



Cooperative intramolecular hydrogen bonding induced azo-hydrazone tautomerism of azopyrrole: Crystallographic and spectroscopic studies



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ABSTRACT

The azo-hydrazone tautomerism of three azopyrrole compounds, which were synthesized by the reactions of 2-acylbenzenediazonium salt with pyrrole and *meso*-diethyl-2,2'-dipyrrromethane, have been studied. In the solid state, 2-(2-acylphenyl)diazopyrrole adopted an azo tautomeric form, whereas 5,5'-bis(2-acylphenyl)diazo-dipyrrromethane and 5-(2-acylphenyl)diazo-dipyrrromethane crystallized in the hydrazone form. In polar solution, all of the compounds mainly adopt an azo form. In an apolar solution, however, 5,5'-bis(2-acylphenyl)diazo-dipyrrromethane and 5-(2-acylphenyl)diazo-dipyrrromethane mainly adopt hydrazone form. It is cooperative intramolecular hydrogen bonds that influence the azopyrrole tautomerisation from the azo to the hydrazone form.

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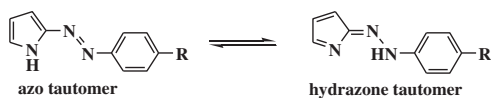
1. Introduction

Azo compounds are the most widely used dyes in various fields such as dyeing of textiles, non-linear optics, photoswitches and optical data storage [1–6]. Heterocyclic azo compounds have shown excellent color and chromophoric strength, compared to azo dyes derived from anilines [7]. Over the past decade, azopyrrole dyes have been attracting much attention because of their rapid increasing role in the design of advanced materials and devices. For example, Dolphin and coworker found a series of symmetrical 2,5-bisazopyrroles and BF₂-azopyrrole complexes with near infrared absorption [8]. Mikroyannidis and coworkers have designed some bulk heterojunction organic solar cells and photovoltaic devices based on azopyrrole compounds [9–11]. Raposo and coworkers have synthesized many azopyrrole based dyes which can act as nonlinear optical materials and photoswitches [12–15]. Many pyrrole azocrown ethers which were designed and synthesized by Wangner-Wysiecka and Biernat are excellent lead(II) chemosensors [16–18]. In previous work, we have demonstrated that 5, 5'-bisdiazo-dipyrrromethane compounds and their dimers are useful building blocks in crystal engineering [19–21].

The azo-hydrazone tautomerism is the characteristic property of azo compounds [22]. Azo-hydrazone tautomerism is quite interesting because each tautomer exhibits distinct properties. The process is also susceptible to environmental conditions such as temperature, solvent, pH and substitution pattern [23]. Azopyrrole is proposed to exhibit azo-hydrazone tautomerization as shown in Scheme 1. Although calculations have proved that the azo tautomer is more stable than hydrazone tautomer [24], the UV–Vis spectra studies have witnessed the existence of the azo-hydrazone tautomeric equilibria in solution [8]. X-ray crystallography is a useful method to study the azo-hydrazone tautomerism from which exact bond distances can be obtained. Previous studies revealed that hydrazone tautomer was the dominant in the crystal structures of boron-azopyrrole complex [8] and Ni(II) complexes [25], whereas azo tautomer dominated in the crystal structures of free azopyrrole ligands [19,20]. Previous studies revealed that intramolecular hydrogen bonds may promote the hydrazone-azo tautomerism [26,27]. We speculate that attaching a hydrogen bond acceptor group in an *ortho* position of benzene may cause the transformation of azopyrrole from azo form to hydrazone form. Bearing this in mind three new azopyrrole compounds (**1–3**) were synthesized and their azo-hydrazone tautomerism has been studied by X-ray diffraction, ¹H NMR and UV–Vis spectroscopy. It was found that cooperative intramolecular hydrogen bonds help the azopyrrole to transfer from azo tautomer to hydrazone form.

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Scheme 1. Azo-hydrazone tautomerism of azopyrrole.

