Structural Basis for the Acidity of Sulfonamides. Crystal Structures of Dibenzenesulfonamide and Its Sodium Salt[1]

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Abstract: To ascertain what role structural factors—and, hence, by implication, bonding factors—play in the pronounced acidity of dibenzenesulfonamide (pK_a = 1.45), the structures of the acid itself, $(C_6H_5SO_2)_2NH$, and the sodium salt, $Na^+(C_6H_5SO_2)_2N^-$, have been determined. For $(C_6H_5SO_2)_2NH$: space group, $P2_1/c$; $Z = 4$; $d_o = 1.470$ g/cm^{-3}; $d_c = 1.468$ g/cm^{-3}; $a = 8.625 \pm 0.004$, $b = 10.164 \pm 0.004$, $c = 15.627 \pm 0.004$ Å; $\beta = 101.09 \pm 0.05°$; $V = 1340$ Å^3. Intensities of 2364 independent reflections were measured using Mo Kα radiation and employing an automated diffractometer. The 1276 reflections accepted as statistically reliable and nonzero were used to solve (by application of the Karle–Hauptman sigma-2 relationship) and refine the structure. For $Na^+(C_6H_5SO_2)_2N^-$: space group, Pbcn; $Z = 8$; $d_o = 1.585$ g/cm^{-3}; $d_c = 1.580$ g/cm^{-3}; $a = 15.218 \pm 0.004$, $b = 17.210 \pm 0.004$, $c = 10.252 \pm 0.004$ Å; $V = 2685$ Å^3. Intensities of 1639 independent reflections were measured using Cu Kα radiation and employing an automated diffractometer. Of these, 1251 reflections were used to solve the structure by the symbolic addition procedure and to refine it. In $(C_6H_5SO_2)_2NH$, the phenyl groups lie above and below the S–N–S plane, giving approximate molecular symmetry C_2; in $[(C_6H_5SO_2)_2N]^-$, they lie on the same side of the S–N–S plane giving approximately C_s symmetry. This difference seems to be caused primarily by steric, electrostatic, and packing forces. The SNS angle, mean S–N distances, and mean S–O distance in $(C_6H_5SO_2)_2NH$ and $[(C_6H_5SO_2)_2N]^-$ are, respectively: 127.7 (3)°, 1.650 (7) Å, and 1.415 (18) Å; and 127.5 (3)°, 1.580 (9) Å, 1.446 (8) Å. Thus, the only major change attributable directly to deprotonation of $(C_6H_5SO_2)_2NH$ is the decrease of 0.070 (16) Å in the mean S–N bond length.

It is well known that sulfonamides are moderately acidic. An extensive tabulation of pK_a values for derivatives of benzenesulfonamide, $PhSO_2NH_2$, has been made by Dauphin and Kergomard.[2] The pK_a for benzenesulfonamide is 10.1, and the introduction of various substitutents on the benzene ring causes the pK_a values to range from 8.75 (3,5 NO_2–) to 10.51 (p-NH_2–). N-Aryl derivatives are somewhat more acidic; examples are $PhSO_2NHPh$ (pK_a = 9.65) and its 3,3′-dinitro derivative (pK_a = 5.51). Dibenzenesulfonamide, $(PhSO_2)_2NH$, with a pK_a of 1.45 is a remarkably strong acid, approximately as strong as phosphoric acid.

We considered that this high degree of acidity would be due, at least in part, to effective delocalization of negative charge in the anion, which would in turn have observable structural consequences, amounting at least to S–N bond shortening as a result of increased dπ–pπ interaction.

In order to establish directly and quantitatively the structural changes which accompany the dissociation of $(C_6H_5SO_2)_2NH$, accurate X-ray crystallographic studies of both the amide and its sodium salt, $Na^+(C_6H_5SO_2)_2N^-$, were undertaken. The results of both studies are reported here.

Experimental Section

Dibenzenesulfonamide. A sample of crystalline dibenzenesulfonamide was furnished by Dr. Anthony Evnin of the Union Carbide Research Institute. Several crystals in the original sample were of appropriate dimensions and appeared free of defects when viewed under polarized light and photographed by precession and Laué techniques. One of these crystals was selected for data collection. It was a monoclinic prism of approximate dimensions 0.4 × 0.3 × 0.2 mm, and was mounted along the b axis.

Precession photography indicated a monoclinic unit cell with the systematic absence $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, uniquely establishing the space group as $P2_1/c$ (C_{2h}^5, no. 14). Unit cell dimensions were determined on a General Electric XRD-5 goniostat using Cu Kα_1 radiation, $\lambda = 1.5405$ Å, with the crystal aligned so that the b^* axis was coincident with the axis of the goniometer. These data are: $a = 8.625 \pm 0.004$, $b = 10.164 \pm 0.004$, $c = 15.627 \pm 0.004$ Å, and $\beta = 101.09 \pm 0.05°$. The unit cell volume is 1340 Å^3, and the calculated density for four molecules per cell of 1.468 g/cm^3 is in excellent agreement with the experimental value of 1.470 g/cm^3 (~ 23°) obtained by flotation.

Intensity data were collected on a General Electric XRD-6 automated diffractometer, equipped with scintillation counter and pulse-height discriminator, which was adjusted to admit 95% of the Kα peak. The crystal was aligned so that the b^* axis was approximately 2° out of coincidence with the ϕ axis. This was done to reduce the possibility of simultaneous diffraction[3] by crystal planes other than the one being counted. Orientation angles and diffractometer settings for this alignment were calculated by a least-squares refinement based on circle settings at the centers of 17 reflections.

The intensities of 2364 independent reflections within the sphere limited by $2\theta = 54°$ were obtained using zirconium-filtered Mo Kα radiation (λ 0.7107 Å) at a takeoff angle of 3°. Scanning was of the θ–2θ type at a scan speed of 1°/min. Angular width of the scans varied as a function of the separation of the α_1–α_2 doublet and included the region ranging from 0.90° below the Kα_1 peak to 0.90° above the Kα_2 peak for each reflection. Backgrounds were estimated by counting for 40 sec at each end of the scan range.

During the first 4-day period of data collection, a 1A sphere of data was measured. During this time the check reflections were entirely stable. Both check peaks and backgrounds then fell some 20% and during the next 3 days, while the high angle data (to d = 0.78 Å, $2\theta = 48°$) were collected, remained completely stable.

The crystal was examined optically after the data had been collected. It showed no signs of decomposition and extinguished sharply when viewed under polarized light. Recorder chart tracings showed no observable increase in peak width or any other degradation of peak shape which would indicate crystal decomposition. The sudden decrease described above affected both peaks and backgrounds in the same way, whereas decomposition would

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[1] Research Supported by the National Science Foundation under Grant No. GP-7034X.

[2] G. Dauphin and A. Kergomard, *Bull. Soc. Chim. France*, 3, 486 (1961).

[3] W. A. Zachariasen, *Acta Cryst.*, **18**, 705 (1965).

have caused background levels to remain unchanged or to rise. It is therefore improbable that this crystal decomposed to any significant extent.

It seems likely that the tube, the counter, or the pulse-height discriminator caused the abrupt decrease, in which case the two portions of the data set might properly be combined without serious error by means of separate scale factors. The overall factor required to bring the intensities of the second (high-angle) portion of the data into relative scale with the first was approximately 1.2. This scaling was accomplished during the refinement process by means of a second varied scale factor as will be described.

Of the 2364 intensities measured, 317 were recorded as less than zero. An additional 768, for which $I/\sigma_F = (P - B_1 - B_2)/(P + B_1 + B_2)^{1/2} < 3$, were rejected as statistically unreliable. In the preceding expression, P = peak counts and B_1, B_2 are the two background counts. The remaining 1279 reflections were corrected for Lorentz–polarization effects and used to solve and refine the structure. Absorption corrections (μ = 4 cm^{-1}) were neglected.

