studies involving squaraine dyes. In our previous paper, we reported results from the synthesis of highly soluble indolenium squaraine dyes and established a correlation between the nature of the N- alkyl groups and the solubility [5,6]. Improvements in solubility have made it possible for us to study the properties of these dyes more completely [7–9]. We believe that studies of this type are important not only to understanding the physical and chemical properties of dye molecules, but also in the design of new dyes.

While multiple conformational isomers maybe written for a given indolenium squarylium dye, do all possible isomers actually exist? If not, which one is the predominant structure? In order to answer these questions, we selected bis(1-isopropyl-2,3,3-trimethylindolenium-2-ylidene)squaraine(SQ) as a model compound, and employed a combination of quantum chemical calculations and enhancement NMR analyses.

In the present study, molecular mechanical (MM +) calculations in the PCMODEL package and AM1 quantum chemical calculations in MOPAC7 were used to conduct geometry optimizations. The AM1-CI method was used to predict transition energies. Distortionless Enhancement by Polarization Transfer (D.E.P.T.), ^{13}C-NMR and ^{13}C-NMR and difference NOE ^{1}H-NMR were used to confirm theoretical predictions. ^{13}C-NMR spectra were assigned with the aid of calculated atomic charge densities.

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2. Results and discussion

2.1. Modeling studies

Theoretically, at least six stable conformational isomers of bis(1-isopropyl-3,3,3-trimethylindolen-2-ylidene)squaraine are expected to exist. As shown in Fig. 1, although all isomers contain alternate single and double bonds at the connection points of the indolenium and squaraine moieties, they can not be interconverted by free rotation because of delocation of the π electrons.

The six structures were subjected to MM+ and AM1 geometry optimizations. The energy valves obtained are listed in Table 1. Heat of formation data calculated by AM1 was used to predict the relative concentration of the various isomers, based on Boltzmann distribution method. The equilibrium concentration for each isomer is also listed in Table 1. These results indicate that isomers **I**, **II** and **III** are plausible structures, while **IV**, **V** and **VI** are unlikely to exist because of their higher energies.

Similarly, a large difference in molecular planarity was found among the six optimized structures. A planarity in the conjugated system was found at the points of attachment between the indolenium and squarylium moieties. The dihedral angles listed in Table 2 correlated with the relative position of the O-atom and *N*-alkyl group. When the isomer with the *N*-alkyl group was close to the O-atom, a large dihedral angle was observed, and when a C-3 methyl group of the indolenium was close to the O-atom, a planar structure formed. So isomers **I** and **II** were planar, **III** and **V** were slightly twisted and **IV** and **VI** were very twisted. Also, the torsion angle depended on the size of *N*-alkyl group, with the *N*-isopropyl giving torsion angle as large as 37°.

Table 1
The energy data for the six conformational isomers optimized by MM+ and AM1

	PCMODEL	AM1			
No.	ΔH_f (kcal/mol)	ΔH_f (kcal/mol)	E (eV)	E_T (nm)	C[a] (%)
I	114.74	110.87	−5642.02	620	9.91
II	114.74	110.42	−5642.03	620	21.16
III	108.94	109.72	−5642.07	626	68.89
IV	116.11	118.29	−5641.69	827	0.00
V	115.24	114.12	5641.87	-	0.04
VI	115.86	118.36	−5641.69	816	0.00

[a] Predicted hypothetical equilibrium percentage concentration by Boltzmann distribution, calculated as follows: $Ni/Nj = \exp[-(Ei - Ej)/RT$, Ni, Nj represents the relative concentration and Ei, Ej =heat of formation calculated by AM1. $Nj = 109.72$, and $T = 298$ K (normalized).

