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Dyes and Pigments 40 (1998) 53–57

DYES
AND
PIGMENT

Three dimensional molecular stacking and functionalities of aminonaphthoquinone by intermolecular hydrogen bondings and interlayer π–π interactions

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Received 9 March 1998; accepted 3 April 1998

Abstract

Three dimensional molecular stacking of aminonaphthoquinones affecting largely on their 3rd order nonline optical property was evaluated by X-ray crystal analysis. It was found that the intermolecular hydrogen bondings a the interlayer π–π interactions played a significant role in producing large bathochromic shifts of absorption maximu in solid state, and gave large 3rd order nonlinear optical susceptibility. Molecular symmetry and substituent effects their physical properties were also correlated with their molecular stacking in crystals. © 1998 Elsevier Science Ltd. A rights reserved.

Keywords: Aminonaphthoquinone dyes; Intra- and intermolecular hydrogen bonding; Interlayer π–π interaction; Three dimensio molecular stacking; X-ray crystal analysis; Nonlinear optical property

1. Introduction

Almost all functionalities of organic materials for electronics and photonics are induced by π-electron oriented intermolecular interactions. Intermolecular interactions including π–π interactions, coupling of molecular transition dipoles, and characterization of molecular stacking are very significant with respect to special functionalities in the solid state. Dye molecules have a large π-conjugated planar structure and are thus valuable candidates for organic functional materials [1]. Solid state chemistry of dye molecules is of current interest with regard to their functionali with their structure in crystals, and aggregates functional materials, these giving color changes crystals [2–4], organic nonlinear optical materia [5], organic photoconductors and emitters f electroluminescence. Many functionalities a caused by intra- and intermolecular π–π intera tions of dye molecules in the solid state.

We have reported some new types of amin naphthoquinone dyes which perform thr dimensional molecular stacking caused by inte molecular hydrogen bondings and interlayer π- interactions [5]. Aminonaphthoquinones have strong intramolecular charge-transfer chrom phoric system in which the amino- and hydrox groups are as donor moieties and the quino

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PII: S0143-7208(98)00029-1

group is an acceptor moiety. In addition, the amino and hydroxyl groups also act as hydrogen donors, and the quinone carbonyl groups act as hydrogen acceptors, and consequently effective molecular stacking in the π-molecular plane is anticipated by the intra- and intermolecular hydrogen bondings in solid state. On the other hand, interlayer $\pi - \pi$ interactions of a charge-transfer character play a significant to be in the three dimensional molecular stacking. The amino nitrogen and the hydroxyl oxygen act as electron donors, and the quinone carbonyl group act as an electron acceptor.

In a previous paper [2], we have discussed the synthesis and solid state absorption properties of aminonaphthoquinone dyes, and their chromophoric systems were evaluated to ascertain the intermolecular π–π interactions of dye molecules using the Pariser–Parr–Pople molecular orbital (PPP MO) method. In this paper, we report the correlation between the 3rd order nonlinear optical property and the three dimensional molecular stacking of aminonaphthoquinones using X-ray crystal analyses data.

2. Experimental

2.1. Materials and equipment

The aminonaphthoquinone dyes **1** and **2** have been previously synthesized and identified [2]. The preparations of vapor deposited thin film of **1** and **2** were performed using the Nippon Shinku Kikou VSP-060 apparatus. Visible spectra were recorded on a U-3410 Hitachi spectrophotometer

2.2. Preparation of a single crystal of 1 and 2

Slow evaporation of an acetonitrile solution of **1** gave red colored crystals after several days, and a benzene solution of **2** gave golden colored crystals. The crystal was collected by filtration and used in this investigation.

2.3. X-ray crystal analysis

X-ray crystal analysis of **1** was carried out by M. Kubata at Sumitomo Electric Industries, Ltd, and that of **2** by A. Nakao at Mac Science C Ltd. The authors are greatly indebted to them.

