Sulfamides and sulfamide polymers directly from sulfur dioxide†

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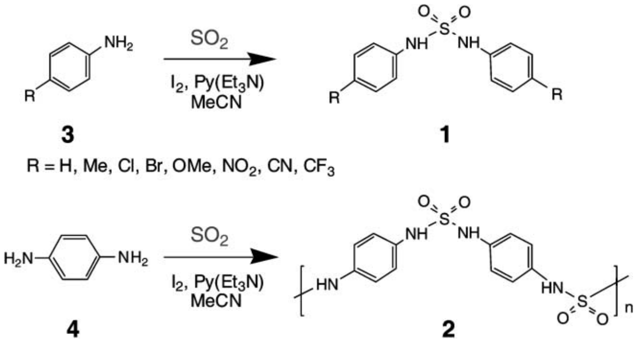
SO_2 gas is effectively used for the preparation of *N*,*N*′-diarylsulfamides and shape-persistent sulfamide polymers, which utilize a network of intermolecular N–H···O=S hydrogen bonds to self-assemble into soft porous materials.

Sulfur dioxide, or SO_2, is an environmentally important gas that is formed upon burning sulfur-containing fuels.[1] SO_2 interacts with moisture and chemicals in the air to generate acid rain, sulfites, sulfates and other toxic products. SO_2 also contributes to respiratory illnesses. The development of novel methods for the chemical utilization of SO_2 are ongoing. Organic reactions of SO_2 include cycloadditions and the synthesis of sulfinic acids, sulfones, sulfoxides and sulfolenes.[2] Additionally, liquid SO_2 is used as a solvent for organic synthesis.[3] In this communication, we present a convenient, one-step procedure for the preparation of diaryl sulfamides **1** directly from SO_2. We further describe how to use SO_2 to make novel materials—sulfamide polymers **2** of unique, persistent shape. Finally, we demonstrate how sulfamides self-assemble into porous nanostructures through self-complementary hydrogen bonds. Taken together, this study continues to explore the use of environmentally toxic gases in the preparation of new materials.[4]

Sulfamides are known for their biological activity.[5] They are also used as chelating agents[6] and in self-assembly.[7] Symmetric *N*,*N*′-sulfamides are typically prepared by reactions of amines with sulfuryl chloride.[8] However, the latter reagent is made from SO_2. Moreover, only dialkylsulfamides can be obtained in reasonable yields from this procedure.[9] Reactions with aromatic amines mostly give complex mixtures, containing chlorination and oxidation products. We found that an excess (~100-fold) of SO_2 together with I_2 and Py or Et_3N in MeCN smoothly and rapidly converted primary anilines into *N*,*N*′-diarylsulfamides (Scheme 1). An ice-cold MeCN solution of Py or Et_3N (3 equiv.) was saturated with SO_2, and then I_2 (1 equiv.) and anilines **3** (1 equiv.) were added. After 2 h at room temperature, sulfamides **1** were isolated in 20–87% yield (see ESI†). The reaction does not work in the absence of the amine base or I_2. Furthermore, when smaller quantities of I_2 were employed, much lower yields were obtained.

It has been known for many years that SO_2 and tertiary amines form stable charge-transfer complexes.[10] Olah *et al.* used these complexes in a synthetic methodology.[11] These complexes are often solids and therefore easy to handle. In a single case, a mixture of Py, I_2 and liquid SO_2 was employed as a dehydrating reagent for the formation of carboxamides and sulfamides.[12] Inconveniently, the liquid SO_2 had to be handled in a high-pressure vessel.



Scheme 1 Preparation of *N*,*N*′-diarylsulfamides **1** from anilines **3** (top) and the synthesis of sulfamide polymer **2** from phenylenediamine (**4**) (bottom).