Solution of the structure was accomplished using the symbolic addition procedure for application of the Karle–Hauptman sigma-2 relationship to determine the phases of 483 of the largest structure factors. The method used has been described in detail by Karle and Karle.[4] Our local version of the FORTRAN package MAGIC, by Robert Dewar and Allen Stone of the University of Chicago, was employed in the following way.

The reduced data (F_o's) out to 1-Å spacings were converted by the preliminary program FAME to normalized structure factors (E's), by the relationship $E^2 = F_o^2 \exp(T \sin^2 \theta/\lambda)/\epsilon K^2 S$, where F_o is the observed structure factor, T is an overall temperature factor, ϵ is an integer to correct for extinct reflections in special zones, K is the scale factor necessary to place the observed structure factor amplitudes on an absolute scale, and S is the sum of the scattering factors of all atoms in the unit cell for the particular value of (h, k, l). The overall temperature factor T and scale factor K may be evaluated from a Wilson plot, which the program calculates as its first order of business. In the present case the Wilson plot was poor. There was wide scatter and no convincing "best" line could be drawn. A second set of E's, employing the "reasonable" value of 3.5 for T and rescaled so that $|E^2| = 1.0$ was computed by the program and these E's were used for the sign determination process.

Using the program MAGIC, which implements the Karle–Hauptmann sigma-2 relationship[5]

$$\mathrm{s}E_h \simeq \mathrm{s}[\textstyle\sum E_k E_{h-k}]$$

where s means "sign of" and h and k are the index triples of the reflections, a most probable set of signs was generated. This most probable set was strongly favored over the next most probable set, involving approximately ten times fewer inconsistencies in the sigma-2 relationships. Reflections whose determination led to an inconsistency were rejected, and the 483 remaining reflections were given signs in accordance with the most probable combination. These were punched in a format suitable for a Fourier calculation based on the signed E's, the so-called E-map. All of the above steps were carried out in one run on an IBM 360/65 computer, which lasted 3.81 min. The preliminary generation of E's required 1.28 min of execution time.

An E-map for the most probable sign combination revealed the location of 18 of the 19 atoms of the molecule, all sharply resolved. Only three noise peaks were of comparable magnitude to the weakest atom peak present. The peak magnitudes of the sulfur atoms were heavily overemphasized, which is expected from their "heavy atom" role in dominating the largest E's. The benzene rings were somewhat underemphasized in general, probably due to their relatively high thermal motion. Subsequent refinement revealed a rough inverse correlation between E-map intensity and isotropic temperature factor for the ring carbon atoms of both this molecule and its sodium derivative.

The coordinates derived from the E-map were used to begin refinement of the structure. The location of the one atom not revealed on the E-map, a ring carbon atom, was easily deduced. The atoms were all assigned an isotropic temperature factor of 3.5, and the scale factor which had been used to rescale the E's, 0.656, was used. Structure factors were then calculated for those reflections within the 1-Å sphere. Three cycles of full-matrix least-squares refinement were carried out, allowing the scale factor and position coordinates of all 19 atoms to vary. The function minimized was

$$\sum w||F_o| - |F_c||^2$$

where the weighting factor w was $1/\sigma_F^2$, σ_F being the estimated standard deviation based on counting statistics, $(P + B_1 + B_2)^{1/2}$. The unweighted residual

$$R = \sum||F_o| - |F_c||/\Sigma|F_o|$$

fell to 16.2% following the third cycle. Four cycles in which the isotropic temperature factors were also allowed to vary resulted in R = 12.7, following which a ΔF synthesis was computed. The map showed no major anomalies, and nearly all of its largest peaks were attributable to anisotropic motion of the sulfur and oxygen atoms.

Accordingly, the next cycles of refinement were carried out with anisotropic temperature factors for the sulfur, oxygen, and nitrogen atoms. At this time the remainder of the data was added, with a separate scale factor. Three cycles of partially anisotropic refinement lowered the unweighted residual R to 7.4%, and the weighed residual, $R_w = \{\Sigma(1/\sigma_F{}^2)(|F_o| - |F_c|)^2/\Sigma(1/\sigma_F{}^2)\,|F_o|^2\}^{1/2}$, using the values of σ_F obtained from counting statistics, was 6.9%. A ΔF synthesis was computed whose largest peak (0.54 e Å^{-3}) was in a position corresponding to the amide hydrogen atom. The positions in which hydrogen atoms bound to the benzene rings were anticipated contained positive electron density of marginal significance (~0.25 e Å^{-3}). The considerable thermal motion of the benzene rings probably accounts in part for the weakness and diffuseness of the ring hydrogen atom peaks relative to the amide hydrogen atom peak.

A final cycle of refinement was carried out in which the coordinates of the amide hydrogen atom were allowed to vary. An isotropic temperature factor of 5.0 was assigned to this atom and was not varied. The final unweighted R = 0.073; R_w = 0.069. No attempt was made to refine ring hydrogen atom coordinates. A correlation matrix computed during the last cycle showed no significant correlations between the varied parameters. The final fractional atomic coordinates are given in Table I and temperature factors of the nonhydrogen atoms are given in Table II. A table of observed and calculated structure factor amplitudes has been deposited with the ASIS National Auxiliary Publication Service.[6] Bond lengths are given in Table III and bond angles are given in Table IV. Figure 1 shows the structure of the $(C_6H_5SO_2)_2NH$ molecule.

Table I. Fractional Atomic Coordinates of Dibenzenesulfonamide

Atom	x	y	z
S(1)	0.4333 (2)	0.3961 (1)	0.2501 (1)
S(2)	0.7702 (2)	0.4746 (1)	0.2725 (1)
O(1)	0.5019 (5)	0.2757 (3)	0.2260 (2)
O(2)	0.3056 (5)	0.4545 (4)	0.1947 (2)
O(3)	0.8393 (5)	0.6014 (4)	0.2915 (2)
O(4)	0.8121 (5)	0.3702 (4)	0.3320 (2)
N	0.5784 (5)	0.5038 (5)	0.2628 (3)
C(1)	0.3845 (6)	0.3759 (5)	0.3535 (3)
C(2)	0.2352 (8)	0.4113 (6)	0.3641 (4)
C(3)	0.1942 (8)	0.3917 (7)	0.4460 (5)
C(4)	0.3049 (8)	0.3402 (6)	0.5151 (4)
C(5)	0.4538 (7)	0.3054 (7)	0.5030 (4)
C(6)	0.4960 (7)	0.3257 (6)	0.4203 (4)
C(7)	0.7967 (7)	0.4250 (6)	0.1689 (3)
C(8)	0.7580 (8)	0.5123 (7)	0.1006 (4)
C(9)	0.7858 (8)	0.4759 (7)	0.0160 (5)
C(10)	0.8538 (8)	0.3573 (7)	0.0064 (4)
C(11)	0.8931 (8)	0.2701 (7)	0.0756 (4)
C(12)	0.8667 (7)	0.3061 (7)	0.1587 (4)
H	0.5626 (6)	0.6005 (6)	0.2633 (3)

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[4] J. Karle and I. L. Karle, *Acta Cryst.*, 21, 849 (1966).

[5] H. Hauptman and J. Karle, "Solution of the Phase Problem, I. The Centrosymmetric Crystal." A.C.A. Monograph No. 3, Polycrystal Book Service, Pittsburgh, Pa.

