Anna Hanft and Crispin Lichtenberg*

Dimerization of 2-[(2-((2-aminophenyl)thio)phenyl)amino]-cyclohepta-2,4,6-trien-1-one through hydrogen bonding, C₁₉H₁₆N₂OS

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 α radiation (0.71073 Å)
μ :	0.22 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART APEX, φ and ω
$\theta_{\max}$, completeness:	28.0°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	9366, 3619, 0.040
Criterion for I_{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 C₇-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

<https://doi.org/10.1515/ncrs-2020-0124>

Received March 5, 2020; accepted April 23, 2020; available online May 5, 2020

Abstract

C₁₉H₁₆N₂OS, triclinic, $P\bar{1}$ (no. 2), $a = 8.1510(3)$ Å, $b = 8.8021(3)$ Å, $c = 11.3953(5)$ Å, $\alpha = 72.546(2)^\circ$, $\beta = 84.568(2)^\circ$, $\gamma = 80.760(2)^\circ$, $V = 768.86(5)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0491$, $wR_{\text{ref}}(F^2) = 0.1494$, $T = 100$ K.

CCDC no.: 1998662

*Corresponding author: Crispin Lichtenberg, Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany, e-mail: 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 (Å²).

Atom	x	y	z	U _{iso} ^a /U _{eq}
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_i 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 R²₂(22) motif, i.e. a ring structure formed by 22 atoms including two hydrogen bond donors and two hydrogen bond acceptors [30]. Using the C₇H₅ONH 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 R²₂(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 CH₂Cl₂ (20 mL) were added, the aqueous phase was separated and extracted with CH₂Cl₂ (2 × 10 mL). The combined organic phases were dried over Na₂CO₃ 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.

¹H-NMR (500 MHz, CDCl₃): δ = 6.72 (td, 1H, ³J_{HH} = 7.50 Hz, ⁴J_{HH} = 1.29 Hz, 18-H), 6.72 (dd, 1H, ³J_{HH} = 8.10 Hz, ⁴J_{HH} = 1.35 Hz, 16-H), 6.78 (m, 1H, 5-H), 6.85 (dd, 1H, ³J_{HH} = 10.3 Hz, ⁴J_{HH} = 0.52 Hz, 3-H), 6.96 (dd, 1H, ³J_{HH} = 7.95 Hz, ⁴J_{HH} = 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, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.5 Hz, 19-H), 8.69 (br. s, 1H, NH) ppm.

¹³C-NMR (125 MHz, CDCl₃): 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 C₁₉H₁₆N₂OS (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_{iso} values of H atoms were set to $1.2 \cdot U_{eq}$ 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.

Acknowledgements: The authors thank Prof. Holger Braunschweig for constant support and the Fonds der Chemischen Industrie (Liebig scholarship to C. L.), the DFG, and the University of Würzburg for generous financial support. This publication was supported by the Open Access Publication Fund of the University of Würzburg.