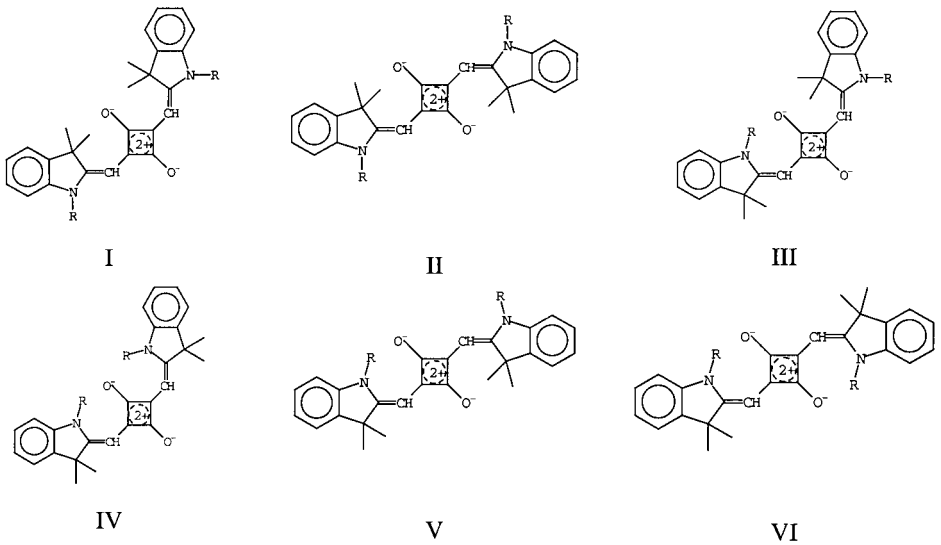
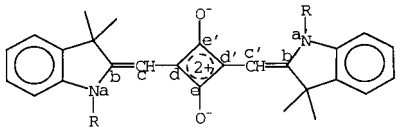


Fig. 1. The six stable conformations of the squarylium dye where $R = i\text{-}Pr$.

Table 2
Torsion angles for six conformation isomers optimized by AM1



Position	I	II	III	IV	V	VI
a-b-c-d	179.17	−179.20	−179.06	4.38	180.00	−4.93
b-c-d-e	179.00	−179.42	178.91	37.62	−178.55	−33.35
a′-b′-c′-d′	−179.08	179.35	−9.90	−37.67	−9.83	33.43
b′-c′-d′-e′	−178.49	178.50	−17.41	−14.75	−26.28	13.03

A planarity in the conjugated system decreases p-orbital overlap, making the transition energy (also listed in Table 1) small. Thus, a bathchromic shift in the VIS-IR region should be observed in nonplanar conformations. Since the present squaraine dye exhibits a sharp and intense absorption in the VIS-IR region, with $\lambda_{max} = 630$ nm in solution and since little change occurs when the *N*-alkyl group is varied [6], it is reasonable to believe that a highly twisted structure cannot be readily obtained.

The *cis*-**I** and *trans*-**II** conformations should have the same absorption because of equivalent π systems.