2.4. Calculations and measurement

The PPP MO calculations were used to evalua the absorption spectra of **1** and **2**. The molecul hyperpolarizability (γ) was calculated usi MOPAC, and the 3rd order nonlinear optical su ceptibility $(\chi)^{(3)}$ for third harmonic generation the vapor deposited thin film of **1** and **2** w determined by Sumitomo Electric Industry [5].

3. Results and discussion

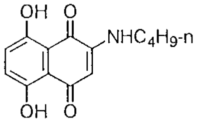
3.1. Solid state absorption spectra

Two alkylaminonaphthoquinones **1** and **2** we previously synthesized and their absorption spe tra in benzene and vapor deposited thin fil determined (Fig. 1). They have same chrom phoric system of an intramolecular charge-transf character and they absorbed in a similar wav length region to **1** (501, 530^{sh} nm) and **2** (463, 50 543 nm). The band splitting of **2** was due to t vibrational levels of the first excitation band. C the other hand, the solid state absorption spe trum of **2** was quite different from that in solutio A large bathochromic shift of 100 nm from sol tion to solid state was observed for **2**, but no significant shift was observed for **1**.

The peak at around 600 nm for **2** arose from t bathochromic shift of the first excitation band o in solution; it was not the new transition band d to the intermolecular charge-transfer band donor–acceptor molecular complex. Large diffe ences in absorption spectra between **1** and **2** we concluded to arise from their intermolecular π- interactions in the solid state. X-ray crystal an lyses of their single crystals were then carried ou

3.2. X-ray crystal analyses

Single crystals of **1** and **2** were obtained fro their acetonitrile and benzene solution respective by slow evaporation of the solvent. To elucida the molecular structure and packing modes of



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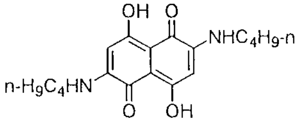

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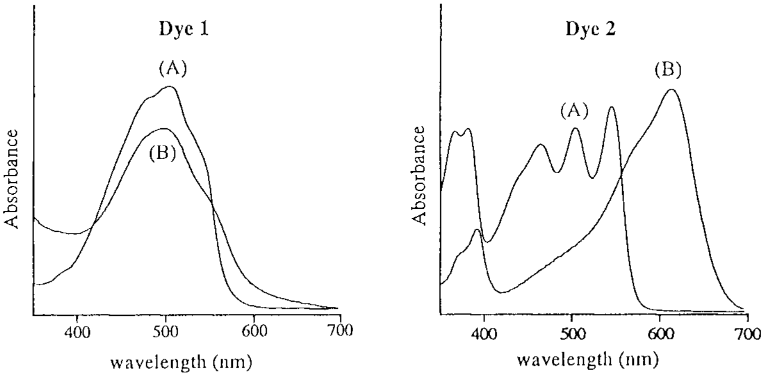


Fig. 1. Differences in absorption spectra of **1** (left) and **2** (right) in (A) benzene and (B) vapor deposited thin film.

and **2** in the crystals, X-ray structure analyses were carried out and the results are summarized in Table 1. The crystal system of **1** is monoclinic and that of **2** is triclinic. The space group of **1** is P21/a and that of **2** is P$\bar{1}$ and the final residual index R was 0.064 for **1** and 0.0537 for **2**. The goodness of fit for **1** is poor of 2.085, but that for **2** is satisfactory at 0.2999. Hydrogen atom treatment was not done for each analysis, but the direction of intermolecular hydrogen bonding between the imino or the hydroxyl hydrogens and the quinone oxygen in the same plane was concluded from the hybridization of each atom.

Molecular structures of **1** and **2** are shown in Fig. 2. The 1,4-quinone form for **1** and the 1,5-quinone form for **2** were confirmed in the crystals, but their tautomerism has been studied in solution [7]. The π-chromophoric systems of **1** and **2** are completely in a planar situation, but the alkyl moieties of the butyl groups are out of plane, especially in the case of **2** (cf. Figs. 4 and 5).

