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Novel colorimetric anion sensors based on *N*-acetylglyoxylic amides containing nitrophenyl signalling units

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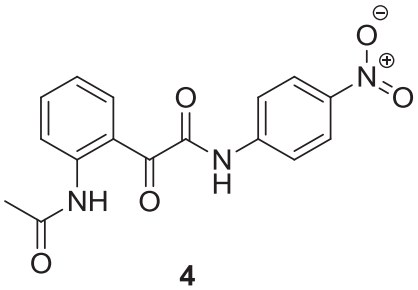
HIGHLIGHTS

- We designed and synthesized *N*-acetylglyoxylic amide-based colorimetric anion sensors.
- Sensors **4** and **5** showed obvious color changes upon addition of CN^- and F^-.
- CN^- and F^- formed hydrogen bonds with the receptors and induced subsequent deprotonation.

GRAPHICAL ABSTRACT

N-acetylglyoxylic amides based anion colorimetric sensors **4** and **5** demonstrated recognition of CN^- and F^- *via* hydrogen bonds and subsequent NH deprotonation which led to the intramolecular charge-transfer resulting in visible color changes.



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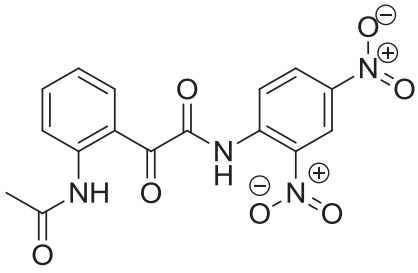

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ABSTRACT

N-acetylglyoxylic amides **4** and **5** bearing pendant 4-nitrophenyl and 2,4-dinitrophenyl groups respectively were synthesized and evaluated as anion sensors. A crystal structure of **4** was obtained by X-ray crystallography. Compounds **4** and **5** behaved as colorimetric sensors for CN^- and F^-, and exhibited naked eye-detectable color changes upon the addition of these anions. The chromogenic properties of **4** and **5** were assessed by UV–Vis and ^1H NMR spectroscopy.

Introduction

Important environmental and human health consequences can result from the presence of excess anions [1–9]. Therefore, increasing attention has been focused upon the development of sensors capable of selectively recognizing and sensing anions. A number of molecular receptors that contain different types of anion-binding groups have been reported [1,10,11]. In particular, NH fragments, such as amide, urea/thiourea [12], pyrrole [13] and imidazolium [14] groups that can act as H-bond donors toward anions have been widely used as anion binding sites for

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recognition and sensing applications. Typically, anions are recognized *via* hydrogen bonding or deprotonation of protons on the receptor-NH group. Isatin has been used as a scaffold for anion recognition. However, only limited number of isatin derivatives have been reported as colorimetric anion sensors and anion receptors [15–18].

Glyoxylamides represent ideal candidates for the potential development of anion sensors due to their NH hydrogen bonding donor group. Nevertheless, the glyoxylamide moiety has not been used previously for the anion recognition. It was therefore of interest to introduce a chromophoric group into *N*-acetylglyoxylic amides derived from *N*-acetylisatin in order to obtain novel colorimetric sensors for anions. In particular, nitrophenyl groups were selected as signalling units because they could be covalently linked to the glyoxylamide NH moiety to enhance both hydrogen-bond donor tendency and acidity of the NH group. Furthermore, the optical properties of the chromogenic nitrophenyl fragment would likely be altered following anion binding, thus providing colorimetric and spectral sensing of the recognition event [19]. It was envisaged that the target anion sensors could be obtained by ring-opening of *N*-acetylisatins with nitrophenyl amines.

Experimental

General

Melting points were obtained using a Mel-Temp melting point apparatus. Infrared spectra were recorded with a Thermo Nicolet 370 FTIR spectrometer. UV–Vis spectra were recorded using a Varian Cary 100 Scan spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX300 (300 MHz) or a Bruker DMX600 (600 MHz) spectrometer and were internally referenced relative to the solvent nuclei. Mass spectrometric analysis was carried out at the Biomedical Mass Spectrometry Facility, UNSW. Microanalyses were performed on a Carlo Erba Elemental Analyzer EA 1108 at the Campbell Microanalytical Laboratory, University of Otago, New Zealand.