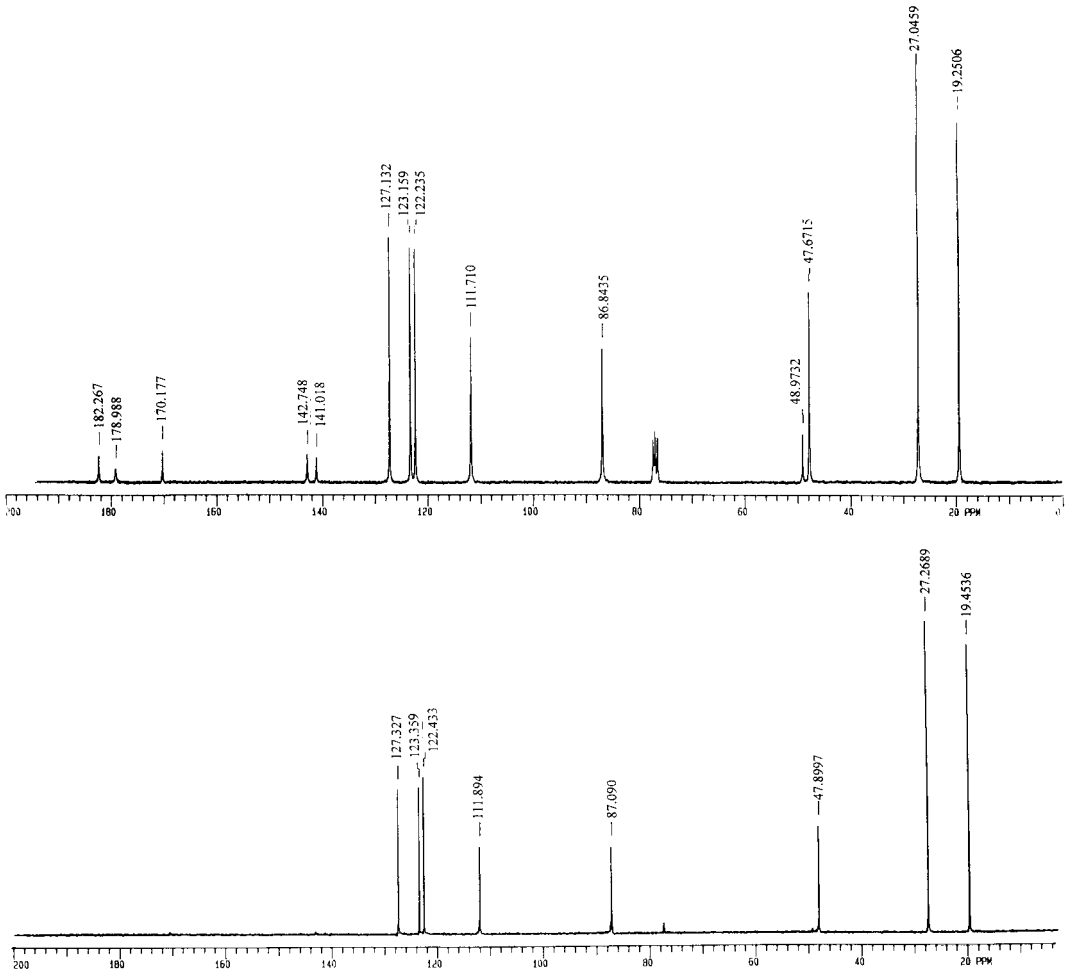


Fig. 2. The ^{13}C-NMR of the SQ dye (the overall ^{13}C-NMR spectrum above and the DEPT ^{13}C-NMR spectrum down).

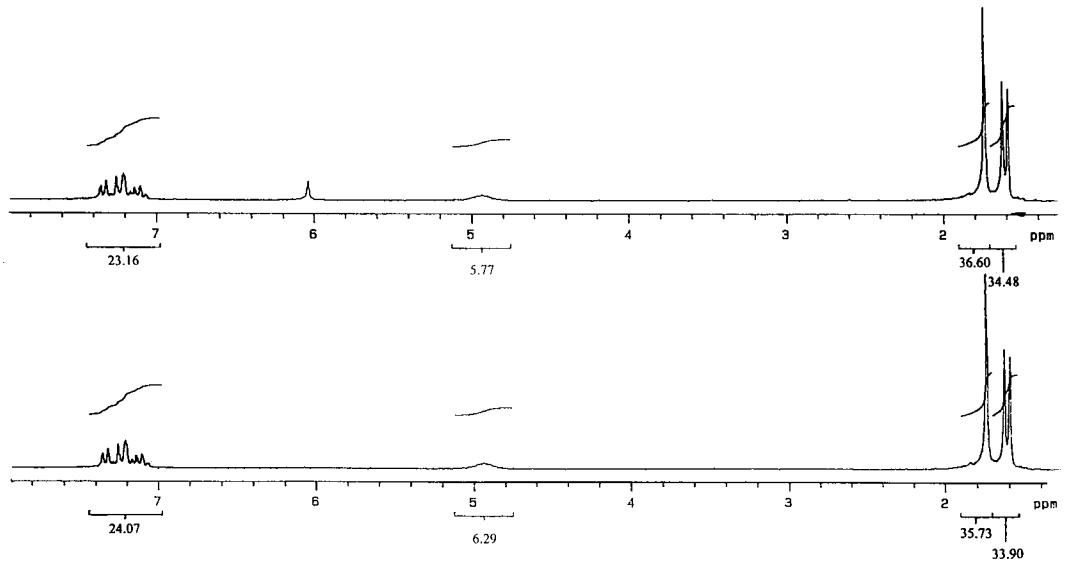


Fig. 3. the NOE difference spectrum with irradiating of proton.

The main difference between the two isomers was their symmetry.

Comparing with the result obtained from the energy calculations, it is apparent that transition energy of isomer **III** is close to that of **I** and **II**. Whether this non-planar isomer exists in large concentrations can be determined by NMR experiments.

2.2. NMR studies

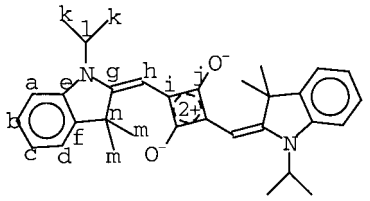
When the C-3 methyl is close to the O-atom, the H-O distance can be as short as 1.4 Å. Because a ^{13}C-NMR chemical shift depends mainly on C-atom density, an assessment of C-atom charge density suggests that *cis*-isomer **II** should give two carbonyl C-peaks in the ^{13}C-NMR spectrum compared to the *trans*-isomer **II**, which would exhibit a single carbonyl C-peak.