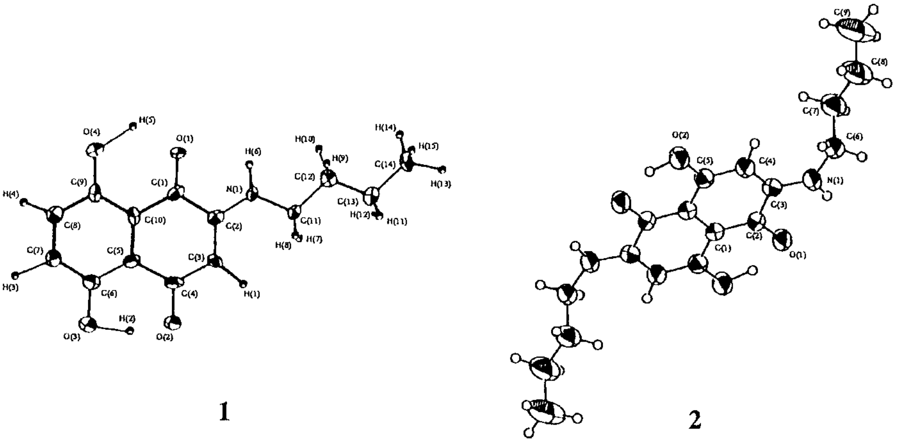
Table 1
Crystal data of **1** and **2**

Dye	**1**	**2**
Formular	$C_{14}H_{15}NO_4$	$C_{18}H_{24}N_2O$
Formular weight	261.27	332.39
Crystal system	Monoclinic	Triclinic
Space group	P21/a	P$\bar{1}$
Cell dimension		
a/Å	8.821 (3)	5.3330 (
b/Å	12.913 (5)	6.9870 (
c/Å	11.753 (4)	12.2980 (
α(°)	90.00	97.61
β(°)	109.98	91.64
γ(°)	90.00	95.11
V(Å^3)	–	214.75
Z	4	1
Dc/g cm^{-3}	1.379	1.200
Total reflections measured	623	1182
Reflection used	172	851
Residuals R	0.064	0.0537
Residuals R_w	0.070	0.0570
Goodness of fit	2.085	0.2999

Differences in intra- and intermolecular hydrogen bondings of **1** and **2** are shown in Fig. 3. In the case of **1** and **2**, intramolecular hydrogen bondings between the imino and/or the hydroxyl hydrogen atoms and the quinone oxygen atom were observed, which gave planar π-systems for **1** and **2** in molecular levels. On the other hand, inte
molecular hydrogen bondings between the imi
hydrogen and the quinone oxygen atoms contr
the intermolecular layered structures for molecul
stacking. The zig-zag intermolecular hydrog

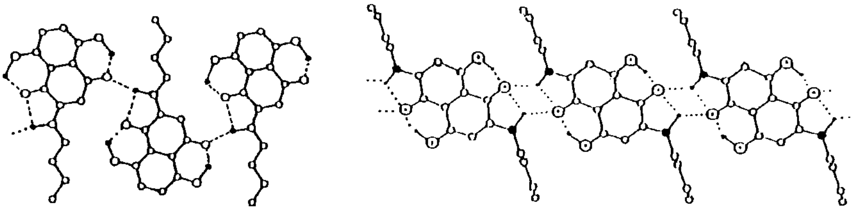
bonding in **1** resulted in some "bent" structures in each pair of molecules, while, four centered intermolecular hydrogen bondings in **2** resulted in planar interlayer structures (Fig. 4). The interlayer distances of **1** is 3.37 Å at the nearest and 4.4 Å at the longest, but that of **2** is 3.3 Å which is almost the summation of the van der Waals radius of each element.

