# Nonpreorganized neutral acyclic anion receptors: Structural investigations of *N*,*N*'-diphenyl-1, 3-benzenedisulfonamide and *N*,*N*'bis(4-*t*-butylphenyl)-1, 3-benzenedisulfonamide<sup>1</sup>

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The structure of *N*,*N'*-diphenyl-1,3-benzenedisulfonamide (**1**) was determined by single crystal X-ray diffraction. It crystallizes in *P*2<sub>1</sub>/*n* with cell dimensions: *a* = 11.8390(6) Å, *b* = 12.3950(10) Å, *c* = 12.1184(10) Å,  $\beta$  = 94.388(6)°, and *V* = 1773.1(2) Å<sup>3</sup>. Its di-*t*-butyl derivative, *N*,*N'*-bis(4-*t*-butylphenyl)-1,3-benzenedisulfonamide (**2**), was prepared and structurally characterized as two solvated structures. Both crystallize in *P*1 with cell dimensions: **2** · CF<sub>3</sub>CH<sub>2</sub>OH, *a* = 9.469(2) Å, *b* = 10.0039(18) Å, *c* = 16.385(3) Å, *a* = 85.561(16)°,  $\beta$  = 83.035(18)°,  $\gamma$  = 72.459(16), and *V* = 1467.7(5) Å<sup>3</sup>; **2** · CICH<sub>2</sub>CH<sub>2</sub>Cl, *a* = 9.559(2) Å, *b* = 9.8125(12) Å, *c* = 17.100(6) Å, *a* = 82.495(19)°,  $\beta$  = 83.47(2)°,  $\gamma$  = 70.100(15), and *V* = 1491.1(6) Å<sup>3</sup>. The structures exhibit hydrogen-bonding, and are evaluated in terms of preorganization for anion binding.

**KEY WORDS:** anion; crystal structure; synthesis; conformation; dual-host; extraction.

## Introduction

Despite its apparent simplicity and versatility, the use of dual-host systems for the extraction of ion pairs remains a relatively unexplored area of separations research.<sup>1,2</sup> We recently demonstrated that simple disulfonamide molecules,

combined with a calix[4]arene-crown ether cation host, can significantly enhance extraction of the CsNO<sub>3</sub> ion pair.<sup>2</sup> In fact, this dual-host system gave the largest synergistic effects yet observed,<sup>2</sup> prompting us to further investigate the origins of these effects. As part of these investigations, we report here the solid-state structures of N,N'diphenyl-1,3-benzenedisulfonamide and N,N'bis(4-*t*-butylphenyl)-1,3-benzenedisulfonamide. The two N-H bonds in these disulfonamide molecules serve as potential sites for hydrogen bonding interactions with anions. If they are structurally predisposed to bind a single anion, this chelation could explain the strong synergistic effects observed in the ion pair extraction of CsNO<sub>3</sub>.

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## Experimental

#### Syntheses

N,N'-Bis-diphenyl 1,3-benzenedisulfona*mide* (1).<sup>3</sup> The compound was synthesized by a modification of the previously published method.<sup>4</sup> 1,3-Benzenesulfonylchloride (2.00 g, 7.3 mmol) was added gradually to a solution of aniline (3.39 g, 36.3 mmol) in 1,2-dichloroethane (50 mL) and was allowed to react for 2 h. The reaction mixture was washed with 1NHCl  $(3 \times 50 \text{ mL})$  to remove the excess aniline, and subsequently with saturated NaHCO<sub>3</sub>  $(2 \times 50 \text{ mL})$ , and water  $(2 \times 50 \text{ mL})$ . The organic layer was dried by using a granular Na<sub>2</sub>SO<sub>4</sub> column, and reduced by rotary evaporation to 10 mL. Slow addition of hexanes gave the crystalline product that was dried in vacuo for 8 h at 60°C. Yield: 2.59 g (91%). The product was found to be spectroscopically identical to the one previously reported.<sup>4</sup>

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*N,N'-Bis*(4-t-butylphenyl)-1,3-benzenedisulfonamide (**2**). The compound was synthesized as earlier with the exception that (2.22 g, 8.1 mmol) of 1,3-benzenesulfonylchloride was gradually added to a solution of 4-(t-Bu)-aniline (6.02 g, 40.3 mmol) in 1,2-dichloroethane (50 mL) and was allowed to react for 2 h. Yield: 1.86 g (46%). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 19.2°C):  $\delta$ (ppm) 8.38 (s,-br, 1H, ar, H-2), 7.77 (dd, 2H, ar, H-4), 7.43 (t, 1H, ar, H-5), 7.29 (d, 4H, Ph, H-2), 6.96 (d, 4H, Ph, H-3), 6.78 (s, br, 2H, N-H), 1.25 (s, 18H t-Bu).