[6] For this table, order NAPS Document No. NAPS-00650 from the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022, remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

Table II. Temperature Parameters in Dibenzenesulfonamide[a]

Atom	*B*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)		0.0162 (3)	0.0085 (2)	0.0028 (1)	−0.0014 (2)	0.0016 (1)	0.0001 (1)
S(2)		0.0153 (3)	0.1116 (2)	0.0034 (1)	−0.0011 (2)	0.0020 (1)	−0.0004 (1)
O(1)		0.0252 (9)	0.0075 (5)	0.0051 (2)	−0.0019 (5)	0.0051 (3)	−0.0013 (2)
O(2)		0.0172 (8)	0.0197 (7)	0.0042 (2)	0.0009 (7)	0.0005 (3)	0.0019 (3)
O(3)		0.0236 (10)	0.0161 (7)	0.0065 (2)	−0.0093 (4)	0.0049 (4)	−0.0043 (4)
O(4)		0.0184 (9)	0.0199 (7)	0.0040 (2)	0.0049 (6)	0.0026 (3)	0.0030 (3)
N		0.0161 (10)	0.0055 (5)	0.0050 (3)	−0.0012 (6)	0.0044 (4)	−0.0001 (3)
C(1)	3.3 (1)						
C(2)	5.1 (1)						
C(3)	6.3 (1)						
C(4)	4.9 (1)						
C(5)	5.0 (1)						
C(6)	4.5 (1)						
C(7)	3.8 (1)						
C(8)	5.7 (1)						
C(9)	6.4 (1)						
C(10)	5.5 (1)						
C(11)	6.0 (1)						
C(12)	5.1 (1)						
H	5.0 (0)						

[a] Estimated errors in the last significant place appear in parentheses.

The Sodium Salt of Dibenzenesulfonamide. The sodium salt of dibenzenesulfonamide was obtained from dibenzenesulfonamide and NaOH in an acetone–water mixture at room temperature. The solvent was removed with a rotary evaporator at −30° and the salt recrystallized by controlled evaporation of an acetone-*n*-butyl alcohol solution. The crystals were long colorless needles. One of these crystals was mounted along the needle (*c*) axis for the X-ray investigation.

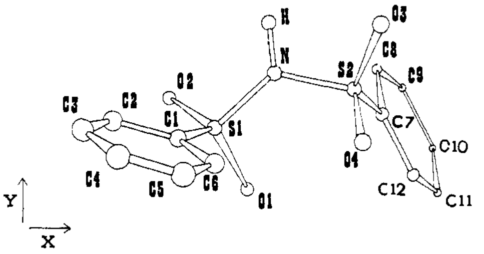

Figure 1. The dibenzenesulfonamide molecule seen in projection down the *c** axis.

The unit cell was found to be orthorhombic from precession photographs. Systematic absences uniquely established the space group as Pbcn (D_{2h}^{14}, no. 60), a centric space group. Unit cell dimensions were determined on the diffractometer in the manner explained above. They are: $a = 15.218 \pm 0.004$, $b = 17.210 \pm 0.005$, $c = 10.252 \pm 0.004$ Å. The calculated density for eight molecules in the cell of volume 2685 Å^3 was 1.580. The crystals remained suspended in CCl_4 (measured density d_{25}, 1.585 g/cm^{-3}).

Three-dimensional intensity data were collected on a General Electric XRD-6 automated diffractometer equipped with scintillation counter and pulse-height discriminator. Cu Kα radiation (λ 1.5418 Å) was used with a target takeoff of 3°. The crystal was an irregular six-sided prism of length 0.52 mm, and approximate cross section 0.5 × 0.3 mm. It was mounted with *c** coincident with the ϕ axis.

Peak intensities were measured with θ–2θ scans of 4°/min over a range of 2.66° about the peak center. Backgrounds were estimated by counting for 10 sec at each end of the scan range. Signal to noise ratios were excellent with this crystal, which had a narrow mosaic spread and very little diffuse scattering; 1639 independent reflections, including those systematically absent, were recorded within the sphere limited by $2\theta = 110°$. A reflection was rejected as statistically unreliable if $F_o < 2\sigma_F$, where

$$\sigma_F = \frac{\mathrm{RLP}}{2F}(P + 4B_T + 0.002\ I^2)^{1/2}$$

where RLP is the reciprocal Lorentz-polarization correction, *P* is total peak counts (40 sec), B_T is total background counts (20 sec), and $I = P - 2B_T$. After elimination of the statistically unreliable and the systematically absent reflections, the remaining 1261 data were used to solve and refine the structure. The data within $2\theta = 60°$ were collected with an additional layer of Ni foil attenuating the diffracted beam to ensure counter linearity. The attenuation factor was calculated from check reflection intensities to be 1.629 and was introduced as a correction factor in the data reduction step. At a later stage in the refinement, an independent scale factor was employed for these reflections which remained closely equal to the scale factor for the higher angle data.

The intensities of several reflections were monitored after every 50 reflections. These showed no significant fluctuations or trends

Table III. Bond Lengths (Å) in Dibenzenesulfonamide[a]

S(1)–N	1.643 (5)	C(4)–C(5)	1.383 (10)
S(1)–O(1)	1.441 (5)	C(5)–C(6)	1.428 (9)
S(1)–O(2)	1.386 (5)	C(6)–C(1)	1.365 (8)
S(1)–C(1)	1.763 (6)	C(7)–C(8)	1.377 (9)
		C(8)–C(9)	1.440 (11)
S(2)–N	1.657 (5)	C(9)–C(10)	1.360 (11)
S(2)–O(3)	1.426 (5)	C(10)–C(11)	1.385 (10)
S(2)–O(4)	1.409 (5)	C(11)–C(12)	1.408 (11)
S(2)–C(7)	1.756 (7)	C(12)–C(7)	1.375 (10)
		N–H	1.01 (6)
C(1)–C(2)	1.379 (9)		
C(2)–C(3)	1.410 (10)		
C(3)–C(4)	1.388 (9)		

[a] Estimated errors in the last significant place appear in parentheses.

Table IV. Bond Angles (deg) in Dibenzenesulfonamide[a]

S(1)–N–S(2)	127.7 (3)	S(2)–C(7)–C(12)	120.3 (5)
O(1)–S(1)–O(2)	121.0 (3)	C(1)–C(2)–C(3)	119.1 (6)
O(1)–S(1)–N	104.7 (2)	C(2)–C(3)–C(4)	119.9 (7)
O(2)–S(1)–N	106.1 (3)	C(3)–C(4)–C(5)	119.9 (6)
C(1)–S(1)–O(1)	109.2 (3)	C(4)–C(5)–C(6)	120.2 (6)
C(1)–S(1)–O(2)	108.2 (3)	C(5)–C(6)–C(1)	118.4 (6)
C(1)–S(1)–N	106.6 (3)	C(6)–C(1)–C(2)	122.3 (6)
O(3)–S(2)–O(4)	120.3 (3)	C(7)–C(8)–C(9)	118.9 (6)
O(3)–S(2)–N	102.8 (3)	C(8)–C(9)–C(10)	119.2 (7)
O(4)–S(2)–N	108.1 (3)	C(9)–C(10)–C(11)	121.3 (7)
C(7)–S(2)–O(3)	108.9 (3)	C(10)–C(11)–C(12)	119.6 (6)
C(7)–S(2)–O(4)	109.0 (3)	C(11)–C(12)–C(7)	119.4 (6)
C(7)–S(2)–N	106.6 (3)	C(12)–C(7)–C(8)	121.4 (6)
S(1)–C(1)–C(2)	119.0 (5)	S(1)–N–H	124 (3)
S(1)–C(1)–C(6)	118.7 (5)	S(2)–N–H	107 (3)
S(2)–C(7)–C(8)	118.0 (5)		

[a] Estimated errors in the last significant place are in parentheses.

