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Pnicogen, halogen and hydrogen bonds in (*E*)-1-(2,2-dichloro-1-(2-nitrophenyl)vinyl)-2-(*para*-substituted phenyl)-diazenes

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ABSTRACT

Schiff base condensation of 2-nitrobenzaldehyde with (*para*-substituted phenyl)hydrazine in the presence of CH_3COONa in EtOH at 80 °C produces (*E*)-1-(*para*-substituted phenyl)-2-(2-nitrobenzylidene)hydrazines [$-OCH_3$ (**1**), $-CH_3$ (**2**), $-H$ (**3**), $-Br$ (**4**), $-Cl$ (**5**), $-F$ (**6**)]. CuCl catalyzed olefination of **1**$-$**6** with CCl_4 in the presence of tetramethylethylenediamine (TMEDA) in DMSO leads to (*E*)-1-(2,2-dichloro-1-(2-nitrophenyl)vinyl)-2-(*para*-substituted phenyl)-diazenes [$-OCH_3$ (**7**), $-CH_3$ (**8**), $-H$ (**9**), $-Br$ (**10**), $-Cl$ (**11**), $-F$ (**12**)], respectively. **1**–**12** were characterized by ^1H and ^{13}C NMR spectroscopies, ESI-MS, elemental and X-ray diffraction (for **8**, **9** and **12**) analysis. The single crystal X-ray analysis of **8**, **9** and **12** evidence the intramolecular N···Cl pnicogen bonds which is significantly strengthened in view of the planarity of the four atoms involved in the 1,4-membered synthon. The intermolecular halogen and hydrogen bonds also contribute to stabilize the crystal structures of **8**, **9** and **12**. In DMSO solution **1**–**12** exist in the *E*-isomeric form, which stabilized by inter- and intramolecular noncovalent interactions. Solvatochromic behavior on UV–vis absorption spectra of azo dyes **7**–**12** were studied in CH_2Cl_2, DMF and MeOH, which λ_{max} is dependent on the attached substituents at *para*-position of aromatic moiety.

1. Introduction

Noncovalent interactions are known to be responsible for the conformation of organic and inorganic molecules [1,2]. Due to the fundamental importance of "σ-hole" interactions, such as halogen bonding, chalcogen bonding, pnicogen bonding, and tetrel bonding, in crystal packing and supramolecular assembly, these specific noncovalent interactions have become a hot topic in synthesis, catalysis and design of materials [3–8]. Similarly, to the hydrogen bonds [9–11], the "σ-hole" bonds can also be classified into several fundamental types: negative charged assisted, positive charged assisted, conventional (or "neutral") and resonance assisted halogen, chalcogen, pnicogen or tetrel bonds. The strength of these directional interactions, and then their ability to organize/control the formation of supramolecular assemblies, depending on their intra- and intermolecular versions. In comparison to intermolecular version, the examples on intramolecular noncovalent interactions are limited, which they can also play a crucial role in synthesis, catalysis, crystal engineering, drug design and delivery, etc. [7,8,11–21]. In the present work, we report the role of intramolecular N···Cl pnicogen bond as well as intermolecular halogen and hydrogen bonds in the synthesis and design of diazene dyes.

In recent years, copper-catalyzed transformation of hydrazones into halogenated diazenes (catalytic olefination) have received increasing research interest [22,23], due to the cooperative actions of conjugated N=N and C=C bonds leading to chromophoric properties [24] (Scheme 1). Intramolecular N···Cl pnicogen bond can also contribute to N=N and C=C conjugation in diazene dyes and absorb some wavelength visible light photon energy. We therefore decided to systematically investigate the structure-property relationship of a series of (*E*)-1-(2,2-dichloro-1-(2-nitrophenyl)vinyl)-2-(*para*-substituted phenyl)-

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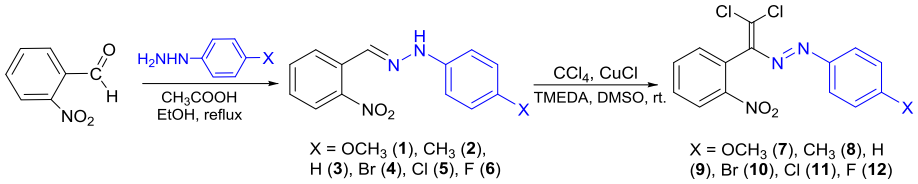

Scheme 1. Synthesis of **1–12**.

diazenes in terms of their intramolecular pnicogen bond as well as intermolecular halogen bond strength (Scheme 1). The *para*-substituents on the aromatic moiety range from typical electron donating groups ($-OCH_3$ and $-CH_3$) to typical electron withdrawing ones ($-Br$, $-Cl$ and $-F$).

