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Structural relationships on conductivities of ortho-hydroxyazo dyes

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Abstract

The solid film conductivities of 23 H/K acid azo dyes and three metallised azo dyes were measured at 25°C and 60° respectively. The data show that the solid conductivities of these ortho-hydroxyazo dyes are determined and controll by the extent of the intramolecular and intermolecular conjugation. It is concluded that the conductivity properties organic materials can be improved by optimizing the positions of electron donors and acceptor substituents. © 19 Elsevier Science Ltd. All rights reserved.

Keywords: Conductivity; Solid film; Azo dyes

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1. Introduction

The study of organic materials for their electrical behaviour is now a dynamic field of research and activity has increased step by step in the recent past, since a number of applications [1] can be foreseen. The mode of conduction is based on delocalization of π-electrons and the excitation of an electron from the highest filled π-MOs to the lowest unfilled MOs (LUMO). Radiation can stimulate the creation of new donor levels or of reasonable number of free electrons [2], and the resistivity, as well as the thermal activation energy, decrease with increasing degree of conjugation of the dyes [3], where the degree of conjugation corresponds to the wavelength of the absorption maximum of the dye. In addition, steric effec and geometrical charge [4] influence the co ductivity of an organic molecule, as well as hi pressures and shear [5] and can significant increase the conductivity; σ- and π-electron effects of coordination play an important role the mechanism of conductivity, as does the inte molecular conjugation for the combined acti of high pressure and shear in a substance wi a developed system of conjugated bonds. T conjugative effect has some significant influen on electrical conductivity [6] and non-line optical properties [7], but experimental data this subject are very scant. The work describ here measures the solid conductivities of 23 H/ acid azo dyes and three metallised azo dyes at and 60°C, and such an investigation of the stru tural effect on the conductivities should be a gui for the synthesis of new functional materials.

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2. Experimental

2.1. Ortho-hydroxyazo dyes

Twenty-three H/K acid azo dyes were synthesized and their structures confirmed by ^{1}H NMR (Table 1) three metal complexes of ortho-hydroxyazo dyes (Table 2) were supplied by BASF.

The sample tablets were formed by a tablet press under 20 MPa, and both sides of the tablets were silvered. To minimize the solvent and water content, the tablets were dried at 120°C for 24 h.

2.2. Apparatus

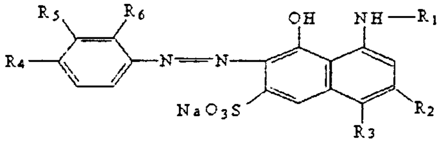
A. C. conductivity measurements from 20 Hz to 1 MHz were carried out using two polished silver electrodes and were made with an HP 4284 Recession LCR Meter. The conductivities we obtained by processing the high frequency da with a computer.

3. Results and discussion

The conductivities at 25°C and 60°C are show in Tables 1 and 2. The results in Table 1 show th D-13, D-25 and D-16 have higher conductio which indicates that the intramolecular bifurat hydrogen bond [8,9] of o-nitro or o-sulfo oxyg to hydroxy hydrogen gives rise to strong ove lapping of the molecular orbitals. Moreover, t intramolecular hydrogen bonds play an importa role in keeping the molecular planar [10], whi

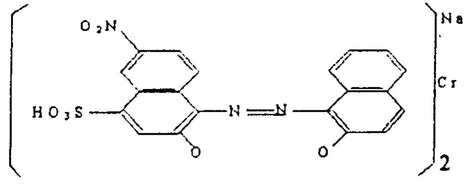
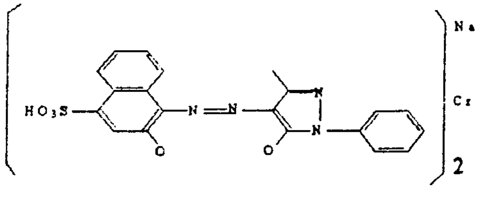
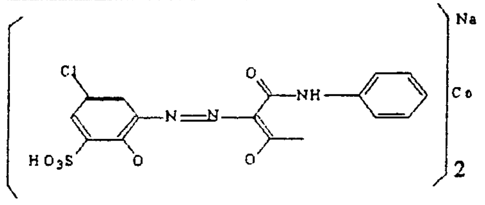
Table 1

Structural formulae of H/K acid azo-dyes and their conductivities (G: S/cm) at 25 and 60°C, respectively