Table V. Fractional Coordinates in Sodium Dibenzenesulfonamide[a]

Atom	x	y	z
S(1)	0.37410 (9)	0.35424 (9)	0.51845 (15)
S(2)	0.37244 (9)	0.51795 (9)	0.48816 (15)
Na(1)	0.50000	0.3986 (2)	0.75000
Na(2)	0.50000	0.5907 (2)	0.75000
N	0.3814 (3)	0.4411 (3)	0.5698 (4)
O(1)	0.4009 (2)	0.3413 (3)	0.3851 (4)
O(2)	0.4208 (2)	0.3086 (2)	0.6159 (4)
O(3)	0.4104 (3)	0.5115 (3)	0.3586 (4)
O(4)	0.4064 (3)	0.5794 (2)	0.5681 (4)
C(1)	0.2619 (3)	0.3200 (3)	0.5281 (5)
C(2)	0.2200 (4)	0.2974 (4)	0.4183 (6)
C(3)	0.1336 (5)	0.2740 (5)	0.4274 (8)
C(4)	0.0904 (5)	0.2777 (4)	0.5455 (7)
C(5)	0.1326 (5)	0.3067 (5)	0.6550 (7)
C(6)	0.2191 (4)	0.3314 (4)	0.6458 (7)
C(7)	0.2593 (4)	0.5373 (3)	0.4654 (6)
C(8)	0.2138 (4)	0.4951 (4)	0.3725 (8)
C(9)	0.1229 (6)	0.5093 (6)	0.3570 (10)
C(10)	0.0827 (6)	0.5651 (5)	0.4344 (9)
C(11)	0.1296 (6)	0.6083 (6)	0.5245 (9)
C(12)	0.2192 (5)	0.5934 (4)	0.5406 (7)

[a] Estimated errors in last significant figure are in parentheses. The x and z coordinates of Na(1) and Na(2) are fixed by symmetry in space group Pbcn.

during the data collection process, indicating both crystal and machine to be stable.

The structure was solved by the symbolic addition procedure described in the preceding section pertaining to dibenzenesulfonamide. E's were generated from the complete set of data following an Lp correction, excluding systematically absent reflections. The overall temperature factor obtained from the Wilson plot was 2.59; the scale factor required to normalize the E's so that $|E^2| = 1$ was 0.64. The 800 largest E's were used for the symbolic addition procedure.

Sign determination proceeded quickly and easily, and in three cycles the signs of 421 independent reflections were determined. Three independent reflections were assigned (+) phases to fix the origin, and the remaining five symbolic knowns evaluated with the aid of 3161 indications of symbol equivalence. These unambiguously favored a single sign combination with all other combinations less probable by a factor of 1000 or more.

An E-map, phased on 395 reflections whose signs were determined without inconsistencies, revealed all atoms in the molecule, although resolution in the vicinity of the S atoms was not as sharp as that found in the dibenzenesulfonamide map. It appears that series termination ripple was responsible for this, as the ring carbon atoms were clear and sharp. Once again the S atoms were overemphasized in this map, while the ring carbon atoms were weak but clearly visible. Noise peaks, except for the ripple, were few in number and minor in magnitude. The only ambiguity in the map was the nitrogen atom position; two peaks of approximately equal amplitude occurred in reasonable positions amidst considerable ripple. Subsequent refinement showed the higher of these to be the correct one. The sodium ion was clearly shown in the special positions $(0, y, {}^3/_4)$ and $({}^1/_2, y, {}^3/_4)$.

Isotropic least-squares refinement of the sulfur, sodium, and carbon atom coordinates was carried out. A ΔF map confirmed the oxygen positions as those indicated by maxima on the E-map, and resolved the ambiguity of the N position. (A Fourier map based only on S and Na did not resolve this ambiguity; it actually gave slight preference to the incorrect location. This map also possessed the ripple around the S atoms found in the E-map.) With all atoms in their proper places, isotropic refinement brought the unweighted residual R down to 0.108.

The data were corrected for absorption (μ = 39 cm^{-1}). The correction was evaluated by measuring the intensity of the 004 reflection, which occurred at $\chi = 90°$, as a function of the ϕ setting in 10° intervals. These data were used to construct a "best ideal" polygonal cross section for use in the correction program. The average deviation of the observed intensity from the mean value was 12.1% in the experimental curve. Application of the correction reduced this deviation to 3.6%.

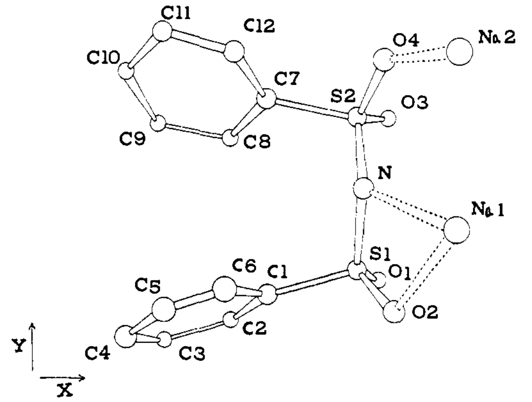

Figure 2. The structure of the sodium salt of dibenzenesulfonamide viewed down the c axis. Dotted lines indicate the presumably strong electrostatic interactions.

Systematically low magnitudes for F_o for reflections of high intensity appeared to be the result of extinction effects. A correction for secondary extinction was therefore made. The secondary extinction parameter[7] was allowed to vary in the refinement and converged at a value of $0.25 \pm 0.02 \times 10^{-6}$.

Refinement was resumed with the sulfur, nitrogen, and oxygen atoms given anisotropic temperature factors, while the rest remained isotropic. For a portion of the refinement the benzene rings were refined as rigid bodies, but this produced excessively large estimated standard deviations for the carbon atoms. The coordinates of all atoms were allowed to vary independently during the last two cycles. The function minimized during refinement was

$$\sum w||F_c| - |F_o||^2$$

The weighting factor was $w = 1/\sigma^2$, where σ is the standard deviation of F_o based on counting statistics. The refinement converged with the unweighted discrepancy index R = 0.077. The weighted residual was 0.107.

An analysis of the weighting scheme showed no significant variation of $w||F_o| - |F_c||^2$ as a function of the magnitude of F_o or of $\sin \theta/\lambda$. A correlation matrix indicated no significant correlations between any of the varied parameters. A final ΔF synthesis showed no anomalous peaks of significant magnitude and phenyl hydrogen atoms were revealed as peaks of marginal significance (~0.25 e/Å). The highest peak on the map, in the vicinity of the nitrogen atom, was of positive density 0.55 e/Å.

The fractional atomic coordinates for the sodium salt of dibenzenesulfonamide are shown in Table V and the temperature factors are shown in Table VI. The observed and calculated structure factors have been deposited with the ASIS National Auxiliary Publications Service.[6] Bond lengths and bond angles are shown in Tables VII and VIII, respectively. Figure 2 shows the structure of the molecule.

Computer Programs. Diffractometer settings for dibenzenesulfonamide were calculated with the IBM 360 program PICK2 (J. Ibers, Northwestern University, 1965) which can handle off-axis crystal alignments, while settings for the sodium salt were obtained using a time-share program SAMEAG (D. C. Richardson and A. Arnone, MIT, 1966). The latter program gave punched paper tape output directly, while for the former a time-share program (A. Parkes and P. F. S.) was written to obtain paper tape output. Preliminary lattice and orientation angle refinement was carried out on the time-share program PICK1 (P. F. Stokely and A. Parkes, MIT, 1968), a variant of PICK2. PICK2 also provides variable scan ranges which increase as the spread of the α_1-α_2 doublet increases.

The 7094 program PMMO (M. J. Bennett, MIT, 1965) was used to convert intensity data to structure factors for the sodium salt. The dibenzenesulfonamide data were processed by the 360 program DIFDAR (A. Parkes, MIT, 1968), which is designed to handle the general settings and variable scan range obtainable when PICK2 is used for computing diffractometer settings. Both programs provide correction for Lorentz and polarization effects and compute esd's for the structure factors. The program GONO9 (W. C. Hamil-

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(7) W. A. Zachariasen, *Acta Cryst.*, **16**, 1139 (1963).

