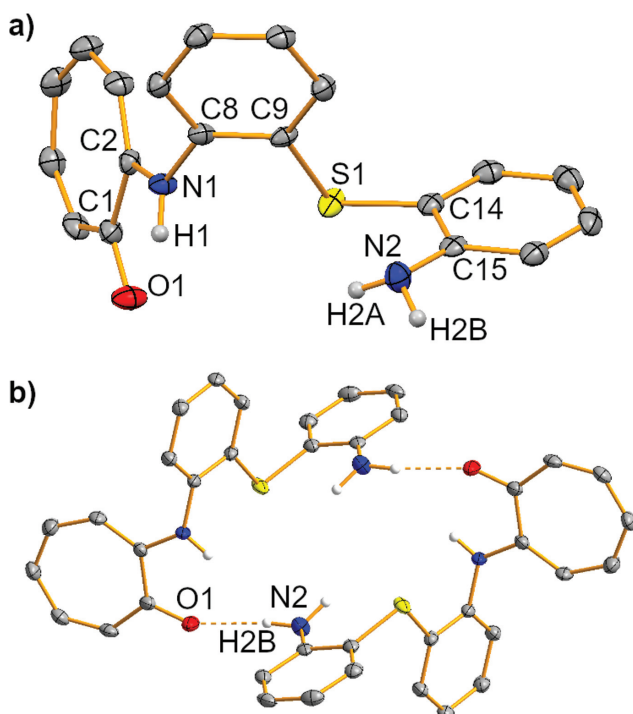


Anna Hanft and Crispin Lichtenberg\*

# Dimerization of 2-[(2-((2-aminophenyl)thio)phenyl)amino]-cyclohepta-2,4,6-trien-1-one through hydrogen bonding, C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>OS



The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

**Table 1:** Data collection and handling.

Crystal:	Colourless plate
Size:	0.21 × 0.16 × 0.04 mm
Wavelength:	Mo K $\alpha$ radiation (0.71073 Å)
$\mu$ :	0.22 mm <sup>-1</sup>
Diffractometer, scan mode:	Bruker SMART APEX, $\varphi$ and $\omega$
$\theta_{\max}$ , completeness:	28.0°, 99%
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ , $R_{\text{int}}$ :	9366, 3619, 0.040
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 2625
$N(\text{param})_{\text{refined}}$ :	220
Programs:	Bruker [1, 2], SHELX [3, 4], Mercury [5], Olex2 [6]

## Comment

Aminotroponimines (ATIs) are monoanionic ligands with applications in fields such as hydroamination and polymerization catalysis and the stabilization of low-valent main group species [7–12]. Their potential to act as redox-active ligands has recently been demonstrated [13–15]. In the coordination chemistry of ATIs, it has been shown that not only their  $N,N'$ -binding pocket, but also their C<sub>7</sub>-ligand backbone can undergo directed bonding interactions with metal centers [16–19]. Thus, ATIs can effectively act as ditopic, tridentate ligands. A strategy to further increase the denticity of this class of ligands is to connect two ATI ligands *via* linkers, generating so-called tropocoronands. These macrocyclic ligands have been employed for the chelation of metal atoms including Co, Ni, Cu, and Rh [20–28]. We became interested in tropocoronands containing unsaturated linker units. Reaction of 2,2'-thio-dianiline (**1**) with *O*-tosyltropone (**2**) in a 1.0:2.5 stoichiometry gave the title compound 2-[(2-((2-aminophenyl)thio)phenyl)amino]-cyclohepta-2,4,6-trien-1-one (**3**) as the main product, which was isolated and fully characterized. The isolation of compound **3** shows that functionalization of the first N atom in **1** hampers functionalization of the second nitrogen atom in this substrate in the protocol that was employed. The asymmetric unit of the

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## Abstract

C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>OS, triclinic,  $P\bar{1}$  (no. 2),  $a = 8.1510(3)$  Å,  $b = 8.8021(3)$  Å,  $c = 11.3953(5)$  Å,  $\alpha = 72.546(2)^\circ$ ,  $\beta = 84.568(2)^\circ$ ,  $\gamma = 80.760(2)^\circ$ ,  $V = 768.86(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_{\text{gt}}(F) = 0.0491$ ,  $wR_{\text{ref}}(F^2) = 0.1494$ ,  $T = 100$  K.