Dye	R$_1$	R$_2$	R$_3$	R$_4$	R$_5$	R$_6$	log G$_{25°C}$	log G$_{60°C}$
D-13	–COPh	–H	$-SO_3Na$	–H	–H	$-SO_3Na$	–5.115	–5.076
D-25	–COPh	–H	$-SO_3Na$	–H	–H	$-NO_2$	–4.944	–4.594
D-16	$-COCH_3$	$-SO_3Na$	–H	–H	–H	$-NO_2$	–5.353	–5.139
D-21	–COPh	$-SO_3Na$	–H	–H	–H	$-OCH_3$	–5.931	–5.621
D-=9	$-COCH_3$	$-SO_3Na$	–H	–H	–H	$-OCH_3$	–6.447	–5.945
D-8	$-COCH_3$	$-SO_3Na$	–H	–H	–H	–COPh	–6.595	–6.502
D-11	$-SO_2Ph$	$-SO_3Na$	–H	–H	–H	–H	–5.718	–5.683
D-30	$-COCH_3$	$-SO_3Na$	–H	–COPhCl	–H	–H	–5.897	–6.694
D-19	–H	$-SO_3Na$	–H	–H	–H	$-OCH_3$	–6.512	–5.970
D-1	–COPh	$-SO_3Na$	–H	–H	–H	–H	–5.987	–5.769
D-4	$-COCH_3$	$-SO_3Na$	–H	–H	–H	–H	–5.997	–5.776
D-14	–COPh	$-SO_3Na$	–H	–H	$-NHCOCH_3$	–H	–5.971	–5.625
D-29	$-SO_2PhCH_3$	$-SO_3Na$	–H	–COPhCl	–H	–H	–5.888	–5.517
D-24	–H	$-SO_3Na$	–H	$-NO_2$	–H	$-NO_2$	–5.650	–5.557
D-5	$-COCH_3$	$-SO_3Na$	–H	$-NO_2$	–H	–H	–5.973	–5.868
D-20	$-COCH_3$	$-SO_3Na$	–H	$-OCH_3$	–H	–H	–5.571	–5.312
D-18	$-COCH_3$	$-SO_3Na$	–H	$-SO_3Na$	–H	$-NO_2$	–5.960	–6.034
D-28	$-COCH_3$	$-SO_3Na$	–H	–OPh	–H	–H	–6.281	–6.175
D-22	–H	$-SO_3Na$	–H	$-OCH_3$	–H	–H	–6.221	–5.998
D-7	–COPh	$-SO_3Na$	–H	–H	$-NO_2$	–H	–5.987	–5.937
D-17	$-C_2H_5$	$-SO_3Na$	–H	–H	–H	$-NO_2$	–6.485	–5.283
D-6	–COPh	$-SO_3Na$	–H	–H	–H	$-NO_2$	–6.033	–5.866
D-3	–COPh	$-SO_3Na$	–H	$-NO_2$	–H	–H	–6.797	–6.643

Table 2
Structural formulae of metallised azo dyes and their conductivities (G: S/cm) at 25 and 60°C, respectively

DYE	Structure Formula	$\log G_{25°C}$	$\log G_{60°C}$
Dye-1		-5.936	-5.868
Dye-2		-6.244	-6.127
Dye-3		-6.380	-6.344

affects and strengths the polarizabilities of donor-acceptor-substituted π systems [11]. The 5-electron-acceptor (EA) sulfo group in the naphthalene nucleus decreases the density of the electron cloud in the coupling component, and strengthens the resonance between the donor and acceptor pairs of the molecules, and between the head and tail parts of the dimer [12], which leads to a better polarizability, and in turn results in a better conduction.

The effect of the polarization of π-electrons on the conductivity was examined with H acid azo dyes as shown in Figs. 1–4.