Table VI. Temperature Parameters of Atoms in Sodium Dibenzenesulfonamide[a]

Atom	B	β_{11}	β_{22}	β_{33}	β_{12}	β_{15}	β_{23}
S(1)		0.00255 (9)	0.00241 (8)	0.00592 (23)	0.00016 (4)	0.00001 (8)	0.00013 (8)
S(2)		0.00251 (9)	0.00255 (9)	0.00610 (24)	0.000010 (4)	0.00008 (8)	0.00019 (7)
Na(1)	3.31 (9)						
Na(2)	3.25 (9)						
		0.0030 (2)	0.0026 (2)	0.0060 (5)	0.00006 (17)	0.0011 (2)	0.0002 (3)
O(1)		0.0039 (2)	0.0037 (2)	0.0074 (5)	−0.0007 (1)	0.0010 (2)	0.0013 (2)
O(2)		0.0034 (2)	0.0030 (2)	0.0097 (5)	0.0005 (1)	−0.0003 (2)	0.0009 (2)
O(3)		0.0038 (2)	0.0037 (2)	0.0068 (5)	−0.0002 (2)	0.0009 (2)	0.0006 (2)
O(4)		0.0046 (2)	0.0023 (2)	0.0099 (6)	−0.0005 (1)	−0.0016 (3)	−0.0006 (2)
C(1)	2.7 (1)						
C(2)	3.8 (1)						
C(3)	4.8 (1)						
C(4)	4.8 (1)						
C(5)	4.8 (1)						
C(6)	3.9 (1)						
C(7)	3.0 (1)						
C(8)	4.5 (1)						
C(9)	6.3 (2)						
C(10)	6.6 (2)						
C(11)	6.4 (2)						
C(12)	4.7 (1)						

[a] Estimated errors in last significant figure are in parentheses.

ton, 1960) in a version for the IBM 360 was used for absorption corrections.

The programs FAME, MAGIC, LINK, and SYMPL (Dewar and Stone, University of Chicago, 1966) for centric space groups of orthorhombic or lower symmetry, were modified for the 360/65 by P. F. Stokely.

Results

The only significant qualitative difference between the molecular geometry of dibenzenesulfonamide (DBSA) and that of its anion (DBSA⁻) is in the rotational orientation of the groups bound to the tetrahedral sulfur atoms. As may be seen in Figure 3, the phenyl rings lie on opposite sides of the S–N–S plane in DBSA and on the same side of this plane in DBSA⁻. The *trans* configuration in the former minimizes the overall steric interference in the molecule, while the *cis* configuration found in the anion permits each of the electronegative nitrogen and oxygen atoms to approach the sodium ions closely. These rotational orientations are equivalent in terms of the kind and amount of covalent bonding permitted between the sulfur atoms and the atoms attached to them.

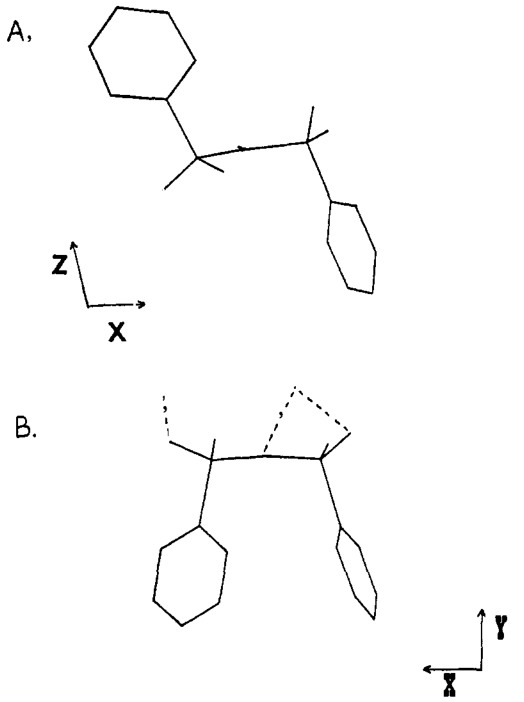

Figure 3. Orthographic projection of (A) dibenzenesulfonamide and (B) the dibenzenesulfonamide anion, showing their rotational orientations.

The idealized point group symmetry of the dibenzenesulfonamide molecule is C_2, while that of the anion, neglecting the tilt of the phenyl rings, is C_s. However,

Table VII. Bond Lengths (Å) in Sodium Dibenzenesulfonamide[a]

S(1)–N	1.598 (5)	C(3)–C(4)	1.379 (11)
S(1)–O(1)	1.441 (5)	C(4)–C(5)	1.386 (11)
S(1)–O(2)	1.456 (5)	C(5)–C(6)	1.386 (11)
S(1)–C(1)	1.777 (6)	C(6)–C(1)	1.374 (9)
S(2)–N	1.571 (5)	C(7)–C(8)	1.382 (10)
S(2)–O(3)	1.453 (5)	C(8)–C(9)	1.414 (12)
S(2)–O(4)	1.435 (5)	C(9)–C(10)	1.387 (14)
S(2)–C(7)	1.769 (6)	C(10)–C(11)	1.383 (14)
C(1)–C(2)	1.384 (9)	C(11)–C(12)	1.397 (13)
C(2)–C(3)	1.379 (10)	C(12)–C(7)	1.377 (10)

[a] Estimated errors in last significant figure are in parentheses.

Table VIII. Bond Angles (deg) in Sodium Dibenzenesulfonamide[a]

S(1)–N–S(2)	127.5 (3)	S(2)–C(7)–C(8)	118.6 (5)
O(1)–S(1)–O(2)	115.8 (3)	S(2)–C(7)–C(12)	119.3 (5)
O(1)–S(1)–N	115.3 (3)	C(1)–C(2)–C(3)	119.2 (7)
O(2)–S(1)–N	104.2 (3)	C(2)–C(3)–C(4)	120.0 (7)
C(1)–S(1)–O(1)	106.6 (3)	C(3)–C(4)–C(5)	120.5 (8)
C(1)–S(1)–O(2)	106.4 (3)	C(4)–C(5)–C(6)	119.6 (8)
C(1)–S(1)–N	107.8 (3)	C(5)–(C6)–C(1)	119.3 (7)
O(3)–S(2)–O(4)	115.7 (3)	C(6)–C(1)–C(2)	121.3 (6)
O(3)–S(2)–N	112.8 (3)	C(7)–C(8)–C(9)	118.5 (8)
O(4)–S(2)–N	106.5 (3)	C(8)–C(9)–C(10)	119.0 (9)
C(7)–S(2)–O(3)	106.4 (3)	C(9)–C(10)–C(11)	121.8 (9)
C(7)–S(2)–O(4)	106.7 (3)	C(10)–C(11)–C(12)	118.9 (9)
C(7)–S(2)–N	108.3 (3)	C(11)–C(12)–C(7)	119.6 (8)
S(1)–C(1)–C(2)	119.6 (5)	C(12)–C(7)–C(8)	122.1 (7)
S(1)–C(1)–C(6)	119.1 (5)		

[a] Estimated errors in last significant figure are in parentheses.

there are no *crystallographic* symmetry requirements on any pairs of bond lengths, so each distance, in general, is determined independently twice. Intermolecular forces, notably hydrogen bonding in DBSA and electrostatic interactions with Na^+ ions in $DBSA^-$, produce significant deviations from the idealized point group symmetry.

The estimated errors given for individual bond lengths and angles take into account both the least-squares estimated standard deviations and the estimated cell edge errors. Neither the bond lengths nor their errors have been corrected for thermal motion. It appears that the estimated standard deviations of some bond lengths, particularly those of the benzene rings, are somewhat underestimated for this reason.

Coordination about Nitrogen. The coordination about the nitrogen atom in DBSA is planar within the estimated errors. The S–N–S angle is 127.7 ± 0.3°, the S(1)–N–H angle is 124.9 ± 2.8°, and the S(2)–N–H angle is 107.3 ± 2.9°. The average S–N distance is 1.650 ± 0.007 and the N–H distance is 1.01 ± 0.06 Å. The nitrogen atom lies in the plane of the S and H atoms within the estimated error of 0.005 Å. As will be discussed, the hydrogen atom is involved in a hydrogen bond to an oxygen atom of a neighboring molecule.