Under the conditions described here, the amine base (for example, Py) most probably forms the known[13,10] donor–acceptor complexes $Py–I^+I^-$ and further $Py–I^+I_3^-$ with I_2, and $Py^+–SO_2^-$ with SO_2. These complexes further lead to iodosulfinate (SO_2I^-) and the still elusive[14] sulfuryl iodide (SO_2I_2), which then successively react with $ArNH_2$ in nucleophilic substitution reactions to produce first $ArNHSO_2I$ and then sulfamides **1**. While further elucidation of this mechanism is ongoing, we disclose some important features of this reaction:

1. Generally, the $Et_3N/SO_2/I_2$ system gives better yields than does the $Py/SO_2/I_2$ system; however, the product is more difficult to purify. Using DMAP or quinuclidine as a base provided better yields and higher purities.
2. Both anilines with electron-donating and electron-withdrawing substituents give reasonable yields (see Table 1 in the ESI†). To our knowledge, this is the only procedure for preparing sulfamides directly from electron-rich anilines.
3. Polymer-supported amines, such as commercial 2% cross-linked polyvinylpyridine and Amberlite IRA-67, can also be used; however, the yields drop significantly (up to 10–20% for *para*-toluidine, for example).
4. Dialkylsulfamides can also be synthesized.

The developed protocol was then applied to the synthesis of polymeric sulfamide material **2** (Scheme 1). There are only a few examples of sulfamide polymers, dating from the early 1960s, and none of them are aromatic.[15] These polyalkylsulfamides were prepared by a condensation between sulfamide ($NH_2SO_2NH_2$) and aliphatic diamines or formaldehyde, affording insoluble solids. In our protocol, the ice-cold MeCN solution of Et_3N was saturated with SO_2, after which I_2 and *para*-phenylenediamine (**4**) were added. The reaction mixture was stirred for 2 h at room

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† Electronic supplementary information (ESI) available: Synthetic procedures and crystallographic details.

temperature, and product **2** was formed in 35% yield as a light-brown crystalline solid that was soluble in DMF, DMSO and larger quantities of acetone, MeOH and MeCN. The ^{1}H NMR spectrum in DMSO-d_6 revealed two singlets at 8.96 and 6.96 ppm for the NH and aromatic protons, respectively. The FTIR spectrum showed the characteristic absorptions at 1152, 1325 and 3277 cm^{-1} due to the symmetric and asymmetric vibrations of the –SO$_2$– group and the NH stretching, respectively. A sample of **2** was then dissolved in 1 M NaOH solution and precipitated with 1 M HCl (see ESI†), after which C, H, N and Cl elemental analyses were performed. The ~4% amount of Cl found for the end amino groups in the hydrochloride salt of **2** corresponds to the lower weight oligomer with degree of polymerization DP = 10 (decamer), and an average molecular weight of ~1700 D. It should be possible to obtain higher polymers by performing reactions in more polar solvents. These studies are currently in progress and also involve other phenylenediamines.

Due to the geometry of sulfamide fragments, compounds **1** and **2** have unique structural features. The solid state structure of *N*,*N*′-diphenylsulfamide (**1**, R = H) was investigated using X-ray crystallography.‡ Compound **1** crystallizes in the *P*-1 space group with two chemically similar molecules in the asymmetric unit. The sulfur atoms adopt a tetrahedral geometry and the phenyl groups lie on the opposite sides of the N–S–N axis (Fig. 1).

Self-complementary hydrogen bonding between the N–H and S=O groups in **1** (R = H) leads to a secondary layer structure (Fig. 2) featuring pseudo octagonally-shaped pores with diameters of about 11–12 Å. Such a widely developed porous network, in principle, can be used for gas entrapment and storage.

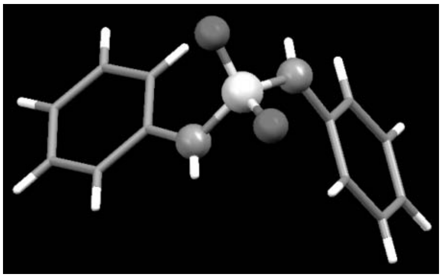

Fig. 1 Molecular structure of **1** (R = H).

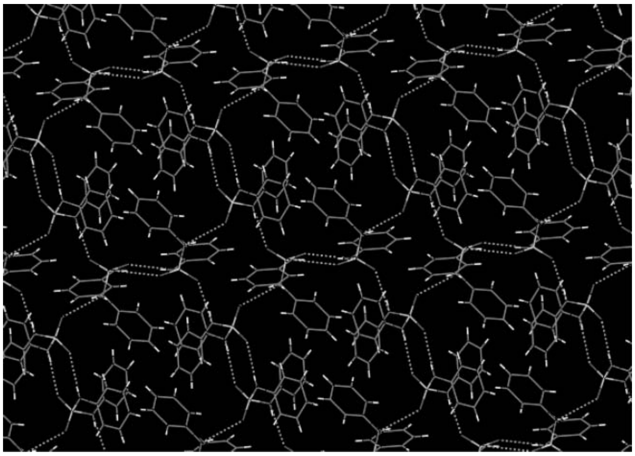

Fig. 2 The packing diagram of **1** (R = H) showing the 2D layer structure formed by hydrogen bonding interactions.