They have no permanent dipole moments and can only act through induced polarization, and conjugation involves the delocalization and polarization σ conjugated π-electrons. The polarized energy of π-electrons depends on structural features, e.g. the oscillator strengths and the conjugation length, which are controlled by the associated effect of conjugated groups. When both termin groups are combined in the same direction polarization, the conjugation stretched to bo terminals. Large conjugated π systems are high polarizable, so the conductivity of dyes D-21, 1 11, D-14 and D-17 attains a high value. In a co jugated molecule, two (valence and conductio bands are coupled with the frontier orbitals of t end groups (the donor and the acceptor, respe tively), and the ground state then consists of hybridization of the valence band and the don orbital. The excited state leading to charge tran fer is expressed by a partially filled acceptor ort tal hybridized with the conduction band. Suzuki al. [13] had introduced a simple model to descri the above electronic structure of donor/co jugated-bridge/acceptor molecules, which interpre the intramolecular adiabatic charge transfer. conjugated molecule, in which the donor-don

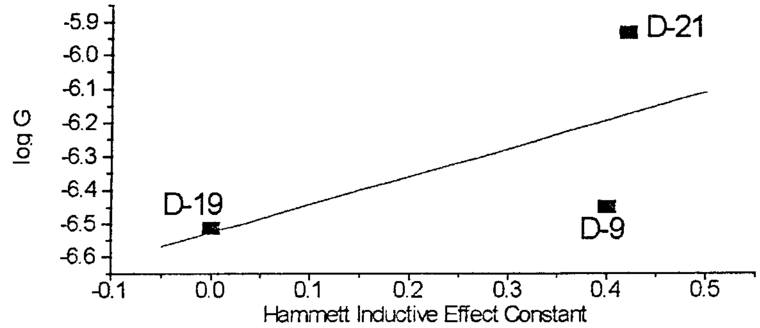


Fig. 1. Conductivities (G: S/cm) of H acid azo dyes with R_4–R_5 = H and R_6 = –OCH_3 at 25°C vs Hammett inductive effect consta (σ_I) of substituents (R_1 = –H) coupled with the 8-amino-group on the naphthalene nucleus.

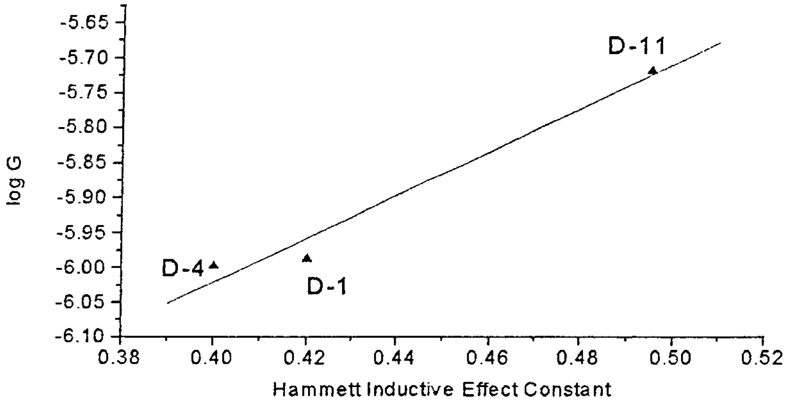


Fig. 2. Conductivities (G: S/cm) of H acid azo dyes with R_4–R_6 = H at 25°C vs Hammett inductive effect constant σ_I of substitue (R_1 = –COPh) coupled with the 8-amino-group in naphthalene nucleus.

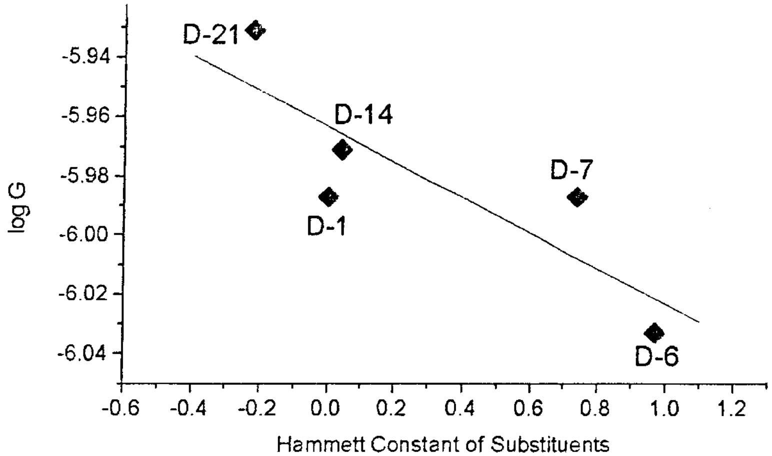


Fig. 3. Conductivities (G: S/cm) of H acid azo dyes with EA substituent, benzoyl–COPh, coupled with the 8-amino-group at 25°C the electronic effect of substituents in the diazo component.