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\*Corresponding author: Crispin Lichtenberg, Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany, e-mail: [crispin.lichtenberg@uni-wuerzburg.de](mailto:crispin.lichtenberg@uni-wuerzburg.de), <https://orcid.org/0000-0002-0176-0939>

Anna Hanft: Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å<sup>2</sup>).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub> <sup>*</sup> / <i>U</i> <sub>eq</sub>
C1	0.2649(3)	0.9263(2)	0.59895(19)	0.0194(5)
C2	0.4020(3)	0.8573(2)	0.68386(19)	0.0170(4)
C3	0.5422(3)	0.7529(3)	0.66942(19)	0.0214(5)
H3	0.612709	0.721509	0.734592	0.026*
C4	0.5961(3)	0.6864(3)	0.5733(2)	0.0262(5)
H4	0.696426	0.617702	0.584103	0.031*
C5	0.5225(3)	0.7078(3)	0.4652(2)	0.0254(5)
H5	0.580316	0.654797	0.411164	0.031*
C6	0.3712(3)	0.7996(3)	0.4269(2)	0.0232(5)
H6	0.340482	0.797943	0.350771	0.028*
C7	0.2605(3)	0.8920(3)	0.48436(19)	0.0223(5)
H7	0.165653	0.941274	0.441153	0.027*
C8	0.4611(3)	0.8454(2)	0.89677(19)	0.0173(4)
C9	0.3829(2)	0.7484(2)	1.00027(19)	0.0172(4)
C10	0.4672(3)	0.6839(3)	1.10903(19)	0.0205(5)
H10	0.416279	0.618802	1.178156	0.025*
C11	0.6259(3)	0.7165(3)	1.1144(2)	0.0210(5)
H11	0.682462	0.671832	1.186693	0.025*
C12	0.7015(3)	0.8159(3)	1.0120(2)	0.0218(5)
H12	0.807463	0.839519	1.016403	0.026*
C13	0.6186(3)	0.8802(3)	0.9025(2)	0.0198(5)
H13	0.669291	0.946235	0.833736	0.024*
C14	0.1056(3)	0.6179(3)	1.13132(19)	0.0193(4)
C15	0.0507(2)	0.7064(3)	1.21541(19)	0.0184(4)
C16	-0.0269(3)	0.6290(3)	1.3276(2)	0.0219(5)
H16	-0.062511	0.684984	1.384912	0.026*
C17	-0.0509(3)	0.4700(3)	1.3539(2)	0.0247(5)
H17	-0.104983	0.421133	1.428000	0.030*
C18	0.0044(3)	0.3819(3)	1.2714(2)	0.0263(5)
H18	-0.009798	0.274248	1.290426	0.032*
C19	0.0811(3)	0.4578(3)	1.1605(2)	0.0229(5)
H19	0.117034	0.400415	1.104136	0.027*
H1	0.282(3)	0.972(3)	0.788(2)	0.034(7)*
H2A	0.100(3)	0.914(3)	1.109(3)	0.041(8)*
H2B	0.013(4)	0.921(3)	1.240(3)	0.046(8)*
N1	0.3736(2)	0.9092(2)	0.78604(16)	0.0194(4)
N2	0.0760(3)	0.8639(2)	1.1906(2)	0.0247(4)
O1	0.14534(19)	1.01392(19)	0.63363(14)	0.0271(4)
S1	0.18083(7)	0.71275(7)	0.98081(5)	0.02337(18)

title compounds contains one formula unit of **3** (triclinic, *P* $\bar{1}$ , *Z* = 2, see the Figure). The three planar ring systems in **3** are twisted towards each other. The angle between the mean planes of the tropolone and the adjacent phenylene ring amounts to 68.3°. The angle between the mean planes of the two phenylene units is 76.3°. The C–N bond lengths in compound **3** suggest partial double bond character for C2–N1 [1.361(3) Å] and C15–N2 [1.374(3) Å], but not for C8–N1 [1.426(3) Å]. This demonstrates the stronger electron withdrawing character of the tropolon-2-yl unit compared to the phenylene unit in **3**. The C–S bond lengths are identical within limits of error and virtually identical to those in the