In $DBSA^-$, the S–N–S angle is 127.5 ± 0.3°, essentially identical with that found in DBSA. The S–N distances, however, are significantly shorter, the average value being 1.580 ± 0.009 Å. The difference between the S–N distances in DBSA and $DBSA^-$ is thus 0.07 Å, which is 14σ and eight times the deviation from the mean of the two independent values for each distance. This is highly significant and is the only large bond length change between DBSA and its anion.

Coordination about Sulfur. The sulfur atoms in both molecules have a distorted tetrahedral coordination. In DBSA there is an appreciable variation of S–O distances between 1.386 ± 0.005 and 1.442 ± 0.005 Å. The average of the deviations from the mean S–O distance, 1.415 Å, is 0.018 Å. The principal reason for the variation is apparently the participation of O(1) in intermolecular hydrogen bonding, which results in the long distance of 1.442 Å for S(1)–O(1) and the short distance of 1.386 Å for S(1)–O(2). The S–O distances about sulfur(2) vary less (1.425 and 1.409 Å) since no hydrogen bonding takes place involving these oxygen atoms. If the disparity in the S(1)–O(1) and S(1)–O(2) distances is discounted because of the hydrogen bonding involved, and only the S(2)–O(3) and S(2)–O(4) distances are taken as representative S–O distances for DBSA, the mean is 1.417 Å with a deviation from the mean of 0.009 Å.

In $DBSA^-$, the S–O distances range from 1.435 to 1.456 Å with standard deviations of 0.005 Å. The average S–O distance is 1.446 Å and the average deviation from this value is 0.008 Å. Thus, the average S–O distance in $DBSA^-$ is 0.030 ± 0.017 Å longer than the average distance in DBSA, which is significant at about the 90% confidence level.

The S–C distances in DBSA are 1.763 and 1.755 ± 0.006 Å, which yield an average value of 1.759 Å with a deviation from the mean of 0.004 Å. In the salt, the two values are 1.769 and 1.777 ± 0.006 Å, which deviate by 0.006 Å from the mean value of 1.773 Å. Therefore, the average S–C value in $DBSA^-$ is 0.014 Å longer than that in DBSA, a difference of just over 2σ.

Thus when DBSA is deprotonated, the S–N distances become substantially shorter, while the S–O and the S–C distances become longer by slight but probably significant amounts.

The bond angles about the sulfur atoms in DBSA are somewhat distorted from ideal tetrahedral angles. This appears to be due to nonbonding intramolecular contacts which are shown in Table IX. The contact distances O(1)–O(2) and O(3)–O(4), and all the N–O contacts are closely bunched in the range 2.4–2.5 Å, indicating that the tetrahedra have been altered in a way that produces a minimum of steric interference.

Table IX. Principal Nonbonding Contact Distances (Å) in Dibenzenesulfonamide[a]

Intramolecular		Intermolecular, under 3.5 Å[b]	
H–O(3)	2.36 (8)	C(3)–O(4′)	3.420 (8)
H–O(2)	2.73 (9)	C(9)–O(2″)	3.301 (9)
O(3)–O(2)	>3.5	H–O(1‴)	1.80 (10)
O(4)–O(1)	2.994 (6)	N–O(1‴)	2.854 (6)
O(1)–O(2)	2.457 (6)	O(3)–O(1‴)	3.399 (7)
O(3)–O(4)	2.470 (7)		
O(1)–C(6)	3.174 (8)		
O(2)–C(2)	2.868 (9)		
O(3)–C(8)	3.057 (8)		
O(4)–C(12)	2.917 (8)		
N–O(1)	2.454 (6)		
N–O(2)	2.426 (6)		
N–O(3)	2.417 (7)		
N–O(4)	2.497 (6)		
N–C(7)	2.751 (8)		
N–C(1)	2.737 (8)		
O(3)–C(7)	2.604 (8)		
O(4)–C(7)	2.586 (8)		
O(1)–C(1)	2.620 (8)		
O(2)–C(1)	2.561 (7)		

[a] Estimated errors in last significant figure are in parentheses.
[b] The translation operations indicated by primed numbers are: (′) = $x - 1, y, z$; (″) = $1 - x, 1 - y, -z$; (‴) = $1 - x, {}^1/_2 - y, {}^1/_2 - z$.

In the sodium salt, the geometry of the molecule is dictated principally by the orientation of the nitrogen and oxygen atoms around the sodium ions due to electrostatic attractions. As can be seen in Figure 2, the angle N–S(1)–O(2), for example, is contracted to 104° because of the location of Na(1) above and between them. The nonbonding contact distances in the salt are given in Table X. The most noteworthy intramolecular contacts are O(1)–O(3), 2.928 ± 0.007 Å, and the two closest contacts between the rings, C(2)–C(8), 3.44 ± 0.01, and C(1)–C(8), 3.40 ± 0.01 Å.

Coordination about the Na^+ Ion. The sodium ions of the salt lie on special positions on twofold axes, and the coordination about each is a distorted octahedron. Na(1) has as its nearest neighbors N, O(2), and O(3), each represented twice from a total of four molecular units. Na(2) is surrounded by O(1), O(3), and O(4), similarly drawn from four different molecules. The distances are given in Table XI.

Benzene Rings. The equations of the best planes describing the benzene rings and the distances of the carbon atoms from these planes are given for DBSA in Table XII and for $DBSA^-$ in Table XIII. The planarity of the rings is quite good; however, the individual

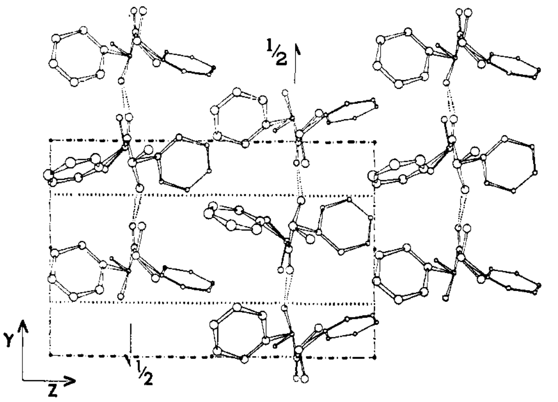

Figure 4. A molecular packing diagram of dibenzenesulfonamide. The projection is down the *a* axis. The molecules are linked together into chains by hydrogen bonds, represented by dotted lines.

bond lengths and angles in DBSA show considerable fluctuation. This may be attributable to the relatively high thermal motion of the carbon atoms of the ring, as indicated by their isotropic temperature factors, which ranged up to six in both structures. It is probable that this thermal motion is highly anisotropic and that the use of isotropic temperature factors provided inadequate allowance for this. There were not sufficient data available for DBSA to permit anisotropic refinement for the carbon atoms and still maintain a high (10:1) data-to-parameter ratio.

Table X. Principal Nonbonding Contact Distances (Å) in Sodium Dibenzenesulfonamide[a]

Intramolecular		Intermolecular[b]	
O(1)-O(2)	2.454 (6)	O(4)-O(1′)	3.260 (6)
O(3)-O(4)	2.446 (6)	O(3)-N(1′)	3.351 (7)
O(1)-O(3)	2.928 (7)	O(3)-O(4′)	3.283 (6)
O(2)-O(4)	>3.5	O(4)-O(3″)	3.366 (7)
N-O(1)	2.562 (7)	N(1)-O(3″)	3.103 (7)
N-O(2)	2.404 (7)	O(2)-C(4‴)	3.408 (9)
N-O(3)	2.520 (7)	O(4)-C(4⁗)	3.420 (9)
N-O(4)	2.411 (7)		
N-C(1)	2.723 (8)		
N-C(7)	2.710 (8)		
C(1)-O(1)	2.589 (7)		
C(1)-O(2)	2.596 (7)		
C(7)-O(3)	2.586 (8)		
C(7)-O(4)	2.578 (9)		
C(2)-O(1)	2.879 (8)		
C(6)-O(2)	3.109 (8)		
C(8)-O(3)	3.009 (9)		
C(12)-O(4)	2.873 (9)		
C(1)-C(8)	3.401 (10)		
C(2)-C(8)	3.438 (11)		

[a] Estimated errors in last significant figure are in parentheses. [b] The translation operations indicated by primed numbers are: (′) = $1 - x, 1 - y, 1 - z$; (″) = $x, 1 - y, {}^1/_2 - z$; (‴) = ${}^1/_2 + x, {}^1/_2 - y, 1 - z$; (⁗) = ${}^1/_2 - x, {}^1/_2 - y, z$.