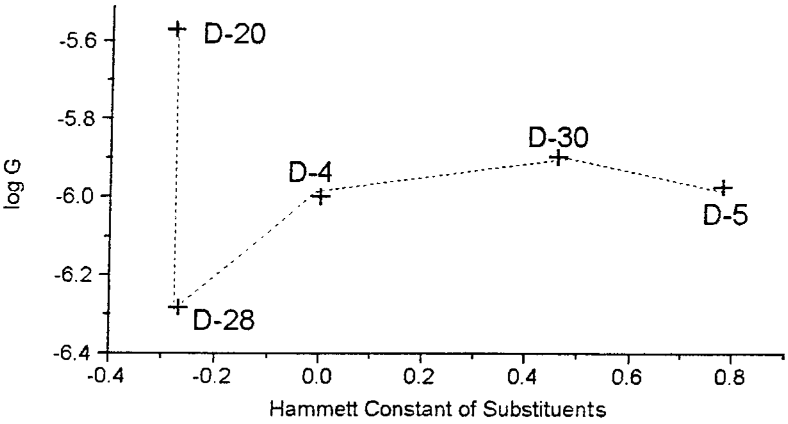


Fig. 4. Conductivities (G: S/cm) of H acid azo dyes with EA substituent, benzoyl–$COCH_3$ coupled with the 8-amino-group at 25°C the electronic effect of substituents in the diazo component.

pairs and acceptor-acceptor pairs alternately appear in the chain, has a narrow energy gap of about 1.6 eV [14]. In Fig. 3, the strong EA substituent (benzoyl–COPh), coupled with the 8-amino-group lowers the density of the electronic cloud in the coupling component and therefore, electron-donor (ED) substitutents in the diazo component promote conjugation. In contrast, when a strong ED group (e.g. $-NH_2$) is present in the naphthalene nucleus, the ED substituents in the diazo component are unfavourable for resonance of the conjugated pair; analogously, then insert insulators in the molecules and dimers of solid dye. Therefore, D-3, D-6, D-7, D-22 and D-18 are poorer conductors. Previous investigations [15] have showed that conjugation occurs when two general conditions are met viz. (i) there is a significant difference between the values of the dipole moments (and polarizabilities) in the first-excited single state, and (ii) push/pull groups should be present in the conjugation system.

The structure of the dye determines whether the conjugative effect occurs, and the intramolecular chemical environment can easily change the orientation of the electron migration in the conjugated pair of o-arylazonaphthols. Since the electronic effect of the acetyl substituent, (Fig. 4), is weaker than that of benzoyl it is unclear as to whether substituents in the diazo component contribute to the conjugate system of *o*-arylazonaphthols. It is clear that the opposite direction of polarizati shortens the length of the conjugation. A previo investigation [6] has shown that in fully co jugated systems (D–π–A) the degree of char separation on excitation is estimated to $30\sim40\%$, and when the conjugation was int rupted by inserting a saturated spacer in the mi dle of the bridge (D–π–A molecules), the chan of the direct charge separation induced in t band maximum was decreased to $7\sim14\%$.

The concept of conjugation length plays important role in theories of conductivity. T data of conductivity in Table 2 also shows th except for the strength of intramolecular a intermolecular conjugation, the length of the co jugation of azo dye molecules or the size of t conjugated π system, plays an important role the polarizability of π electrons on the macr scopic conductivity of chromium or cobalt co plexes of otho-hydroxyazo dyes.

The metal–ligand bond may be one of a wi variety of types, depending on the nature of t ligand and of the metal ion leading to a lar number of structural possibilities, but it is certa that the conjugated π systems include the atom orbitals of the metal ion. The character of t associated effect of the oxygen atoms changes wi the terminal group. So, in Dye-1, the polarizati of the strong terminal electro-acceptor (EA), t NO_2, is in the same direction as that of the O-grou which donates electrons to the π-electron system. the strong conjugation between the donor and the acceptor residues increases the resonance energy in the molecules, and leads to a higher conductivity. Therefore, Dye-1 and Dye-2 have larger delocalised π bonds, and so have better conduction then Dye-3.

4. Conclusions

The conductivities of 23 H/K acid azo dyes and three metallised azo dyes were measured at 25°C and 60°C, respectively. The data show that the solid conductivities of the dyes are determined and controlled by the conjugative effect. It is concluded that the conductivity properties of organic materials can be improved by optimizing the substitution positions of pertinent electron donor and acceptor substituents.

Acknowledgements

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