2. Experimental

2.1. Materials and apparatuses

^1H NMR spectra were recorded in CDCl_3 and $\text{DMSO}-d_6$, with TMS as internal standard, on a BRUKER AV-400 MHz spectrometer. Mass spectra were obtained on an AEIMS-50/PS 30 mass spectrometer. Analyses of C, H and N were determined on a Perkin-Elmer 240 elemental analyzer. The IR spectra were recorded on a SHIMADZU IR-480 spectrophotometer in KBr pellets. UV–Vis spectra were recorded on SHIMADZU UV-2550 spectrometer. Melting points (m.p.) were recorded on an electro-thermal digital melting point apparatus and uncorrected. *Meso*-diethyl-2,2'-dipyrrromethane was prepared according to literature procedures [28]. Other reagents were commercially available and used without further purification.

2.2. Preparation of compounds 1–3

2.2.1. 2-(2-acylphenyl)diazopyrrole (Compound 1)

A suspension of the 2-aminoacetophenone (0.54 g, 4.0 mmol) in water (5.0 mL) was added concentrated hydrochloric acid (1.6 mL) until the mixture was homogeneous. The solution was cooled and kept at 0–5 °C in an ice bath and diazotized by addition of a solution of sodium nitrite (0.283 g, 4.1 mmol) in water (5.0 mL), stirring for 30 min at 0–5 °C. A solution of pyrrole (0.27 g, 4.0 mmol) and pyridine (4.0 mL) in methanol (25.0 mL) was slowly added a solution of diazonium salt at 0–5 °C. The resulting mixture was stirred for 2 h and then evaporated under vacuum to dryness. CAUTION The authors note that diazonium salts can decompose explosively and extreme caution should be exercised during this work up procedure in case of residual diazonium ion content. The residues were purified with the use of column chromatography, eluting with the mixture of ethyl acetate-petroleum (V:V = 1:5), giving compound 1613 mg, brown powder, yield 72%, m.p. = 115–116 °C. IR (KBr), $\nu_{\text{max}}/\text{cm}^{-1}$: 3310, 3111, 1679, 1590, 1535, 1356, 1281, 1124, 1035, 871, 760; ^1H NMR (400 MHz, CDCl_3): δ 2.58 (s, 3H, $-\text{CH}_3$), 6.42–6.44 (m, 1H, PyCH), 7.02–7.03 (m, 1H, PyCH), 7.05–7.07 (m, 1H, PyCH), 7.37–7.41 (m, 1H, ArCH), 7.50–7.54 (m, 1H, ArCH), 7.56–7.58 (m, 1H, ArCH), 7.71–7.73 (m, 1H, ArCH), 9.29 (s, 1H, NH); ^{13}C NMR (100 MHz, CDCl_3): δ 31.6, 111.7, 116.0, 117.4, 122.8, 127.2128.1, 130.7, 136.2, 145.5, 149.5, 202.4; ESI-MS: 214($\text{M}+1^+$). Elemental analysis: $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}$: Calcd: C, 67.59; H, 5.20; N, 19.71. Found: C, 67.77; H, 5.43; N, 19.81.

2.2.2. 5,5'-bis(2-acylphenyl)diazo-dipyrrromethane (compound 2) and 5-(2-acylphenyl)diazo-dipyrrromethane (compound 3)

Compounds 2 and 3 were synthesized as for compound 1 except that *meso*-diethyl-2,2'-dipyrrromethane (0.4 g for compound 2 and 0.8 g for compound 3) was used in place of pyrrole.

Compound 2 632 mg, orange powder, yield 64%, m.p. = 133–134 °C. IR (KBr), $\nu_{\text{max}}/\text{cm}^{-1}$: 3364, 3338, 3174, 2964, 2933, 1642, 1570, 1512, 1431, 1360, 1269, 1255, 1228, 1202, 1158, 933; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 0.74 (t, 6H, $J = 7.2$ Hz, $-\text{CH}_3$), 2.25 (q, 4H, $J = 7.2$ Hz, $-\text{CH}_2-$), 2.45 (s, 6H, $-\text{CH}_3$), 6.29 (s, 2H, PyCH), 6.84 (s, 2H, PyCH), 7.41–7.44 (m, 2H, ArCH), 7.51–7.53 (m, 2H, ArCH), 7.57–7.60 (m, 4H, ArCH), 11.60 (s, 2H, PyNH); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 8.3, 26.9, 32.3, 44.1, 110.9, 118.5, 128.0, 128.4, 131.5, 136.2, 144.0, 146., 151.0, 202.0; ESI-MS: 495($\text{M}+1^+$). Elemental analysis:

$\text{C}_{29}\text{H}_{34}\text{N}_6\text{O}_2$: Calcd: C, 70.42; H, 6.11; N, 16.99. Found: C, 70.35; H, 6.12; N, 17.04.