2. Experimental

2.1. Materials and instrumentation

All the chemicals were obtained from commercial sources (Aldrich) and used as received. Infrared spectra (4000–400 cm^{-1}) were recorded on a Vertex 70 (Bruker) instrument in KBr pellets. Carbon, hydrogen, and nitrogen elemental analyses were done using a "2400 CHN Elemental Analyzer" (Perkin Elmer). The ^1H and ^{13}C NMR spectra were recorded on Bruker Advance II+ 300.13 (75.468 carbon-13) MHz (UltraShield™ Magnet) spectrometer at ambient temperature. The chemical shifts are reported in ppm using tetramethylsilane as the internal reference. Electrospray mass spectra (ESI-MS) were run with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from *m/z* 0 to 1100 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80–105 V). The UV–vis absorption spectra in the 200–700 nm regions were recorded with a scan rate of 240 nm·min^{-1} by using a Lambda 35 UV–vis spectrophotometer (Perkin-Elmer) in 1.00 cm quartz cells at room temperature, with a concentration of **7** − **12** of 1.00·10^{-6} mol L^{-1} in CH_2Cl_2, DMF or MeOH.

2.2. Synthesis of 1–6

Schiff bases **1–6** were synthesized according to the reported method [23,24]. A mixture of 2-nitrobenzaldehyde (10 mmol), CH_3COONa (0.82 g), ethanol (50 mL) and corresponding (*para*-substituted phenyl) hydrazine (10.2 mmol) was refluxed at 80 °C with stirring for 2 h. The reaction mixture was cooled to room temperature and water (50 mL) was added to give a precipitate of crude product, which filtered off, washed with diluted ethanol (1:1 with water) and dried in vacuo of rotary evaporator.

1: pink solid (91%); mp 180–184 °C. Anal. Calcd for $C_{14}H_{13}N_3O_3$ (*M* = 271.28): C, 61.99; H, 4.83; N, 15.49; found: C, 61.93; H, 4.81; N, 15.43%. ^1H NMR (300 MHz, DMSO-d_6): δ 10.76 (s, 1H, NH), 8.19 (s, 1H, CH), 8.15 (d, *J* = 7.72 Hz, 1H, arom), 7.95 (d, *J* = 8.10 Hz, 1H, arom), 7.69 (t, *J* = 7.36 Hz, 1H, arom), 7.46 (t, *J* = 7.54 Hz, 1H, arom), 7.04 (d, *J* = 9.04 Hz, 2H, arom). 6.88 (d, *J* = 8.85 Hz, 2H, arom), 3.70 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 149.26, 146.89, 138.86, 133.52, 129.64, 128.14, 127.18, 125.00, 115.17, 113.93, 55.73. ESI-MS: *m/z*: 272.22 $[M+H]^+$.

2: red solid (90%); mp 140–142 °C. Anal. Calcd for $C_{14}H_{13}N_3O_2$ (*M* = 255.28): C, 65.87; H, 5.13; N, 16.46; found: C, 65.83; H, 5.08; N, 16.40%. ^1H NMR (300 MHz, DMSO-d_6): δ 10.82 (s, 1H, NH), 8.22 (s, 1H, CH), 8.16 (d, *J* = 7.91 Hz, 1H, arom), 7.96 (d, *J* = 8.10 Hz, 1H, arom), 7.70 (t, *J* = 7.54 Hz, 1H, arom), 7.47 (t, *J* = 7.35 Hz, 1H, arom), 7.07 (d, *J* = 8.48 Hz, 2H, arom), 7.01 (d, *J* = 8.29 Hz, 2H, arom), 2.50 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 162.23, 147.03, 142.69, 133.57, 130.28, 130.12, 128.37, 127.28, 125.01, 112.88, 20.74. ESI-MS: *m/z*: 256.26 $[M+H]^+$.

3: red solid (92%); mp 150 °C. Anal. Calcd for $C_{13}H_{11}N_3O_2$ (*M* = 241.25): C, 64.72; H, 6.81; N, 17.03; found: C, 64.66; H, 6.77; N, 17.00%. ^1H NMR (300 MHz, DMSO-d_6): δ 10.89 (s, 1H, NH), 8.26 (s, 1H, CH), 8.16 (d, *J* = 8.10 Hz, 1H, arom), 7.96 (d, *J* = 8.29 Hz, 1H, arom), 7.70 (t, *J* = 7.54 Hz, 1H, arom), 7.48 (t, *J* = 7.54 Hz, 1H, arom), 7.26 (t, *J* = 7.35 Hz, 2H, arom), 7.12 (d, *J* = 7.91 Hz, 2H, arom), 6.82 (t, *J* = 6.97 Hz, 1H, arom).^{13}C NMR (75 MHz, DMSO-d_6): δ 147.19, 145.00, 133.54, 131.10, 129.68, 128.57, 127.42, 124.96, 120.25, 112.89. ESI-MS: *m/z*: 242.18 $[M+H]^+$.