While polymer **2** was very difficult to crystallize, we prepared shorter oligomer **5** for structural studies. It has three aromatic units and two sulfamide groups (for further details of this and even longer oligomers, see the ESI†). Compound **5** crystallizes with two molecules of acetone (Fig. 3).‡ The bridging aryl amine moiety sits on an center of inversion. The backbone adopts a Z-shaped configuration. In addition, the packing diagram shows that **5** also forms a 2D layer porous structure due to hydrogen bonding between N–H groups of the bridging aryl amine moiety and S=O groups. The terminal aryl amine fragments lie above and below the plane, and their N–H groups show hydrogen bonding to the acetone oxygens (Fig. 4). Similar structural features are expected from decamer **2** and its analogs. Such nanoscale, shape-persistent objects could be important building blocks for supramolecular chemistry.

In conclusion, a convenient, one-step procedure for the preparation of various sulfamides and their polymers is now available that simply utilizes SO$_2$ gas. SO$_2$ is activated through the formation of donor–acceptor, non-covalent complexes with amine bases. We are currently working on widening the scope of this reaction. Sulfamide oligomers and polymers are particularly interesting as their shape-persistence means they can be used as units for nanoscaffolding in larger-scale architectures and functional molecular devices. They utilize a network of inter-molecular N–H···O=S hydrogen bonds to self-assemble into soft

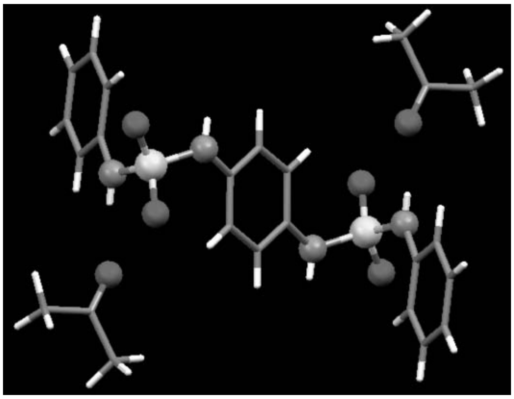

Fig. 3 Molecular structure of oligomer **5**–2 acetone.

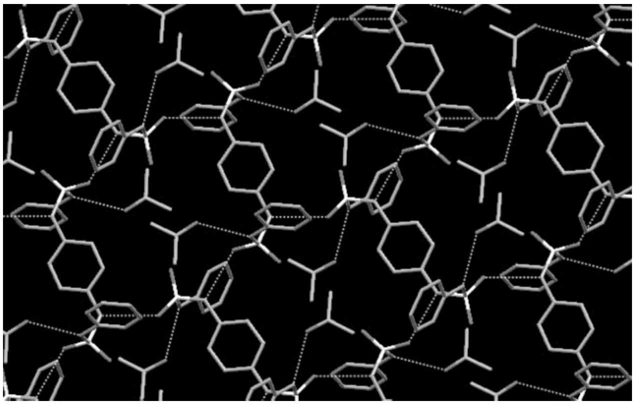

Fig. 4 The packing diagram of **5**–2 acetone showing the 2D layers formed by hydrogen bonding. Hydrogen atoms have been omitted for clarity.

porous materials. Moreover, increased electrical conductivity in these polymers can be envisioned due to the conjugation between the nitrogen and sulfur atoms, and also the aromatic rings. The thermal stability is also among the promising features as a result of extensive intermolecular hydrogen bonding.