References

1. Bruker. APEX2 ver. 2014.9. Bruker AXS GmbH, Karlsruhe, Germany (2014).
2. Bruker. SAINT+ ver. 8.38A. Bruker AXS GmbH, Karlsruhe, Germany (2019).
3. Sheldrick, G.: SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
4. Sheldrick, G.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **A64** (2008) 112–122.
5. Macrae, C. F.; Sovago, I.; Cottrell, S. J.; Galek, P. T. A.; McCabe, P.; Pidcock, E.; Platings, M.; Shields, G. P.; Stevens, J. S.; Towler, M.; Wood, P. A.: Mercury 4.0: from visualization to analysis, design and prediction. *J. Appl. Crystallogr.* **53** (2020) 226–235.
6. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42** (2009) 339–241.
7. Hanft, A.; Lichtenberg, C.: New perspectives for aminotroponiminates: coordination chemistry, redox behavior, cooperativity, and catalysis. *Eur. J. Inorg. Chem.* **2018** (2018) 3361–3373.
8. Roesky, P. W.: The coordination chemistry of aminotroponiminates. *Chem. Soc. Rev.* **29** (2000) 335–345.
9. Roesky, P. W.: Bulky amido ligands in rare earth chemistry – syntheses, structures, and catalysis. *Z. Anorg. Allg. Chem.* **629** (2003) 1881–1894.
10. Dias, H. V. R.; Wang, Z.; Jin, W.: Aminotroponiminato complexes of silicon, germanium, tin and lead. *Coord. Chem. Rev.* **176** (1998) 67–86.
11. Kuehl, O.: *N*-heterocyclic germylenes and related compounds. *Coord. Chem. Rev.* **248** (2004) 411–427.
12. Jenter, J.; Luhl, A.; Roesky, P. W.; Blechert, S.: Aminotroponiminate zinc complexes as catalysts for the intramolecular hydroamination. *J. Organomet. Chem.* **696** (2011) 406–418.
13. Lichtenberg, C.; Krummenacher, I.: Aminotroponiminates as tunable, redox-active ligands: reversible single electron transfer and reductive dimerisation. *Chem. Commun.* **52** (2016) 10044–10046.
14. Hanft, A.; Lichtenberg, C.: Aminotroponiminates: ligand-centred, reversible redox events under oxidative conditions in sodium and bismuth complexes: *Dalton Trans.* **47** (2018) 10578–10589.
15. Hanft, A.; Krummenacher, I.; Lichtenberg, C.: Alkali-metal aminotroponiminates: selectivities and equilibria in reversible radical coupling of delocalized π -electron systems. *Chem. Eur. J.* **25** (2019) 11883–11891.
16. Lichtenberg, C.: Aminotroponiminates: alkali metal compounds reveal unprecedented coordination modes. *Organometallics* **35** (2016) 874–902.
17. Hanft, A.; Lichtenberg, C.: Rationalizing the effect of ligand and substitution patterns on coordination and reactivity of alkali metal aminotroponiminates. *Organometallics* **37** (2018) 1781–1787.
18. Hanft, A.; Jürgensen, M.; Bertermann, R.; Lichtenberg, C.: Sodium aminotroponiminates: ligand-induced disproportionation, mixed-metal compounds, and exceptional activity in polymerization catalysis. *ChemCatChem* **10** (2018) 4018–4027.
19. Pittracher, M.; Frisch, U.; Kopacka, H.; Wurst, K.; Müller, T.; Oehninger, L.; Ott, I.; Wuttke, E.; Scheerer, S.; Winter, R. F.; Bildstein, B.: π -Complexes of tropolone and its *N*-derivatives: ambidentate $[O,O]/[N,O]/[N,M]$ -cycloheptatrienyl pentamethylcyclopentadienyl ruthenium sandwich complexes. *Organometallics* **33** (2014) 1630–1643.
20. Jaynes, S.; Doerrer, L. H.; Liu, S.; Lippard, S. J.: Synthesis, tuning of the stereochemistry, and physical properties of cobalt(II) tropocoronand complexes. *Inorg. Chem.* **34** (1995) 5735–5744.
21. Davis, M.; Roberts, M. M.; Zask, A.; Nakanishi, K.; Nozoe, T.; Lippard, S. J.: Stereochemical and electronic spin state tuning of the metal center in the nickel(II) tropocoronands. *J. Am. Chem. Soc.* **107** (1985) 3864–3870.
22. Davis, M.; Zask, A.; Nakanishi, K.; Lippard, S. J.: Copper(II) tropocoronands: synthesis, structure, and properties of mononuclear complexes. *Inorg. Chem.* **24** (1985) 3737–3743.
23. Villacorte, M.; Gibson, D.; Williams, I. D.; Lippard, S. J.: Dicotroponand complexes: synthesis, X-ray crystal structure, and spectral properties of neutral binuclear copper(I) complexes bridged by symmetrically substituted alkynes. *J. Am. Chem. Soc.* **107** (1985) 6732–6734.
24. Kozhukh, J.; Minier, M. A.; Lippard, S. J.: Synthesis and characterization of mononuclear, pseudotetrahedral cobalt(III) compounds. *Inorg. Chem.* **54** (2015) 418–424.
25. Hopmann, K. H.; Conradie, J.; Zangen, E.; Tonzetich, Z. J.; Lippard, S. J.: Singlet-triplet gaps of cobalt nitrosyls: insights from tropocoronand complexes. *Inorg. Chem.* **54** (2015) 7362–7367.
26. Davis, M.; Lippard, S. J.: Tropocoronands as binucleating ligands. synthesis, structure, and properties of a $(\mu$ -acetato)(μ -methoxy)dicopper(II) derivative. *Inorg. Chem.* **24** (1985) 3688–3691.
27. Jaynes, S.; Ren, T.; Masschelein, A.; Lippard, S. J.: Stereochemical control of reactivity in Co(III) alkyl complexes of the tropocoronand ligand system. *J. Am. Chem. Soc.* **115** (1993) 5589–5599.
28. Shindo, K.; Wakabayashi, H.; Kurihara, T.; Zhang, L.-C.; Ebata, K.; Sakurai, H.; Nozoe, T.: Synthesis and crystal structure of tritropocryptands. *J. Chin. Chem. Soc.* **50** (2003) 47–50.
29. Yuan, Y.-Q.; Guo, S.-R.; Wang, L.-J.: Crystal structure of 2,2'-diaminodiphenyl sulfide, $C_{12}H_{12}N_2S$. *Z. Kristallogr. NCS* **223** (2008) 507–508.
30. Etter, M. C.; MacDonald, J. C.; Bernstein, J.: Graph-set analysis of hydrogen-bond patterns in organic crystals. *Acta Crystallogr.* **B46** (1990) 256–262.

31. Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C.: The Cambridge Structural Database. *Acta Crystallogr.* **B72** (2016) 171–179.
32. Roesky, P. W.; Bürgstein, M. R.: Bridged aminotroponimate complexes of the lanthanides. *Inorg. Chem.* **38** (1999) 5629–5632. (LIGVOM).
33. Dwivedi, A. D.; Binnani, C.; Tyagi, D.; Rawat, K. S.; Li, P.-Z.; Zhao, Y.; Mobin, S. M.; Pathak, B.; Singh, S. K.: Troponate/aminotroponate ruthenium-arene complexes: synthesis, structure, and ligand-tuned mechanistic pathway for direct C-H bond arylation with aryl chlorides in water. *Inorg. Chem.* **55** (2016) 6739–6749. (OTIMUB).
34. Barret, M. C.; Bhatia, P. H.; Kociok-Köhn, G.; Molloy, K. C.: New copper(II) 2-(alkylamino)troponates. *Transition Met. Chem.* **39** (2014) 543–551. (NOPRUH).
35. Nishinaga, T.; Aono, T.; Isomura, E.; Watanabe, S.; Miyake, Y.; Miyazaki, A.; Enoki, T.; Miyasaka, H.; Otani, H.; Iyoda, M.: Structural, electronic and magnetic properties of Cu(II) complexes of 2-substituted tropones bearing a ferrocenyl group at 5-position. *Dalton Trans.* **39** (2010) 2293–2300. (FULHIE).
36. Hicks, F. A.; Brookhart, M.: A highly active anilinetropone-based neutral nickel(II) catalyst for ethylene polymerization. *Organometallics* **20** (2001) 3217–3219. (MIXLOU).
37. Steyl, G.: 2-(4-Flouroanilino)tropone. *Acta Crystallogr.* **E63** (2007) o4353. (SIMQAH).
38. Ito, Y.; Amimoto, K.; Kawato, T.: Prototropic tautomerism and solid-state photochromism of *N*-phenyl-2-aminotropones. *Dyes Pigments* **89** (2011) 319–323. (SAPLOM).
39. Kubo, K.; Matsumoto, T.; Ideta, K.; Mori, A.: Crystal structures of 3-methylpyrrolo[2,3-**b**]tropone and its copper(II) complex. *Heterocycles* **90** (2015) 104–107. (KUHSIR).
40. Kubo, K.; Tsujimoto, T.; Mori, A.: 3-Phenylpyrrolo[2,3-**b**]tropone. *Acta Crystallogr.* **E57** (2001) o225–o227. (HUFTUX).
41. Kubo, K.; Tsujimoto, T.; Kato, N.; Mori, A.: 2,3-Cyclohexanopyrrolo[2,3-**b**]tropone. *Acta Crystallogr.* **E57** (2001) o370–o371. (QIBMUJ).
42. Wahlström, N.; Stensland, B.; Bergman, J.: Synthesis of the marine alkaloid caulersin. *Tetrahedron* **60** (2004) 2147–2153. (ITIJIIE).
43. Jansen van Vuuren, L.; Visser, H. G.; Schutte-Smith, M.: Crystal structure of 2-(methylamino)tropone. *Acta Crystallogr.* **E75** (2019) 1128–1132. (WOLQUM).
44. Huczyński, A.; Majcher, U.; Maj, E.; Wietrzyk, J.; Janczak, J.; Moshari, M.; Tuszyński, J. A.; Bartl, F.: Synthesis, antiproliferative activity and molecular docking of Colchicine derivatives. *Bioorg. Chem.* **64** (2016) 103–112. (XAJCOD).
45. Siwatch, R. K.; Kundu, S.; Kumar, D.; Nagendran, S.: Bulky aminotroponimate-stabilized germylene monochloride and its alkyne derivatives. *Organometallics* **30** (2011) 1998–2005. (OZINUH).