Molecular overlaps of **2** in crystals are shown Fig. 5. Four centered intermolecular charg transfer interactions of **2** were observed betwe the molecular layer; the amino nitrogen a hydroxyl oxygen act as donors and the quino carbonyl act as acceptor. The distance between t nitrogen and the carbon was calculated in 3.31 and that of the oxygen and the carbon at 3.35



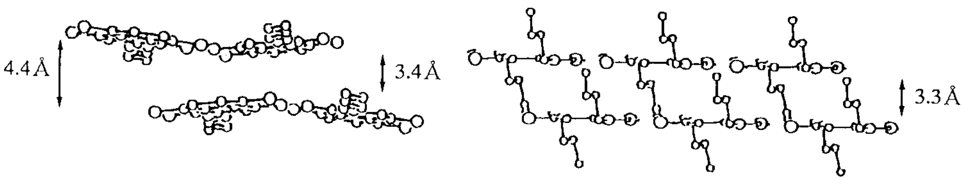
1 **2**

Fig. 2. Molecular structures of **1** and **2**.



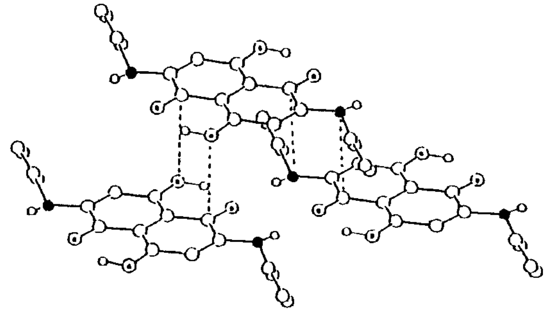
1 **2**

Fig. 3. Intra- and intermolecular hydrogen bondings in crystals of **1** and **2**.



1 (4 molecules) **2** (6 molecules)

Fig. 4. Interlayer structures and distances of **1** and **2**.



2

Fig. 5. Molecular overlaps and the four-centered interatomic charge–transfer interactions of **2** in the two layered structure.

These results indicate that strong interatomic charge-transfer interactions play an important role in producing strong three dimensional molecular stacking. In the case of **1**, such types of interatomic charge–transfer interactions were not observed.

These differences in the crystal structures of **1** and **2** produced large differences in their solid state absorption spectra and 3rd order nonlinear susceptibility [5].

3.3. *Differences in solid state properties of 1 and 2*

Some physical properties of **1** and **2** are summarized in Table 2. Dye **2** has a higher melting point of around 60°C than that of **1** which may attribute to differences in their rigid molecular stacking behavior, but not be due to differences in their molecular weight, and/or numbers of the n-butyl groups which may cause a decrease in me ing point.

Table 2
Some characterization data of dyes **1** and **2**

Dye	**1**	**2**
m.p.	127–128°C	189–190°C
λ max in solution	501, 530^{sh} nm	463, 502, 543 nm
λ max in solid	498 nm	604 nm
$\Delta\lambda^{a}$	−3 nm	102 nm
calcd. $\lambda_{max}{}^{b}$	452 nm	504 nm
γ-calcd. (esu)^{c}	34×10^{-36}	50×10^{-36}
χ [3]$_{THG}$ (esu)	1×10^{-13}	4.8×10^{-11}

[a] $\Delta\lambda=\lambda_{solid}-\lambda_{soln}$.
[b] PPP MO method.
[c] MOPAC method [6].

The reason why **2** in the solid state produc large bathochromic shift of 100 nm compared that in solution is not yet obvious, but dipol dipole interaction [3,4] and intermolecular π- interaction [2,8] need to be considered. The dire tion of the transition moment of **2** in the sol state is the same as that in the molecular level, a is not oriented perpendicular against the π-mol cular plane (interlayer charge–transfer direction) [

The 3rd order molecular hyperpolarizability (of **1** and **2** is almost the same, which arises fro the π-electron system in the molecular level, b the 3rd order nonlinear optical susceptibility $\chi^{(3)}$ of **2** is 500 times larger than that of **1**.

As conclusion, it is concluded that **1** has so bent structure in each pair of molecules in t layered structure but **2** has a rigid plane layer structure in crystals, which arise from the diffe ences in numbers of the intermolecular hydrog bonding sites. Rigid and strong intermolecular π interactions in **2** produced a large bathochrom shift of absorption maximum in the solid state a gave large 3rd order nonlinear optical susce ibility $\chi^{(3)}$. These differences are attributed to t differences in interlayer distance and to the mo cular overlap between the upper and lower mo cular layer.

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