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Notes and references

‡ *Crystal data for* **1** (R = H): $C_{12}H_{12}N_2O_2S$, $M = 248.30$, $T = 100(2)$ K, triclinic, space group P-1, $a = 10.0786(6)$, $b = 11.3145(7)$, $c = 11.3378(7)$ Å, $\alpha = 78.4390(10)$, $\beta = 72.4410(10)$, $\gamma = 74.6320(10)^\circ$, $V = 1178.34(12)$ Å^3, $Z = 4$, $\mu = 0.265$ mm^{-1}, 9448 reflections collected, 4608 unique ($R_{\text{int}} = 0.0196$), final R values (all data): $R1 = 0.0442$, w$R2 = 0.0988$. CCDC 283533. *Crystal data for* **5**: $C_{24}H_{30}N_4O_6S_2$, $M = 534.64$, $T = 100(2)$ K, monoclinic, space group $P2(1)/c$, $a = 8.8506(6)$, $b = 9.9988(7)$, $c = 15.2627(11)$ Å, $\beta = 101.1520(10)^\circ$, $V = 1325.17(16)$ Å^3, $Z = 2$, $\mu = 0.246$ mm^{-1}, 9052 reflections collected, 2571 unique ($R_{\text{int}} = 0.0211$), final R values (all data): $R1 = 0.0407$, w$R2 = 0.0970$. CCDC 603875. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605063h

1 http://www.epa.gov/air/urbanair/so2/.
2 Z. Florjanczyk and D. Raducha, *Pol. J. Chem.*, 1995, **69**, 481.
3 N. Tokura, *Synthesis*, 1971, 639.
4 (*a*) Y. Kang, G. V. Zyryanov and D. M. Rudkevich, *Chem.–Eur. J.*, 2005, **11**, 1924; (*b*) Y. Kang and D. M. Rudkevich, *Tetrahedron*, 2004, **60**, 11219 (NO_x gases); (*c*) D. M. Rudkevich and H. Xu, *Chem. Commun.*, 2005, 2651 (CO_2 gas).
5 J. M. Dougherty, D. A. Probst, R. E. Robinson, J. D. Moore, T. A. Klein, K. A. Snelgrove and P. R. Hanson, *Tetrahedron*, 2000, **56**, 9781.
6 R. C. Mills, P. Doufou, K. A. Abboud and J. M. Boncella, *Polyhedron*, 2002, **21**, 1051.
7 (*a*) F. Hof, C. Nuckolls, S. L. Craig, T. Martin and J. Rebek, Jr., *J. Am. Chem. Soc.*, 2000, **122**, 10991; (*b*) B. Gong, C. Zheng, E. Skrzypczak-Jankun and J. Zhu, *Org. Lett.*, 2000, **2**, 3273; (*c*) B. Gong, C. Zheng, H. Zeng and J. Zhu, *J. Am. Chem. Soc.*, 1999, **121**, 9766.
8 S. D. McDermott and W. J. Spillane, *Org. Prep. Proced. Int.*, 1984, **16**, 49.
9 (*a*) R. Ohme and H. Preuschhof, *Justus Liebigs Ann. Chem.*, 1968, **713**, 74; (*b*) M. Bermann and J. R. Wazer, *Synthesis*, 1972, 576.
10 (*a*) J. Grundnes and S. D. Christian, *J. Am. Chem. Soc.*, 1968, **90**, 2239; (*b*) D. L. A. de Faria and P. S. Santos, *Magn. Reson. Chem.*, 1987, **25**, 592.
11 (*a*) G. A. Olah, Y. D. Vankar and M. Arvanaghi, *Synthesis*, 1979, 984; (*b*) G. A. Olah, Y. D. Vankar and A. P. Fung, *Synthesis*, 1979, 59; (*c*) G. A. Olah, Y. D. Vankar and B. G. Gupta, *Synthesis*, 1979, 36; (*d*) G. A. Olah and Y. D. Vankar, *Synthesis*, 1978, 702; (*e*) G. A. Olah, M. Arvanaghi and Y. D. Vankar, *Synthesis*, 1980, 660.
12 M. Nojima, S. Hasegawa and N. Tokura, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 1254.
13 (*a*) C. Reid and R. S. Mulliken, *J. Am. Chem. Soc.*, 1954, **76**, 3869; (*b*) S. S. Barton and R. H. Pottier, *J. Chem. Soc., Perkin Trans. 2*, 1984, 731.
14 V. K. Manzel and R. Minkwitz, *Z. Anorg. Allg. Chem.*, 1978, **441**, 165.
15 (*a*) A. Vandi, T. Moeller and L. F. Audrieth, *J. Org. Chem.*, 1961, **26**, 3478; (*b*) H. Q. Smith and F. L. Scott, *J. Polym. Sci., Part A: Gen. Pap.*, 1964, **2**, 481; (*c*) R. A. Florentine, G. Barth-Wehrenalp, I. Mockrin, I. Popoff and R. Riordan, *J. Polym. Sci., Part A: Gen. Pap.*, 1964, **2**, 489.