4: red solid (95%); mp 170–174 °C. Anal. Calcd for $C_{13}H_{10}BrN_3O_2$ (*M* = 320.15): C, 48.77; H, 3.15; N, 13.13; found: C, 48.71; H, 3.07; N, 13.08%. ^1H NMR (300 MHz, DMSO-d_6): δ 11.01 (s, 1H, NH), 8.26 (s, 1H, CH), 8.16 (d, *J* = 7.91 Hz, 1H, arom), 7.98 (d, *J* = 8.10 Hz, 1H, arom), 7.72 (t, *J* = 7.54 Hz, 1H, arom), 7.52 (t, *J* = 8.10 Hz, 1H, arom), 7.41 (d, *J* = 8.85 Hz, 2H, arom), 7.06 (d, *J* = 8.85 Hz, 2H, arom). ^{13}C NMR (75 MHz, DMSO-d_6): δ 147.32, 144.33, 133.66, 132.35, 130.09, 128.95, 127.56, 125.04, 123.52, 114.78, 111.17. ESI-MS: *m/z*: 321.12 $[M+H]^+$.

5: pink solid (80%); mp 183 °C. Anal. Calcd for $C_{13}H_{10}ClN_3O_2$ (*M* = 275.69): C, 56.64; H, 3.66; N, 15.24; found: C, 56.59; H, 3.58; N, 15.20%. ^1H NMR (300 MHz, DMSO-d_6): δ 11.01 (s, 1H, NH), 8.26 (s, 1H, CH), 8.16 (d, *J* = 7.72 Hz, 1H, arom), 7.98 (d, *J* = 8.29 Hz, 1H, arom), 7.72 (t, *J* = 7.35 Hz, 1H, arom), 7.52 (t, *J* = 7.35 Hz, 1H, arom), 7.29 (d, *J* = 8.67 Hz, 2H, arom), 7.10 (d, *J* = 8.67 Hz, 2H, arom). ^{13}C NMR (75 MHz, DMSO-d_6): δ 147.32, 143.95, 133.65, 132.12, 130.10, 128.92, 127.56, 125.02, 114.29. ESI-MS: *m/z*: 276.56 $[M+H]^+$.

6: red solid (93%); mp 150 °C. Anal. Calcd for $C_{13}H_{10}FN_3O_2$ (*M* = 259.24): C, 60.23; H, 3.89; N, 16.21; found: C, 60.19; H, 3.81; N, 16.15%. ^1H NMR (300 MHz, DMSO-d_6): δ 10.90 (s, 1H, NH), 8.23 (s, 1H, CH), 8.15 (d, *J* = 7.91 Hz, 1H, arom), 7.97 (d, *J* = 8.10 Hz, 1H, arom), 7.71 (t, *J* = 7.54 Hz, 1H, arom), 7.49 (t, *J* = 7.91 Hz, 3H, arom), 7.10 (d, *J* = 6.59 Hz, 4H, arom). ^{13}C NMR (75 MHz, DMSO-d_6): δ 158.46, 155.34, 147.17, 141.65, 133.57, 131.15, 128.62, 127.44, 124.99, 116.40, 116.10, 113.93. ESI-MS: *m/z*: 260.20 $[M+H]^+$.

2.3. Synthesis of 7–12

Diazene dyes **7–12** were synthesized according to the reported method [23,24]. A 20 mL screw neck vial was charged with DMSO (10 mL), **1**, **2**, **3**, **4**, **5** or **6** (1 mmol), tetramethylethylenediamine (TMEDA) (295 mg, 2.5 mmol), CuCl (2 mg, 0.02 mmol) and CCl_4 (20 mmol, 10 equiv). After 1–3 h (until TLC analysis showed complete consumption of corresponding Schiff base) reaction mixture was poured into ~0.01 M solution of HCl (100 mL, ~pH = 2–3), and extracted with dichloromethane (3 × 20 mL). The combined organic phase was washed with water (3 × 50 mL), brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo of the rotary evaporator. The residue was purified by column chromatography on silica gel using appropriate mixtures of hexane and dichloromethane (3/1-1/1), and corresponding diazene dyes **7–12** were obtained.

7: yellow solid (50%); mp 93–95 °C. Anal. Calcd for $C_{15}H_{11}Cl_2N_3O_3$ (*M* = 352.17): C, 51.16; H, 3.15; N, 11.93; found: C, 51.09; H, 3.11; N, 11.90%. ^1H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, *J* = 9.04 Hz, 1H, arom), 7.71 (t, *J* = 7.72 Hz 1H, arom), 7.69 (d, *J* = 8.85 Hz, 2H, arom), 7.63 (t, *J* = 9.04 Hz, 1H, arom), 7.34 (d, *J* = 7.72 Hz, 1H, arom), 6.92 (d, *J* = 8.85 Hz, 2H, arom), 3.86 (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$):