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Crystal structure of (Z)-2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazineyl) terephthalic acid-dimethylsulfoxide (1/1),

$C_{18}H_{15}N_3O_6 \cdot C_2H_6OS$

Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	0.16 × 0.13 × 0.08 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.21 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	25.6°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	24106, 3810, 0.082
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2387
$N(\text{param})_{\text{refined}}$:	283
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 NaNO₂ 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 C₂₀H₂₁N₃O₇S ($M = 447.46$): C, 53.69; H, 4.73; N, 9.39. Found: C, 53.58; H, 4.70; N, 9.36%. **IR (KBr):** 3441 (br.) $\nu(\text{H}_2\text{O})$, 2498 $\nu(\text{NH})$, 1664 $\nu(\text{C}=\text{O})$, 1600 $\nu(\text{C}=\text{N})$ cm⁻¹. **MS (ESI)** (positive ion mode): m/z : 370.10 [M–DMSO + H]⁺

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Abstract

$C_{18}H_{15}N_3O_6 \cdot C_2H_6OS$, $P2_1/c$ (no. 14), $a = 15.762(9)$ Å, $b = 6.013(4)$ Å, $c = 22.264(11)$ Å, $\beta = 103.522(19)^\circ$, $V = 2052(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0484$, $wR_{\text{ref}}(F^2) = 0.1348$, $T = 296(2)$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
S1	0.16958(6)	0.59889(12)	0.58433(3)	0.0497(2)
O1	0.17080(15)	0.1222(3)	0.51448(9)	0.0564(6)
H1O	0.171057	0.025021	0.542264	0.085*
O2	0.07960(16)	−0.1156(4)	0.45720(10)	0.0678(7)
O3	0.12752(13)	0.4501(3)	0.19721(8)	0.0500(5)
H3O	0.131810	0.537652	0.168089	0.075*
O4	0.14698(15)	0.7723(3)	0.24669(8)	0.0537(6)
O5	0.28494(13)	1.0473(3)	0.32101(9)	0.0474(5)
O6	0.41696(16)	1.1628(4)	0.50389(9)	0.0717(7)
O7	0.17262(15)	0.8413(3)	0.60476(8)	0.0574(6)
N1	0.22718(14)	0.7114(3)	0.36826(9)	0.0356(5)
H1N	0.228421	0.795282	0.334998	0.043*
N2	0.27689(14)	0.7683(3)	0.42174(9)	0.0360(5)
N3	0.38148(15)	1.2718(4)	0.38409(10)	0.0437(6)
H3N	0.406549	1.284842	0.424617	0.052*
C1	0.17745(16)	0.5170(4)	0.36289(11)	0.0330(6)
C2	0.13361(16)	0.4438(4)	0.30374(11)	0.0350(6)
C3	0.08753(17)	0.2463(4)	0.29796(13)	0.0406(7)
H3A	0.058976	0.196253	0.258949	0.049*
C4	0.08340(18)	0.1229(4)	0.34923(12)	0.0400(7)
H4A	0.051529	−0.008685	0.344740	0.048*
C5	0.12660(17)	0.1942(4)	0.40753(12)	0.0358(6)
C6	0.17394(17)	0.3903(4)	0.41447(12)	0.0363(6)
H6A	0.203356	0.437210	0.453606	0.044*
C7	0.32522(16)	0.9480(4)	0.42659(12)	0.0364(6)
C8	0.32830(17)	1.0927(4)	0.37279(12)	0.0367(6)
C9	0.39780(17)	1.4298(4)	0.34107(12)	0.0394(6)
C10	0.45815(19)	1.5942(5)	0.36409(14)	0.0486(7)
H10A	0.485977	1.596794	0.405813	0.058*
C11	0.4766(2)	1.7534(5)	0.32477(16)	0.0566(8)
H11A	0.517846	1.862167	0.340206	0.068*
C12	0.4356(2)	1.7556(5)	0.26347(16)	0.0564(8)
H12A	0.448534	1.865053	0.237473	0.068*
C13	0.3753(2)	1.5947(5)	0.24091(14)	0.0507(8)
H13A	0.346666	1.595906	0.199342	0.061*
C14	0.35629(19)	1.4303(5)	0.27910(13)	0.0457(7)
H14A	0.315751	1.320378	0.263166	0.055*
C15	0.13728(17)	0.5748(5)	0.24744(12)	0.0382(6)
C16	0.12196(19)	0.0521(5)	0.46152(13)	0.0432(7)
C17	0.37487(19)	0.9915(5)	0.49014(13)	0.0498(8)
C18	0.3744(2)	0.8217(6)	0.53924(14)	0.0684(10)
H18A	0.424802	0.842014	0.572581	0.103*
H18B	0.375495	0.675354	0.522229	0.103*
H18C	0.322531	0.838962	0.554404	0.103*
C19	0.0702(2)	0.4970(6)	0.59526(18)	0.0715(10)
H19A	0.022907	0.569861	0.567148	0.107*
H19B	0.066321	0.525533	0.636956	0.107*
H19C	0.066943	0.339705	0.587675	0.107*
C20	0.2413(2)	0.4575(5)	0.64531(15)	0.0623(9)
H20A	0.299885	0.508223	0.648365	0.093*
H20B	0.238091	0.300484	0.637250	0.093*
H20C	0.224803	0.486924	0.683410	0.093*

and 79.10 [DMSO + H]⁺. ¹H NMR (DMSO-*d*⁶): δ 2.44 (s, 3H, CH₃), 2.50 (s, 6H, 2CH₃ 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). ¹³C{¹H} (DMSO-*d*⁶): δ 26.33 (CH₃), 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} (C,N,O) and 1.5 *U*_{eq}(C) (for CH₃).

Comment

No covalent interactions have been extensively used as a synthetic tool in the synthesis, catalysis and design of materials [5–14]. “σ-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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