## Crystallography

A summary of crystallographic data is given in Table 1, and selected bond lengths and angles are given in Tables 2 and 3. Complete crystallographic data are available as supplementary material. Intensity data were obtained using a Nonius CAD4 diffractometer fitted with a 1.1 mm collimator using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å)

Table 1. Crystal Data and Structure Refinement

Compound	1	$2 \cdot CF_3CH_2OH$	$2 \cdot ClCH_2CH_2Cl$
CCDC deposit no.	CCDC-1003/6122	CCDC-1003/6123	CCDC-1003/6124
Color/shape	Colorless/block	Colorless/fragment	Colorless/fragment
Chemical formula	$C_{18}H_{16}N_2O_4S_2$	$C_{28}H_{35}F_3N_2O_5S_2$	$C_{28}H_{36}Cl_2N_2O_4S_2$
Formula weight	388.47	600.7	599.6
Temperature, K	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	a = 11.8390(6)  Å	a = 9.469(2)  Å	a = 9.559(2)  Å
	b = 12.3950(10)  Å	b = 10.0039(18)  Å	b = 9.8125(12)  Å
	c = 12.1184(10)  Å	c = 16.385(3)  Å	c = 17.100(6)  Å
		$\alpha = 85.561(16)^{\circ}$	$\alpha = 82.495(19)^{\circ}$
	$\beta = 94.388(6)^{\circ}$	$\beta = 83.035(18)^{\circ}$	$\alpha = 83.47(2)^{\circ}$
		$\gamma = 72.459(16)^{\circ}$	$\gamma = 70.100(15)^{\circ}$
Volume, Å <sup>3</sup>	1773.1(2)	1467.7(5)	1491.1(6)
Ζ	4	2	2
$D_{\text{calc}},(\text{g cm}^{-3})$	1.45	1.36	1.34
Absorption coefficient	0.327	0.240	0.393
$\theta$ range, deg	2.3-27.5	2.1-26.5	2.2-24.0
Reflections measured	7207	8867	6011
Independent reflections	$4062(R_{\rm int} = 0.026)$	$6032(R_{\rm int} = 0.026)$	$4646(R_{\rm int} = 0.030)$
Data/restraints/parameters	4062/0/241	6032/0/392	4646/230/403
Goodness of fit on $F^2$	1.03	1.06	1.04
$R1 \left[ I > 2\sigma(I) \right]$	0.034	0.050	0.066
wR2 (all data)	0.094	0.146	0.218

	1	$2 \cdot CF_3CH_2OH$	$2 \cdot ClCH_2CH_2Cl$
C(12)-C(11)-N(1)-S(1)	124.7(2)	-129.8(2)	-133.5(5)
C(11)-N(1)-S(1)-C(1)	-53.1(1)	54.3(2)	57.4(4)
N(1)-S(1)-C(1)-C(2)	124.0(1)	47.6(3)	40.4(5)
C(2)-C(3)-S(2)-N(2)	127.8(1)	48.5(3)	54.8(5)
C(3)-S(2)-N(2)-C(21)	-47.4(2)	55.0(3)	55.7(5)
S(2)-N(2)-C(21)-C(22)	125.8(2)	-150.6(2)	-147.3(5)

Table 2. Selected Torsion Angles (deg)

and an Oxford Cryosystems 600 series low temperature device. Calculations were carried out using XCAD4<sup>5</sup> (data reduction), SHELXTL<sup>6</sup> (absorption correction, structure solution/refinement, and molecular graphics), and PLATON<sup>7</sup> (structure analysis). All non-hydrogen atoms were refined anisotropically. Except as noted below, each H atom was placed in a calculated position, refined using a riding model, and given an isotropic displacement parameter equal to 1.2 (CH, CH<sub>2</sub>) or  $1.5(CH_3, NH, OH)$  times the equivalent isotropic displacement parameter of the atom to which it is attached. When warranted, methyl H atomic positions were allowed to rotate about the adjacent C-C bond. H atoms attached to N or O were located in a difference map, and their positional parameters refined. Chemically equivalent N-H distances were restrained to be equal in the structures of 2. Full-matrix least squares refinement against  $|F|^2$  of the quantity  $\sum w(F_o^2 - F_c^2)^2$  was used to adjust the refined parameters.

*N*, *N'*-Diphenyl-1, 3-benzenedisulfonamide (1). The crystals were grown by slow evaporation of a 1,1,1-trifluoroethanol solution. Cell constants and an orientation matrix were obtained from a crystal measuring  $0.44 \times 0.43 \times$  $0.30 \text{ mm}^3$ , by least-squares refinement, using the setting angles of 25 reflections in the range  $10 < \theta < 20^\circ$ . The highest peak in the final difference map measured  $0.34 \text{ e} \cdot \text{Å}^{-3}$ .