free 2,2'-thiodianiline substituent [1.772(2) Å] [7–12, 29] In the solid state, the title compound is linked *via* two N–H···O hydrogen bonds, forming dimers with C<sub>i</sub> symmetry (see the Figure). In this scenario, O1 acts as a H-bond acceptor, while H2B represents the H-bond donor. Overall, this leads to a so-called R<sup>2</sup><sub>2</sub>(22) motif, i.e. a ring structure formed by 22 atoms including two hydrogen bond donors and two hydrogen bond acceptors [30]. Using the C<sub>7</sub>H<sub>5</sub>ONH fragment, 15 structures of 2-(amino)tropolones can be found in the Cambridge Structural Database [31]. The majority of these compounds form dimers in the solid state through N–H···O hydrogen bonding [32–42]. In comparison to the title compound, all of these dimers form R<sup>2</sup><sub>2</sub>(10) motifs, i.e. the rings generated through hydrogen bonding are significantly smaller. In addition, two examples of hydrogen-bonded coordination polymers and two monomeric species have been reported in the literature [14, 43–45].

### Source of material

Ethanol (30 mL) was added to a mixture of 2,2'-thio-dianiline (**1**) (157 mg, 0.726 mmol) and *O*-tosyltropone (**2**) (500 mg, 1.81 mmol). The reaction mixture was heated under reflux for 3 d. Aqueous sodium hydroxide (2 M, 20 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) were added, the aqueous phase was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). The combined organic phases were dried over Na<sub>2</sub>CO<sub>3</sub> and all volatiles were removed *in vacuo*. The crude reaction product was purified by column chromatography (Hexan/Ethyl acetate 5:1). The product was obtained as colourless crystals. Yield: 70 mg, 0.220 mmol, 30%.

The atom labeling used for the NMR spectroscopic characterization is the same as the atom labeling in the single crystal X-ray structure analysis.

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): δ = 6.72 (td, 1H, <sup>3</sup>J<sub>HH</sub> = 7.50 Hz, <sup>4</sup>J<sub>HH</sub> = 1.29 Hz, 18-H), 6.72 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 8.10 Hz, <sup>4</sup>J<sub>HH</sub> = 1.35 Hz, 16-H), 6.78 (m, 1H, 5-H), 6.85 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 10.3 Hz, <sup>4</sup>J<sub>HH</sub> = 0.52 Hz, 3-H), 6.96 (dd, 1H, <sup>3</sup>J<sub>HH</sub> = 7.95 Hz, <sup>4</sup>J<sub>HH</sub> = 1.42 Hz, 10-H), 7.11 (m, 1H, 4-H), 7.14 (m, 1H, 11-H), 7.20 (m, 1H, 17-H), 7.22 (m, 1H, 12-H), 7.32 (m, 3H, 6-H, 7-H, 13-H) 7.36 (dd, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz, 19-H), 8.69 (br. s, 1H, NH) ppm.

<sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>): δ = 110.83 (s, 3-C), 113.31 (s, 14-C), 115.66 (s, 16-C), 119.15 (s, 18-C), 124.84 (s, 5-C), 126.33 (s, 13-C), 126.63 (s, 12-C), 127.46 (s, 11-C), 128.19 (s, 10-C), 131.09 (s, 7-C), 131.38 (s, 17-C), 134.45 (s, 9-C), 135.58 (s, 8-C), 136.05 (s, 4-C), 137.42 (s, 19-C), 137.60 (s, 6-C), 149.09 (s, 15-C), 153.96 (s, 2-C), 177.17 (s, 1-C) ppm.

**Anal.** calc. for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>OS (320.41 g/mol): C, 71.22; H, 5.03; N, 8.74; found: C, 70.99; H, 4.95; N, 8.61.

**m. p.:** 175 °C.

## Experimental details

The  $U_{\text{iso}}$  values of H atoms were set to  $1.2 \cdot U_{\text{eq}}$  of the parent atoms. Coordinates of hydrogen atoms bound to N were refined without any constraints or restraints. All other hydrogen atoms were refined with riding coordinates.

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