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Color tuning donor–acceptor-type azobenzene dyes by controlling the molecular geometry of the donor moiety

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ABSTRACT

Two series of donor–acceptor (D–A)-type azobenzene dyes with a tertiary amine as the donor were synthesized, and their photophysical and thermal properties were investigated. Although tertiary amines with the same Hammett constant were used, the properties of the molecules varied considerably depending on the molecular geometry of the tertiary amine. We found that the electron-donating properties could be controlled by the molecular geometry of the donor, as the geometry strongly affected the orientation of the n orbital of the donor relative to the p orbitals of the π-conjugated system of the phenyl ring. When the n orbital was fixed parallel to the p orbitals, the donor exhibited strong electron-donating properties. These results suggest that the molecular geometry should be considered in addition to the primary molecular structure for the design of highly functional materials.

1. Introduction

Organic dyes have attracted considerable attention, not only as conventional dyestuffs, but also as promising photofunctional materials for optical devices, photovoltaic cells, and biosensors [1]. Azobenzenes are one of the most fundamental and useful organic dyes owing to their availability and their color tunability based on facile modulation of the electronic structure [2]. Azobenzenes are also well-known photochromic molecules, which undergo reversible isomerization between *trans* and *cis* isomers by photoirradiation; thus, such compounds have been used in photoresponsive material systems as phototrigger molecules [3]. Recently, enormous interest has been paid to donor–acceptor (D–A)-type azobenzene derivatives, which have both electron-donating and electron-accepting groups on the π-conjugated system of the azo chromophore (Fig. 1). D–A-type azobenzenes show a π–π* absorption band in the visible light region and their absorption maximum, namely the color can be controlled by the strength of the D–A pair.

Owing to the intriguing photophysical properties of D–A azobenzene molecules, extensive studies have been conducted to develop new D–A azobenzene derivatives for practical applications, such as dyes and pigments, as well as photoresponsive materials. As a result, various D–A azobenzene derivatives, *e.g.*, liquid-crystalline azobenzenes, have been discovered with fascinating optical-switching properties that allow fast responses and real-time holography to be achieved through phase transitions [3–5]. To employ such D–A azobenzenes practically, it is of great importance to gain a deeper understanding of the relationship between molecular structure and color, *e.g.*, absorption wavelength, as well as thermal properties. In the application of photoresponsive materials, the absorption properties determine the wavelength of actinic light; thus, understanding the molecular structure–absorption wavelength relationship is pivotal for realizing effective molecular design.

In general, the absorption wavelength of D–A azobenzenes is determined by the strength of the electron-donating and of electron-accepting groups, which can be discussed quantitatively using Hammett substituent constants (σ) [6]. In this study, we synthesized new D–A azobenzene derivatives with tertiary amines as the donor and various electron acceptors, and investigated the effect of molecular geometry on the absorption spectra and thermal stabilities. We found that not only the σ values of the electron-donating and electron-accepting moieties, but also the molecular geometry made a significant contribution towards controlling the color, *i.e.*, absorption wavelength, of D–A azobenzene dyes. Thus, in two series of D–A azobenzenes carrying electron-donating moieties with the same σ values, a significant color change (~60 nm shift in absorption) was induced by stereoelectronic effects caused by the molecular geometry. Herein, we report that the color and thermal stability of D–A azobenzenes can be controlled by the molecular geometry of the donor as well as the electron-donating and electron-withdrawing properties of the D–A pair. These results offer a new guideline for the rational molecular design of dyes and pigments

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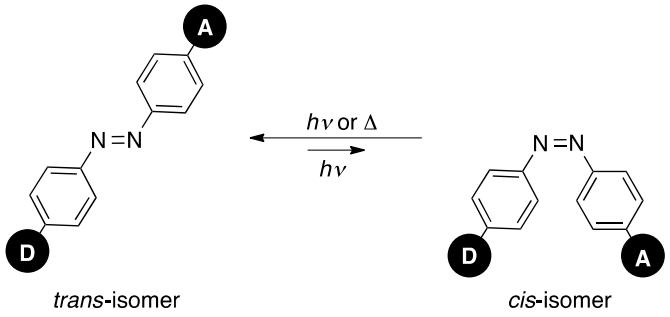

Fig. 1. Donor–acceptor azobenzene derivatives.

with desired colors.