^{13}C-NMR spectra arising from the dye employed in this study are given in Fig. 2. The fact that only one carbonyl C-peak was observed suggests that the dye exists as the trans isomer (**II**). These results were confirmed by an ^{1}H-NMR NOE difference determination. The NOE difference spectrum produced by irradiating the methine proton (h) is given in Fig. 3. It is clear that the proton 1 was enhanced largely and signals for the methyl groups at C-3 (m) and *N*-isopropyl methyl groups (*k*) decrease a little (Table 3). This indicates that only the structure with the *N*-methyl groups close to proton h exists in our sample and is consistent with single crystal X-ray structure data. The reason why the isomers **I** and **III** cannot exist in practice may be stemmed from the formation of the reaction intermediate.

2.3. ^{13}C-NMR assignments

With the aid of the distortionless enhancement by polarization transfer analysis (DEPT) and atom charge density data calculated by AM1, we assigned the ^{13}C-NMR peaks as shown in Table 3 The chemical shift correlated with the atom charge and their bond type. The primary C-atoms had low δ values quaternary C-atoms gave the highest δ values, with secondary and tertiary C-atoms falling in between. Carbon-K had the lowest δ value, followed by Carbon-m, with Carbon-n having the highest δ value among the saturated C-atoms. For the sp2 carbon atoms, Carbon-h appeared at high field, while the quaternary C-atoms appeared at low field. Their atom charge densities were in the order Cj < Cg < Ci, with their chemical shifts in reverse order. The indolenium quaternary Carbon-atoms were at higher field because of the ring effect, and the chemical shift of

Table 3
The ^{13}C-NMR data and C-atom charge densities of the SQ dye used in this study



		^{13}C-NMR/d(ppm)	$Q_{Ci}(e)$[a]
a	=CH-	111.71	−0.1567
b	=CH-	127.13	−0.1045
c	=CH-	122.23	−0.1543
d	=CH-	123.16	−0.0793
e	=C-	142.75	0.0551
f	=C-	141.02	−0.1238
g	=C-	178.99	0.1423
h	=CH-	86.84	−0.2299
i	>C=	170.18	−0.1102
j	>C=O	182.27	0.2246
k	-CH_3	19.25	−0.2315
l	N-CH<	47.67	0.0317
m	-CH_3	27.05	−0.2038
n	>C<	48.97	0.0223

[a] The atom charge densities are based on AM1 calculations.

Carbon-f was smaller than that of Carbon-e because of larger charge density. In the same way, we assigned the chemical shifts of C-a∼d.

3. Experimental methods

3.1. Material

The SQ dye was synthesized by condensation the *N*-isopropyl-2, 3,3-trimethylindolen iodinate with squaric acid in *n*-butanol/pyridine (5:1). the product was purified by recrystalization from methanol–water [6]. The ^{1}H- and ^{13}C-NMR were recorded on a VARIAN JEMINI-300 spectrometer. A $CDCl_3$ solution of concentration ca. 12 mg/ml was used.

3.2. Calculations

The MM+ calculations were conducted with a PCMODEL6 software package, and the geometry optimization results were used to generate an AM1 input file. AM1 calculations employed MOPAC7 software and an EF converger for geometry optimizations. The geometry convergence criteria used the default value (0.0001 kcal/mol). When the change in energy on successive configuration interactions was less than this value, the optimization was believed to be successful. The computer used for the calculations was a Pentium MMX166, and the memory size was 32 MHz. All calculations were conducted on an MSDOS 6.22 platform, with MM+ optimizations often fast and AM1 calculations taking several hours.

The configuration interaction calculations employed four occupied molecular orbits and four unoccupied molecular orbits (CI = 4).

4. Conclusions

Using MMX and AM1 calculations and ^{13}C-NMR experiments, five conformation isomers of a model SQ dye eliminated as possible structures. Further considerations revealed the trans-conformation as the most logical structure. Its ^{13}C-NMR spectrum was assigned with the aid of atomic charge densities calculated by AM1. The nonplanar structures are believed to be unstable probably due to a high energy transition state. Twisted SQ dyes are not practical. This is of significance in the design of new squarine compounds.

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