Compound 3 710 mg, orange powder, yield 51%, m.p. = 99–100 °C. IR (KBr), $\nu_{\text{max}}/\text{cm}^{-1}$: 3302, 3187, 2996, 2915, 1664, 1651, 1590, 1563, 1503, 1458, 1430, 1400, 1349, 1334, 103, 998, 931; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 0.67 (t, 6H, $J = 7.2$ Hz, $-\text{CH}_3$), 2.04–2.20 (m, 4H, $-\text{CH}_2-$), 2.45 (s, 3H, $-\text{CH}_3$), 5.91–5.93 (m, 2H, PyCH), 6.18 (s, 1H, PyCH), 6.63–6.64 (m, 1H, PyCH), 6.80 (s, 2H, PyCH), 7.40–7.43 (m, 1H, ArCH), 7.50–7.52 (m, 1H, ArCH), 7.56–7.60 (m, 2H, ArCH), 10.41 (s, 1H, NH), 11.19 (s, 2H, NH); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 8.3, 27.6, 32.4, 43.5, 105.4, 106.5, 110.6, 116.8, 117.0, 118.3, 128.0, 128.2, 131.5, 134.9, 135.0, 136.3, 146.0, 150.9, 202.1; ESI-MS: 349($\text{M}+1^+$). Elemental analysis: $\text{C}_{21}\text{H}_{24}\text{N}_4\text{O}$: Calcd: C, 72.39; H, 6.94; N, 16.08. Found: C, 72.44; H, 6.80; N, 15.89.

2.3. X-ray crystallography

Single crystals of compound 1 which were suitable for X-ray crystallography studies were grown by slowly evaporating its $\text{CHCl}_3/\text{CH}_3\text{OH}$ (1:1) solution and crystals for compound 2 were grown by slowly evaporating its ethyl acetate/petroleum (1:2) solution. The diffraction data were measured on a BRUKER SMART APEX II CCD diffractometer equipped with a graphite-monochromatic $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) using an ω scan mode. All data were corrected by semi-empirical method using SADABS program. The program SAINT [29] was used for integration of the diffraction profiles. The structure was solved by direct methods using SHELXS program and refined with SHELXL [30]. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2 . The hydrogen atoms were added according to the theoretical models. The crystal data were summarized in Table 1.

3. Results and discussion

3.1. Syntheses and spectral characterizations

Compound 1 was synthesized by the reaction of 2-acylbenzenediazonium salt with pyrrole. Compounds 2 and 3 were synthesized by the reaction of 2-acylbenzenediazonium salt with *meso*-diethyl-2,2'-dipyrrromethane in 2:1 and 1:1

Table 1
Crystal data of compounds 1–3.

Crystals	1	2	3
CCDC No.	953933	953934	953932
Empirical Formula	$\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}$	$\text{C}_{29}\text{H}_{30}\text{N}_6\text{O}_2$	$\text{C}_{21}\text{H}_{24}\text{N}_4\text{O}$
Formula Weight	213.24	494.50	348.44
Temperature (K)	173(2)	173(2)	296(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	Pbca	P-1	P2(1)/c
<i>a</i> (Å)	13.3210(16)	6.9719(4)	20.353(3)
<i>b</i> (Å)	11.6396(14)	12.2842(7)	23.391(4)
<i>c</i> (Å)	14.2645(18)	15.155(10)	8.3511(13)
α (°)	90	95.3560(10)	90
β (°)	90	98.6770(10)	96.104(3)
γ (°)	90	102.2150(10)	90
$V(\text{Å}^3)$	2211.7(5)	1243.47(13)	3953.2(11)
<i>Z</i>	8	2	8
$D_{\text{calc.}}(\text{g}/\text{cm}^3)$	1.281	1.321	1.171
$\mu(\text{mm}^{-1})$	0.085	0.086	0.074
$F(000)$	896	524	1488
Total reflections	10,532	6476	20,069
Unique reflections	1935	4361	6955
R_1/wR_2 [$I > 2\sigma(I)$]	0.0399/0.1024	0.0380/0.0907	0.0435/0.1175
R_1/wR_2 (all data)	0.0454/0.1070	0.0445/0.0954	0.0775/0.1457
GoF on F^2	1.075	1.041	1.014

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