2. Experimental

2.1. General

All solvents and reagents were reagent grade and commercially available, and were used without further purification unless otherwise stated. Column chromatography was carried out on silica gel using CH_2Cl_2 as an eluent (Wakosil® C-200, 64–210 μm) and TLC analysis was performed on silica-gel TLC plates (Merck, Silica-gel 60F $_{254}$). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ at 400, 100, and 372 MHz, respectively, using a JEOL ECS-400 spectrometer. Chemical shifts are reported in parts per million (ppm), using the residual proton in the NMR solvent as an internal reference for ^{1}H and ^{13}C NMR or C_6F_6 (δ −163 ppm) as an internal standard for ^{19}F NMR. IR spectra were obtained using the KBr disk method with an FT/IR-610 spectrometer (JASCO), and all spectra are reported in wavenumbers (cm^{-1}). HRMS were recorded with a JEOL JMS-700 spectrometer. Elemental analyses for C, H, and N were conducted with a MICRO CORDER JM10 analyzer (J-SCIENCE). UV-Vis absorption spectra of dilute solution samples (~10^{-5} mol L^{-1} in AcOEt) were recorded using a JASCO V-500 absorption spectrophotometer. Melting points were recorded as the onset of an exothermic peak during the phase transition from solid to liquid using differential scanning calorimetry (DSC, SII X-DSC7000). The phase transition was observed using an Olympus BX51 microscope equipped with an Instec HCS302 hot-stage and an mK1000 controller. The thermal stabilities were assessed by thermogravimetric analysis (TGA)-differential thermal analysis (DTA) using a DTG-60AH analyzer (Shimadzu) at a heating rate of 5.0 °C·min^{-1}.

2.2. Typical procedure for preparing trans-1-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizin-9-yl)diazenyl]-4-nitrobenzene (3a) from 4-nitroaniline (1a)

4-Nitroaniline (**1a**, 0.069 g, 0.50 mmol), 42% aqueous tetrafluoroboric acid (0.26 g, 1.3 mmol), and H_2O (4.0 mL) were placed in a round-bottomed flask (100 mL) equipped with a magnetic stirring bar, and the mixture was cooled to 0 °C. Then, a solution of sodium nitrite (0.045 g, 0.65 mmol) in H_2O (4.0 mL) was added dropwise to the mixture. After stirring at 0 °C for 0.5 h, a solution of 2,3,6,7-tetrahydro-*1H,5H*-benzo[*ij*]quinolizine (**2**, 0.11 g, 0.64 mmol) in acetic acid (2.0 mL) was slowly added at 0 °C, and a red precipitate began to form. The resultant suspension was stirred at 0 °C for 0.5 h, followed by the addition of sodium acetate (0.082 g, 1.1 mmol). After further stirring at room temperature for 2 h, the precipitate was collected, washed with H_2O, and dried under high vacuum at 70 °C for 1 h. Purification by recrystallization from methanol afforded *trans*-**3a** in 48% yield (0.077 g, 0.24 mmol) as a red solid.

2.2.1. trans-1-[2-(2,3,6,7-Tetrahydro-1H,5H-benzo[ij]quinolizin-9-yl)diazenyl]-4-nitrobenzene (3a) prepared from 4-nitroaniline (1a)

Yield: 48%; mp: 216 °C (Dec.); ^{1}H NMR ($CDCl_3$): δ 8.32 (2H, d, J = 9.1 Hz, *ortho-H* from NO_2 group), 7.85 (2H, d, J = 9.1 Hz, *meta-H* from NO_2 group), 7.46 (2H, s, Ar-*H* in julolidine), 3.39 (4H, t, J = 5.0 Hz, C*H*$_2$-N in julolidine), 2.77 (4H, t, J = 6.3 Hz, C*H*$_2$-Ar in julolidine), 1.91 (4H, dd, J = 6.3, 5.0 Hz, CH_2-C*H*$_2$-CH_2-); ^{13}C NMR ($CDCl_3$): δ 157.1, 147.1, 146.8, 142.8, 124.7, 123.9, 122.2, 121.1, 50.2, 27.7, 21.3; IR (KBr): ν 2939, 2848, 1603, 1511, 1331, 1307, 1277, 1124, 1101 cm^{-1}; HRMS (FAB): m/z [M + H]$^+$ calcd for $C_{18}H_{19}N_4O_2$, 323.1508; found, 323.1503.

2.2.2. trans-1-Cyano-4-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizin-9-yl)diazenyl]benzene (3b) prepared from 4-cyanoaniline (1b)

Yield: 83%; mp: 190 °C (Dec.); ^{1}H NMR ($CDCl_3$): δ 8.02 (1H, brs, Ar-*H*), 7.78 (2H, d, J = 8.6 Hz, *meta-H* from N=N group), 7.69 (2H, d, J = 8.6 Hz, *ortho-H* from N=N group), 7.17 (1H, brs, Ar-*H* in julolidine), 3.71 (4H, brs, C*H*$_2$-N in julolidine), 2.99 (4H, brs, C*H*$_2$-Ar in julolidine), 2.77 (4H, brs, C*H*$_2$-Ar in julolidine), 2.10 (4H, brs, CH_2-C*H*$_2$-CH_2-); IR (KBr): ν 3249, 3053, 2950, 2854, 2220, 1602, 1531, 1476, 1348, 1264, 1212, 1082 cm^{-1}; HRMS (FAB): m/z [M + H]$^+$ calcd for $C_{19}H_{19}N_4$, 303.1610; found, 303.1609.

