Crystal structure of (Z)-2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazineyl) terephthalic acid-dimethylsulfoxide (1/1), C_{18}H_{15}N_{3}O_{6} · C_{2}H_{6}OS

Table 1: Data collection and handling.

| Crystal: | Yellow plate |
| Size: | 0.16 × 0.13 × 0.08 mm |
| Wavelength: | Mo Ka radiation (0.71073 Å) |
| μ: | 0.21 mm⁻¹ |
| Diffractometer, scan mode: | Bruker APEX-II, φ and ω |
| θ_{max}, completeness: | 25.6°, >99% |
| N(hkl)_{measured}, N(hkl)_{unique}, R_{int}: | 24106, 3810, 0.082 |
| Criterion for I_{obs}, N(hkl)_{gt}: | I_{obs} > 2 σ(I_{obs}), 2387 |
| Programs: | Bruker [1], SHELX [2] |

Source of material

(Z)-2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazineyl) terephthalic acid was synthesized by aqueous diazotization of 2-aminoterephthalic acid with subsequent coupling with 3-oxo-N-phenylbutanamide [3, 4].

Diazotization: A 10 mmol portion of 2-aminoterephthalic acid was dissolved in 50 mL of water upon addition of 0.80 g of solid NaOH. The solution was cooled in an ice bath to 0 °C and 10 mmol of NaNO_{2} were added with subsequent addition of 2 mL 33% HCl in portions of 0.4 mL for 1 h, under vigorous stirring. During the reaction, the temperature of the mixture must not exceed +5 °C. The obtained diazonium salt was used for the next stage (see below).

Azocoupling: 10 mmol of NaOH were added to a mixture of 10 mmol of 3-oxo-N-phenylbutanamide in 50 mL ethanol. The solution was cooled in an ice bath, and a suspension of the diazonium salt (prepared according to the procedure described above) was added in two equal portions under rigorous stirring for 1 h. The formed yellow precipitate of (Z)-2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazineyl) terephthalic acid was filtered off, recrystallized from a mixture methanol-dimethylsulfoxide (50:1, v/v) and dried in air. Yield 84% (based on 3-oxo-N-phenylbutanamide), yellow powder, soluble in DMSO, ethanol and dimethylformamide and insoluble in non-polar solvents. The formed yellow precipitate of the title was filtered off, recrystallized from a mixture methanol-dimethylsulfoxide (50:1, v/v) and dried in air. Anal. Calcd. for C_{20}H_{12}N_{2}O_{5}S (M = 447.46): C, 53.69; H, 4.73; N, 9.39. Found: C, 53.58; H, 4.70; N, 9.36%. IR (KBr): 3441 (br. v(OH)), 2980 v(NH), 1666 v(C=O), 1600 v(C=N) cm⁻¹. MS (ESI) (positive ion mode): m/z: 370.10 [M–DMSO + H]⁺
and 79.10 \(\text{[DMSO} + \text{H}]^+\). \(^1\)H NMR (\text{DMSO-d}_6\): \(\delta\) 2.44 (s, 3H, CH\(_3\)), 2.50 (s, 6H, CH\(_2\)) signals of DMSO overlapped with the solvent peak), 7.25—8.40 (8H, Ar—H), 12.85 and 13.11 (s, 2H, OH), 16.00 (s, 1H, NH). \(^{13}\)C\({}^{[1]}\text{H}\) (DMSO-d\(_6\)): \(\delta\) 26.33 (CH\(_3\)), 39.52 (signals of DMSO overlapped with the solvent peak), 115.69 (Ar—H), 116.44 (Ar—H), 120.73 (2Ar—H), 124.13 (Ar—H), 124.94 (Ar—H), 129.41 (2Ar—H), 131.15 (Ar—COOH), 131.79 (Ar—COOH), 135.23 (C—N), 137.89 (Ar—CNH), 143.93 (Ar—NH—N), 161.18 and 166.44 (—COOH), 168.89 and 199.47 (C=O).

**Experimental details**

H atoms were located in the difference Fourier map, but refined with fixed individual displacement parameters, using riding models with C—H distances of 0.93 Å (for aromatic rings), N—H distances of 0.90 Å; O—H distances of 0.85 Å and C—H distances 0.96 for methyl group with \(U(H)\) values of 1.2 \(U_{eq}\) (N,O) and 1.5 \(U_{eq}\) (for CH\(_3\)).

**Comment**

No covalent interactions have been extensively used as a synthetic tool in the synthesis, catalysis and design of materials [5–14]. “o-hole” directed bonding interactions, such as halogen bonding, chalcogen bonding, pnictogen bonding and tetrel bonding, plays a crucial role in controlling the molecular arrangement and further properties of crystal materials due to its moderate strength, directionality and tunability [10, 11, 14–21].

In the title structure, the organic hydrazine molecule is essentially planar, (r.m.s. deviation = 0.174 Å) with a maximum deviation of 0.646(2) and –0.491(2) Å for the O3 and O4 atoms. All carbonyl groups O atoms are involved in intramolecular hydrogen bond interactions to hydrogen atoms of amino and phenyl groups, giving a S(6) motif in each case (cf. the figure) [22]. Both hydroxyl groups H atoms are involved in intermolecular hydrogen bond interactions to O atoms of dimethyl sulfoxide molecules linking the molecules into chains with graph-set notation C(13) along the [001] direction [22]. The bond lengths and angles are in the expected ranges.

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**References**