Table XI. Contact Distances (Å) about the Sodium Ions in Sodium Dibenzenesulfonamide[a]

Contact	Distance	Symmetry operation generating second atom
Na(1)-N(1)	2.683 (5)	x, y, z; $1 - x, y, {}^3/_2 - z$
Na(1)-O(2)	2.396 (5)	x, y, z; $1 - x, y, {}^3/_2 - z$
Na(1)-O(3)	2.342 (5)	$1 - x, 1 - y, 1 - z$; $x, 1 - y, {}^1/_2 - z$
Na(2)-O(4)	2.354 (5)	x, y, z; $1 - x, y, {}^3/_2 - z$
Na(2)-O(1)	2.349 (5)	$1 - x, 1 - y, 1 - z$; $x, 1 - y, {}^1/_2 + z$
Na(2)-O(3)	2.489 (5)	$1 - x, 1 - y, 1 - z$; $x, 1 - y, {}^1/_2 + z$

[a] Estimated errors in last significant figure are in parentheses.

Table XII. Equations of the Best Planes of the Benzene Rings in Dibenzenesulfonamide and the Distances (Å) of the Carbon Atoms from the Planes

Ring 1: $0.2741x + 0.9219y + 0.2738z - 5.6056 = 0$	
C(1)	−0.0058
C(2)	0.0037
C(3)	−0.0034
C(4)	0.0059
C(5)	−0.0102
C(6)	0.0099
Ring 2: $0.8782x + 0.4138y + 0.2398z - 7.9727 = 0$	
C(7)	−0.0101
C(8)	0.0085
C(9)	−0.0051
C(10)	0.0034
C(11)	−0.0080
C(12)	0.0115

Table XIII. Equations of the Best Planes of the Benzene Rings of Sodium Dibenzenesulfonamide and Distances (Å) of the Carbon Atoms from the Planes

Ring 1: $0.3081x - 0.9233y + 0.2296z + 2.7125 = 0$	
C(1)	0.0038
C(2)	0.0021
C(3)	−0.0094
C(4)	0.0083
C(5)	0.0014
C(6)	−0.0062
Ring 2: $-0.2070x - 0.6918y + 0.6918z + 3.9201 = 0$	
C(7)	0.0066
C(8)	−0.0077
C(9)	0.0004
C(10)	0.0129
C(11)	−0.0106
C(12)	−0.0015

Molecular Packing. A drawing of the molecular packing of the DBSA unit cell appears in Figure 4. The molecules are seen to be linked together into chains by rather strong N-H···O(1) hydrogen bonds. These chains run parallel to each other and to the *b* axis. The N-H···O(1) distance is 2.854 ± 0.006 Å, which may be compared to N-H···O distances of 3.03 Å in methanesulfonanilide,[8] 2.94–3.17 Å in α-sulfanilamide,[9] 3.03–3.11 Å in β-sulfanilamide,[10] and 2.96–3.24 Å in γ-sulfanilamide,[11] all of whose molecules are linked pairwise by two or three hydrogen bonds. The N-H···O(1) angle is approximately 168°. The intermolecular contacts of less than 3.5 Å are listed in Table IX, and range from 3.30 Å for C(9)-O(2), upward.

The molecular packing of DBSA$^-$ is shown in Figure 5. The molecules are grouped about the sodium ions in such a way that all of the most electronegative atoms, the nitrogen atom and the four oxygen atoms, are in close proximity to at least one Na$^+$ ion. One oxygen atom, O(3), is near both sodium ions. Most of the

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(8) H. Klug, *Acta Cryst.*, **B24**, 792 (1968).
(9) B. H. O'Connor and E. N. Maslin, *ibid.*, **18**, 363 (1965).
(10) (a) A. M. O'Connell and E. N. Maslen, *ibid.*, **22**, 134 (1967); (b) M. Alléaume and J. Decap, *ibid.*, **18**, 931 (1965).
(11) M. Alléaume and J. Decap, *ibid.*, **19**, 934 (1965).

Table XIV. Comparison of Bond Distances in Dibenzenesulfonamide and Its Sodium Salt with Data for Similar Sulfonamides

	Sulfonamides					Sodium salts	
		p-$NH_2C_6H_4SO_2NH_2$					
Distances	p-$NH_2C_6H_4SO_2$-$NHCH_3$[b]	α[c]	β[d]	γ[e]	$(C_6H_4SO_2)_2$-NH[f]	$(C_6H_4SO_2)_2$-N^- [f]	p-$NH_2C_6H_4$-SO_2NH^- [g]
S–O	1.443 (2)	1.47 (1)	1.45 (17)	1.452 (14)	1.441 (5) 1.386 (5)	1.441 (5) 1.453 (5)	1.460[a]
	1.425 (2)	1.41 (1)	1.448 (14)	1.438 (19)	1.426 (5) 1.409 (5)	1.456 (5) 1.435 (5)	1.449
S–N	1.633 (2)	1.61 (1)	1.620 (16)	1.666 (15)	1.643 (5) 1.657 (5)	1.589 (5) 1.571 (5)	1.540
S–C	1.746 (2)	1.74 (1)	1.750 (18)	1.739 (14)	1.763 (7) 1.756 (6)	1.776 (6) 1.769 (6)	1.781

[a] Esd's not stated. [b] Reference 8. [c] Reference 9. [d] Reference 10. [e] Reference 11. [f] This work. [g] Reference 12.

shortest intermolecular contacts, 3.1–3.35 Å, are between the atoms surrounding the sodium ions. The closest intermolecular approach to a ring carbon atom is made by an oxygen atom at a distance of 3.41 Å.

Discussion

The crystallographic results indicate that, aside from a change in rotational configuration, there is no qualitative difference between the molecular geometry of DBSA and the DBSA⁻ anion. To facilitate comparison of these results with data for similar aromatic sulfonamides, the important bond lengths obtained in the present study are presented in Table XIV alongside the equivalent data for methanesulfonanilide,[6] p-$NH_2C_6H_4SO_2NHCH_3$, three crystalline polymorphs of sulfanilamide,[9–11] p-$NH_2C_6H_4SO_2NH_2$, and the sodium salt of sulfanilamide.[12]

Comparing DBSA with the other sulfonamides, it may be seen that there is general agreement of the results. The S–O distances are mostly in the range 1.40–1.45 Å. The S–N distances range from 1.61 to 1.666 Å, while the S–C distances are 1.74–1.76 Å. There are no significant differences between the DBSA bond lengths and those in the other compounds listed. The structure of yet another crystalline form of sulfanilamide, the monohydrate, has recently been reported[13] and the molecular dimensions do not differ significantly from those tabulated.

The one salt of a sulfonamide whose structure has been determined previously, the sodium salt of sulfanilamide,[12] is seen to be similar in its interatomic distances to $DBSA^-$. The bond length differences between sulfanilamide and its anion are similar to those found in this study, but are a little more pronounced. In particular, the S–N distance in the salt of sulfanilamide is 1.540 Å, significantly shorter than the average value of 1.580 Å obtained for $DBSA^-$. The hydrogen atom positions in the sulfanilamide salt were not reported, so it is impossible to compare the nitrogen coordination in the two salts. The available evidence, however, indicates that there is no significant qualitative difference between dibenzenesulfonamide and sulfanilamide with respect to the changes in molecular dimensions which occur following deprotonation. The great difference in acidity between the two sulfonamides (the pK_a of sulfanilamide is 10.5, or essentially the same as benzenesulfonamide[2]) thus does not result from any atypical structural characteristic of DBSA, or of its conjugate base.