Synthesis

Synthesis of 2-(2-acetamidophenyl)-N-(4-nitrophenyl)-2-oxoacetamide **4**

A mixture of *N*-acetylisatin (5.29 mmol, 1.02 g), 4-nitroaniline (5.29 mmol, 0.73 g) and triethylamine (2.5 mL) in dry dichloromethane (50 mL) was stirred at room temperature for 24 h under nitrogen. The resulting precipitate was collected and washed with hydrochloric acid (0.5 M, 75 mL) and subsequently with dichloromethane (75 mL). The title compound was obtained as an off-white solid (1.09 g, 63%). M.p. 232 °C; UV(MeOH): λ_{max} 230 (ε 28,050 cm^{-1} M^{-1}), 321 (22,050); IR (KBr): ν_{max} 3244, 3213, 3051, 3018, 1702, 1671, 1654, 1591, 1542, 1508, 1453, 1410, 1374, 1335, 1296, 1243, 1165, 1041, 997, 853, 763 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6): δ 2.13 (s, 3H, $COCH_3$), 7.24–7.28 (m, 1H, ArH), 7.64–7.69 (m, 1H, ArH), 7.97 (dd, J = 8.0, 1.6 Hz, 1H, ArH), 8.13 (d, J = 9.3 Hz, 2H, ArH), 8.18 (dd, J = 8.4, 1.0 Hz, 1H, ArH), 8.32 (d, J = 9.3 Hz, 2H, ArH), 10.42 (s, 1H, COCONH), 10.48 (s, 1H, NHCO), ^{13}C NMR (75 MHz, acetone-d_6): δ 23.6 ($CO\underline{C}H_3$), 119.4, 120.71, 120.4, 123.0, 124.8, 132.7, 135.0 (7 × ArCH), 119.9, 124.3, 125.3, 143.9 (4 × ArC), 162.0, 168.8, 189.9 (3 × C=O); HRMS (ESI) m/z calculated for $C_{16}H_{14}N_3O_5$ $(M+H)^+$ 328.0855. Found 328.0922; Anal. Calcd. for $C_{16}H_{13}N_3O_5$: C, 58.72; H, 4.00; N, 12.84. Found: C, 58.98; H, 3.95; N, 13.00%.

Synthesis of 2-(2-acetamidophenyl)-N-(2,4-dinitrophenyl)-2-oxoacetamide **5**

This compound was prepared by the same method as compound **4** from *N*-acetylisatin (5.29 mmol, 1.01 g), 2,4-dinitroaniline (5.29 mmol, 0.97 g) and triethylamine (2.5 mL) as an off-white solid (1.11 g, 56%). M.p. 174 °C; UV(MeOH): λ_{max} 228 (ε 50,086 cm^{-1} - M^{-1}), 261 (29,350), 330 (26,650); IR (KBr): ν_{max} 3448, 3336, 3226, 3110, 2770, 2497, 1957, 1739, 1632, 1581, 1520, 1453, 1388, 1324, 1262, 1168, 1127, 1061, 982, 925, 834, 743 cm^{-1}, ^{1}H NMR (300 MHz, acetone-d_6): δ 2.20 (s, 3H, $COCH_3$), 7.23–7.28 (m, 2H, Ar-H), 7.67–7.74 (m, 1H, ArH), 7.82 (dd, J = 8.0, 1.6 Hz, 1H, ArH), 7.94 (s, 1H, COCONH), 8.22 (dd, J = 9.3, 2.7 Hz, 1H, ArH), 8.61(dd, J = 8.5, 0.9 Hz, 1H, ArH), 8.92 (d, J = 2.7 Hz, 1H, ArH), 10.87 (s, 1H, NHCO); ^{13}C NMR (75 MHz, acetone-d_6): δ 24.10 ($CO\underline{C}H_3$), 117.84, 119.37, 120.19, 141.79, 149.5 (5 × ArC), 119.45, 120.27, 122.60, 123.14, 129.24, 133.20, 136.25 (7 × ArCH), 164.16, 168.78, 190.93 (3 × C=O); MS (TOF–ESI) m/z calculated for $C_{16}H_{13}N_4O_7$ $(M+H)^+$ 373.07. Found 373.08; Anal. Calcd. for $C_{16}H_{12}N_4O_7$. H_2O: C = 49.24; H = 3.62; N = 14.35. Found: C, 49.57; H, 3.49; N, 14.26%.

Anion binding studies

Titration experiments of compounds **4** or **5** with anions were performed in acetone with a constant concentration of compounds **4** or **5** through the stepwise addition of a standard solution containing both the respective compound and anions (as tetrabutylammonium salts).

Structure determination

A suitable single crystal of **4**, selected under the polarizing microscope (Leica M165Z), was picked up on a MicroMount (MiTeGen, USA) consisting of a thin polymer tip with a wicking aperture. The X-ray diffraction measurement was carried out on a Bruker KAPPA APEX II CCD diffractometer at 155 K using graphite-monochromated Mo-Kα radiation (λ = 0.710723 Å). The single crystal, mounted on the goniometer using cryo loops for intensity measurements, was coated with paraffin oil and then quickly transferred to the cold stream using an Oxford Cryo stream attachment. Symmetry related absorption corrections using the program SADABS [20] were applied and the data were corrected for Lorentz and polarization effects using Bruker APEX2 software [21]. Structure was solved by direct methods and the full-matrix least-squares refinement was carried out using SHELXL [22]. The non-hydrogen atoms were refined anisotropically. The molecular graphic was generated using Mercury [23].

Results and discussion

Synthesis of N-nitrophenylglyoxylic amides

The starting material *N*-acetylisatin **1** was prepared by treatment of isatin with acetic anhydride at reflux for 4 h as previously described by Silva et al. [24]. *N*-acetylisatin **1** was then reacted with 4-nitroaniline **2** or 2,4-dinitroaniline **3** in the presence of triethylamine at room temperature for 24 h in dry dichloromethane under nitrogen (Scheme 1). The desired products **4** and **5** were obtained in 63% and 56% yields, respectively.

Analysis of the *N*-nitrophenylglyoxylic amides **4** and **5** by ^{1}H NMR spectroscopy revealed the characteristic singlet resonance for glyoxylamide NH protons at 10.42 and 7.94 ppm respectively, which is indicative of successful ring opening of *N*-acetylisatin **1**. The ^{1}H NMR spectra also revealed resonances for aromatic protons with an integration of eight and seven aromatic protons for