*N,N'-Bis*(4-*t*-butylphenyl)-1,3-benzenedisulfonamide  $\cdot$  1,1-trifluoroethanol, (**2**  $\cdot$  CF<sub>3</sub>CH<sub>2</sub>OH). The crystals were grown by slow evaporation of a 1,1,1-trifluoroethanol solution. Cell constants and an orientation matrix were obtained from a crystal measuring 0.57  $\times$  0.39  $\times$  0.13 mm<sup>3</sup>, by least squares refinement, using the setting angles of 24 reflections in the range 10  $< \theta < 16^{\circ}$ . One

	$D-H\cdots A$	$H \cdots A$	$D \cdots A$	$\angle D - H \cdots A$
1	$N1 - H1 \cdots O4^{i}$ $N2 - H2 \cdots O1^{ii}$	2.20(2) 2.07(2)	3.059(2) 2.862(2)	160(2) 167(2)
$2 \cdot CF_3CH_2OH$	$N1 - H1 \cdots O2^{iii}$	2.03(3)	2.845(3)	175(3)
$2 \cdot CF_3CH_2OH$ $2 \cdot CF_2CH_2OH$	$N2-H2\cdots O3^{iv}$ $O5-H5\cdots O4^{v}$	2.07(3) 2.04(4)	2.878(3) 2.810(3)	175(4) 165(3)
$2 \cdot CF_3CH_2OH$	$C7-H7A\cdots Cg1^{vi}$	3.28	3.941(4)	126
$2 \cdot ClCH_2CH_2Cl$ $2 \cdot ClCH_2CH_2Cl$	$N1 - H1 \cdots O2^{iii}$ $N2 - H2 \cdots O3^{vi}$	2.06(5) 2.05(6)	2.886(6) 2.911(6)	158(5) 168(6)
$2 \cdot CICH_2CH_2CI$	$C/-H/A\cdots O4$	2.50	3.213(9)	129

Table 3. Hydrogen Bond Geometry (Å, deg)<sup>a</sup>

<sup>a</sup>No su's are given for some parameters because the positional parameters of those H atoms involved were not refined. Cg1 refers to the calculated centroid of the arene ring C1-6. Symmetry codes: (i) 1/2 + x, 1/2 − y, 1/2 + z; (ii) 1/2 − x, 1/2 + y, 3/2 − z; (iii) 1 − x, −y, 1 − z; (iv) −x, −y, 1 − z; (v) −x, 1 − y, 1 − z; (vi) 1 − x, 1 − y, 1 − z.

*t*-butyl group is disordered and is modeled over two sites (52:48 for C18–C20). No restraints were applied to the refinement of the disordered atoms. The highest peak in the final difference map measured  $0.54 \text{ e} \cdot \text{Å}^{-3}$ .

N,N'-Bis(4-t-butylphenyl)-1,3-benzenedisulfonamide  $\cdot$  1,2-dichloroethane, (2  $\cdot$  ClCH<sub>2</sub>CH<sub>2</sub> Cl). Suitable crystals were obtained from 1,2dichloroethane. Cell constants and an orientation matrix were obtained from a crystal measuring  $0.44 \times 0.24 \times 0.11 \text{ mm}^3$ , by least squares refinement, using the setting angles of 25 reflections in the range  $10 < \theta < 19^{\circ}$ . Both *t*-butyl groups are disordered, and are modeled as a twofold disorder (68:32 for C17-C20 and 60:40 for C27-C30). All chemically equivalent bond distances and angles between and within the two disordered groups are restrained to be roughly equal. Within each disordered group, the  $U_{ij}$  components of bonded atoms or disordered atoms within 0.7 Å of each other are restrained to be similar. Despite these restraints the thermal ellipsoids of some disordered atoms exhibit unusual elongation, suggesting further, unresolved disorder. The positional parameters for amide H atoms were allowed to refine, although the two N-H distances were restrained to be approximately equal. The highest peak in the final difference map measured 0.90 e  $\cdot$  Å<sup>-3</sup>, and the lowest valley  $-0.70 \text{ e} \cdot \text{Å}^{-3}$ .