The lengths of the bonds connecting nitrogen and oxygen atoms to sulfur atoms in DBSA are all significantly shorter than the values predicted for pure single bonds, *viz.* S–O = 1.69 Å, S–N = 1.74 Å, by Shomaker and Stevenson.[14] Similar shortening of bonds to sulfur atoms has been observed in the structures of sulfonamides[8–13] and attributed to π bonds involving the sulfur d orbitals and lone pair p orbitals of the coordinated atoms. The nature of π bonding to tetrahedral sulfur has been discussed by Cruickshank,[15] who pointed out that while group theoretical treatment of the d orbitals of tetrahedral sulfur yielded five possible π-bonding molecular orbitals, only two of these are of strongly π-bonding character. These utilize the $d_{x^2-y^2}$ and d_{z^2} orbitals which comprise the E_g representation. These two orbitals are available for both parallel and perpendicular π bonding with the attached atoms. Thus bonds to coordinated atoms with available p orbitals may assume a fractional π-bond character so that the total double bond order is approximately two.

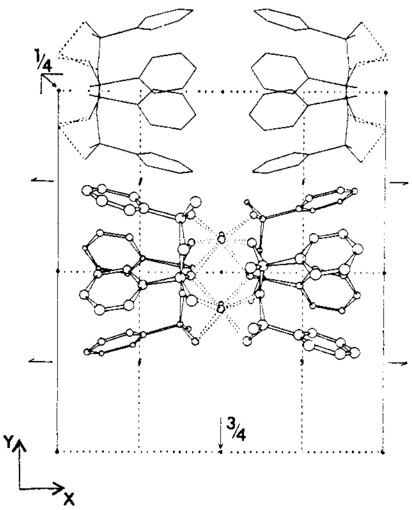

Figure 5. A molecular packing diagram of the sodium salt of dibenzenesulfonamide. The projection is down the *c* axis. Na–O and Na–N coordinate bonds are represented by dotted lines.

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(12) J. Moréno and M. Alléaume, *Compt. Rend.*, **C267**, 64 (1968).

(13) M. Alléaume and J. Decap, *Acta Cryst.*, **B24**, 214 (1968).

(14) V. Shomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941).

(15) D. W. J. Cruickshank, *J. Chem. Soc.*, 5486 (1961).

Cruickshank cites bond order data to show that in sulfates and sulfamides the total double bond order is, in fact, very nearly two. In other words, the π molecular orbitals in these compounds are substantially occupied by lone pair electrons. Two of Cruickshank's examples have particular relevance to dibenzenesulfonamide. The pyrosulfate ion, $O_3S{-}O{-}SO_3^{2-}$, possesses a bent structure[16] with an S–O–S angle of 124°. The S–O(bridge) distance is 1.645 ± 0.005 Å and the other S–O distances are 1.437 ± 0.004 Å. Cruickshank assigns a double bond order of 0.2 to the bridge bonds and 0.60 to the terminal bonds. Closely similar dimensions are found when the bridge oxygen atom is replaced by an NH group, as in the iminodisulfonate ion, $O_3SNHSO_3^{2-}$. In $K_2NH(SO_3)_2$ the data[17] are S–N–S = 125.5°, S–N(bridge) = 1.662 ± 0.005 Å, and S–O = 1.453 ± 0.005 Å.

The results obtained for dibenzenesulfonamide in this study are S–N = 1.650 ± 0.007 Å, S–O = 1.415 ± 0.018 Å, and S–N–S = 127.7°. The distances are seen to be somewhat shorter than those in iminodisulfonate, presumably because the π bond order in the S–C bond is less than that of a third S–O(terminal) bond, resulting in higher bonding electron densities in the remaining bonds. Alléaume and Decap[18] have estimated the S–C double bond order in sulfanilamides to be approximately 40%, which is probably greater than is the case in DBSA, in which the average S–C distance of 1.759 ± 0.004 Å is somewhat longer than those (1.74–1.75 Å) found in sulfanilamides. Cruickshank assigns a π bond order of approximately 0.7 to S–O bonds of length 1.42 Å. Assuming the S–N bond order to be similar to that in the iminodisulfonate ion, or approximately 0.2, the total π bond order to each sulfur atom due to oxygen and nitrogen atoms alone is 1.6. There is probably also a small contribution from the carbon atoms, as the average S–C distance in DBSA, 1.759 Å, is somewhat shorter than the value of 1.77 Å found in compounds where no π bonding between carbon and sulfur atoms is possible, *e.g.*, methyl sulfones.[18] Thus the maximum π bond order of two apparently is nearly realized in DBSA.

There is evidence other than bond length data to support the conclusion of a strong π bond character of the S–N bond in DBSA and related molecules. The planarity of the coordination about the nitrogen atom in DBSA indicates, as has been mentioned, that the orbital hybridization of the nitrogen orbitals is very close to sp^2. This places a nearly pure p orbital in suitable position for π bonding to both sulfur atoms.

This planarity is observed in methanesulfonanilide,[8] in which the S–N–C angle is 120°. The structure of $(CH_3)_2NSO_2N(CH_3)_2$, reported by Jordan, *et al.*,[19] contains S–N–C angles which average 119°, with the nitrogen atom just 0.27 Å out of the plane of the atoms bound to it. In an accompanying[19] LCAO–MO calculation of the isoelectronic $F_2NSO_2NF_2$ molecule, those workers reported results consistent with significant dπ–pπ interactions in the bonds involving sulfur atoms.

Studies of the basicities of sulfonamides lend further support to this conclusion. Proton nmr data[20–22] of sulfonamides in acidic media indicate that protonation occurs on the nitrogen atom. The chemical shift changes of the methyl hydrogen atoms in the group $CH_3SO_2NCH_3$ indicate that protonation on the nitrogen atom causes less deshielding of the NCH_3 group than of the SCH_3 group.[22,23] Since a positive charge must be localized on the nitrogen atom in the protonated species, this result indicates that the unprotonated sulfonamide also has a substantial positive charge on the nitrogen atom and a considerable negative charge on the sulfur atom. This is consistent only with a formulation of the S–N bond in which dπ–pπ bonding draws substantial electron density from the nitrogen lone pair orbital into the sulfur d orbital system.

The results obtained in the present study, indicating that the nitrogen atom of DBSA fails to assume sp hybridization following deprotonation, show that it is not energetically favorable to create a second N–S dπ–pπ molecular orbital. The lengthening of the S–O and S–C distances of the conjugate bases of both DBSA and sulfanilamide indicates that the N–S bond can be strengthened only at the expense of weakening the other bonds to the sulfur atom. This provides confirmation that the available dπ–pπ bonding orbitals in sulfonamides are essentially filled to capacity with electron density drawn from lone pair orbitals. The formal negative charge on the nitrogen atom of the conjugate base cannot, for this reason, be effectively delocalized throughout the system. The increased polarity of the S–N bond caused by the formal negative charge results in the shortening and strengthening of this bond in the anion, but there is evidently no further capacity in the sulfur d orbitals to make effective use of a second S–N π orbital.

The great acidity of dibenzenesulfonamide relative to benzenesulfonamide must therefore be attributed to the inherent electron-withdrawing power of the second phenylsulfonyl group. That this is sufficient to explain the magnitude of the difference in acidity between the two may be illustrated using aniline as an example. The pK_a of the deprotonation of aniline, $C_6H_5NH_2$, is 27.[24] Substituting a phenylsulfonyl group for an amine hydrogen atom results in N-phenylbenzenesulfonamide, $C_6H_5NHSO_2C_6H_5$. The pK_a for this compound[2] is 8.65, or nearly 20 p*K* units lower. In view of this, the reduction of the pK_a of benzenesulfonamide by 9 p*K* units, through an analogous replacement of an amide hydrogen atom by a phenylsulfonyl group, is not an incongruous result.

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