2.2.3. trans-1-(Trifluoromethyl)-4-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizin-9-yl)diazenyl]benzene (3c) prepared from 4-(trifluoromethyl)aniline (1c)

Yield: 73%; mp: 133.1–134.8 °C; ^{1}H NMR ($CDCl_3$): δ 7.86 (2H, d, J = 8.2 Hz, *ortho-H* from CF_3 group), 7.69 (2H, d, J = 8.2 Hz, *meta-H* from CF_3 group), 7.48 (2H, s, Ar-*H* in julolidine), 3.31 (4H, t, J = 5.4 Hz, C*H*$_2$-N in julolidine), 2.82 (4H, t, J = 6.3 Hz, C*H*$_2$-Ar in julolidine), 1.99 (4H, dd, J = 6.3, 5.4 Hz, -CH_2-C*H*$_2$-CH_2-); ^{13}C NMR ($CDCl_3$): δ 155.4, 146.3, 142.5, 129.8 (q, J = 32.4 Hz), 126.0 (q, J = 3.9 Hz), 124.2 (q, J = 271.6 Hz), 123.2, 122.0, 120.9, 50.1, 27.7, 21.4; ^{19}F NMR ($CDCl_3$): δ −63.49 (s, C*F*$_3$); IR (KBr): ν 2950, 2842, 1604, 1516, 1390, 1308, 1123, 1062, 853 cm^{-1}; HRMS (FAB): m/z [M + H]$^+$ calcd for $C_{19}H_{19}F_3N_3$, 346.1531; found, 346.1528; Anal. Calcd for $C_{19}H_{18}F_3N_3$: C, 66.08; H, 5.25; N, 12.17. Found: C, 65.94; H, 5.11; N, 12.13.

2.2.4. Methyl trans-1-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizin-9-yl)diazenyl]-4-benzoate (3d) prepared from 4-(methoxycarbonyl)aniline (1d)

Yield: 28%; mp: 162.3–163.1 °C; ^{1}H NMR ($CDCl_3$): δ 8.11 (2H, d, J = 8.6 Hz, *ortho-H* from CO_2CH_3 group), 7.81 (2H, d, J = 8.6 Hz, *meta-H* from CO_2CH_3 group), 7.49 (2H, brs, Ar-*H* in julolidine), 3.93 (3H, s, C*H*$_3$), 3.34 (4H, t, J = 5.9 Hz, C*H*$_2$-N in julolidine), 2.82 (4H, t, J = 6.3 Hz, C*H*$_2$-Ar in julolidine), 2.00 (4H, dd, J = 6.3, 5.9 Hz, -CH_2-C*H*$_2$-CH_2-); ^{13}C NMR ($CDCl_3$): δ 166.9, 156.1, 146.4, 142.7, 130.5, 129.5, 123.3, 121.7, 120.9, 52.1, 50.1, 27.7, 21.4; IR (KBr): ν 2935, 2833, 1714, 1599, 1379, 1306, 1267, 1119 cm^{-1}; HRMS (FAB): m/z [M + H]$^+$ calcd for $C_{20}H_{22}N_3O_2$, 336.1712; found, 336.1716.

2.2.5. trans-1-[2-(2,3,6,7-Tetrahydro-1H,5H-benzo[ij]quinolizin-9-yl)diazenyl]-3,5-dinitrobenzene (3e) prepared from 3,5-dinitroaniline (1e)

Yield: 16%; mp: 248 °C (Dec.); ^{1}H NMR ($CDCl_3$): δ 8.91 (2H, brs, *ortho-H* from N=N group), 8.89 (1H, dd, J = 2.0, 2.0 Hz, *para-H* from N=N group), 7.56 (2H, brs, Ar-*H* in julolidine), 3.40 (4H, t, J = 5.4 Hz, C*H*$_2$-N in julolidine), 2.84 (4H, t, J = 6.3 Hz, C*H*$_2$-Ar in julolidine), 2.03 (4H, dd, J = 6.3, 5.4 Hz, -CH_2-C*H*$_2$-CH_2-); ^{13}C NMR ($CDCl_3$): δ 155.1, 148.9, 147.8, 142.1, 124.3, 121.5, 121.1, 116.4, 50.3, 27.7, 21.2; IR (KBr): ν 3101, 2935, 2837, 1603, 1531, 1356, 1306, 1271, 1201, 1132 cm^{-1}; HRMS (FAB): m/z [M]$^+$ calcd for $C_{18}H_{17}N_5O_4$, 367.1281; found, 367.1285; Anal. Calcd for $C_{18}H_{17}N_5O_4$: C, 58.85; H, 4.66; N, 19.06. Found: C, 58.64; H, 4.52; N, 19.49.