#### **Results and Discussion**

The structures of 1,  $2 \cdot CF_3CH_2OH$  and  $2 \cdot CICH_2CH_2CI$  are illustrated in Figs. 1–3, respectively. The configuration of each disulfonamide molecule can be expressed in terms of the six torsion angles for the six single bonds that lie between the three arene rings (Table 2). In terms of orienting the N–H groups for anion binding, only rotation about the C–S and S–N bonds are important, as rotation about the N–C bonds only determines the relative position of the outer arene rings (C11–C16 and C21–C26). As can be seen in Table 2, the two N,N'-bis(4-*t*-butylphenyl)-1,3-



**Fig. 1.** Molecular structure of N, N'-diphenyl-1,3-benzenedisulfonamide, (1), showing 50% probability displacement ellipsoids. Most H atoms are omitted for clarity.

benzenedisulfonamide structures ( $2 \cdot CF_3CH_2OH$ and  $2 \cdot ClCH_2CH_2Cl$ ) adopt the same overall conformation, while **1** adopts a different conformation. The primary difference is in the C–C–S–N (rotation about the C–S bond) torsion angles, which are 124.0(1) and 127.8(1)° in **1**, and range from 40.4(5) to 54.8(5)° in the structures of **2**. Basically this places the central arene group between the N–H groups in **1**, while these groups appear to have mostly empty space between them in **2**. These relative orientations of the N–H groups have been termed "*anti–anti*" and "*syn–syn*," respectively.<sup>4</sup> The syn–syn conformation, as



**Fig. 2.** Molecular structure of N,N'-bis(4-*t*-butylphenyl)-1,3-benzenedisulfonamide  $\cdot$  1,1,1-trifluoroethanol, ( $2 \cdot CF_3$ CH<sub>2</sub>OH), showing 50% probability displacement ellipsoids. Minor disorder components and most H atoms are omitted for clarity.



**Fig. 3.** Molecular structure of N,N'-bis(4-*t*-butylphenyl)-1,3-benzenedisulfonamide  $\cdot$  1,2-dichloroethane, ( $2 \cdot ClCH_2$ CH<sub>2</sub>Cl), showing 50% probability displacement ellipsoids. Minor disorder components and most H atoms are omitted for clarity.

observed in the structures of **2**, would appear to be preferable for anion binding.

All three structures exhibit hydrogen bonding between symmetry equivalent disulfonamide molecules (Table 3). One amide hydrogen atom binds to a sulfonyl oxygen atom of a symmetry-related disulfonamide molecule while the amide hydrogen atom on the symmetryequivalent molecule binds to the equivalent sulfonyl oxygen atom of the original molecule, forming an eight-member ring (Fig. 4). The two N—H



**Fig. 4.** Example of hydrogen bonding between disulfonamide molecules. For clarity, only fragments of the two molecules are shown. Fragments shown are from  $2 \cdot CF_3CH_2OH$ . Symmetry code (i) 1 - x, -y, 1 - z.

groups of a single disulfonamide molecule bind two separate disulfonamide molecules in this manner, resulting in the formation of 1-D chains.

While the structure of **1** is not coordinated to a solvent molecule, nor does it contain solvent in the crystal lattice, both structures of **2** crystallized with a solvent molecule acting as a hydrogen bond donor to a sulfonyl oxygen atom (see Figs. 2 and 3 and Table 3). No other hydrogen bonding to or from the solvent molecules is observed. As would be expected, the hydrogen bond formed by CF<sub>3</sub>CH<sub>2</sub>OH is apparently much stronger than that formed by ClCH<sub>2</sub>CH<sub>2</sub>Cl, since it has a much shorter H ··· · A separation (2.04(4) Å *versus* 2.50 Å) and much better directionality  $(\angle D-H \cdots A = 165(3) \text{ and } 129^\circ).^8$ 

No  $\pi$ -stacking is observed in 1, but a couple of edge-face arene interactions are present. Edges of both outer arene rings (C11-C16 and C21-C26) interact with either face of the central arene ring (C1-C6), forming an odd sandwich.  $\pi$ -Stacking of the central ring is observed in the structures of 2, with interplanar distances of 4.041(2) and 3.900(3) Å for 2 · CF<sub>3</sub>CH<sub>2</sub>OH and  $2 \cdot ClCH_2CH_2Cl$ , respectively. Edge-face interactions like those seen in 1 are not observed in 2, presumably because of the presence of the bulky *t*-butyl group on the outer arene rings. However, the central ring (C1-C6) interacts with one of the outer rings (C11-C16), and the two outer rings  $(C11-C16 \rightarrow C21-C26)$  interact with each other in both structures of **2**.

In conclusion, we have observed two conformations for disulfonamide molecules which have demonstrated strong synergistic effects observed in the ion pair extraction of  $CsNO_3$ .<sup>1</sup> The conformation observed for the *t*-butyl derivative appears to be more conducive towards anion binding, but intermolecular hydrogen bonding and arene– arene interactions, observed in all three structures, may play a role in stabilizing the observed conformations. We are currently investigating the interactions of disulfonamide molecules with anions, through structural, theoretical, and liquid–liquid extraction studies. The results of this work will be reported shortly.

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