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A Database Study of the Bonding and Conformation of Bis-sulfonylamide/-imide Moieties

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Abstract

The bonding and conformational characteristics of bis-sulfonylamides and analogous imides are compared. Structures (44 altogether) containing $R—SO_2—NQ—SO_2—R'$ units were retrieved from the Cambridge Structural Database. They are either neutral ($Q = H$, alkyl or aryl groups, hereto atoms such as O and S) or charged ($Q = e^-$) and bearing the functions R, $R' = Me$, Et or Ph, respectively. The principal conformations of the $—SO_2—NQ—SO_2—$ bridge (open *versus* folded) are represented by sodium dibenzenesulfonamide (BSULFA) and dibenzenesulfonimide (NABSUF). In addition to the compounds possessing $Q =$ alkyl or aryl functions, complexes with N-metal bonds could clearly be distinguished. The dominant forms of $S^{VI}—X$ ($X = O$, N C) bonds are characterized and correlated with the bond angles formed around the S atoms. The marked difference between the archetypes of the S—N bonds (*i.e.* nitrogen charged or neutral) indicated that the interdependence of the $S—X$ bonds, *i.e.* the size and the shape of the $S^{VI}[O,O',N,C]$ tetrahedra, are principally governed by the environment of the N atoms. The conformation symmetry and dissymmetry of the charged and neutral $—SO_2—NQ—SO_2—$ moieties are described in terms of the internal rotations about the bonds in the $R—S—N—S—R'$ fragment.

1. Introduction

While preparing 2-nitro-4-trifluoromethylbenzenesulfonamide (Holdrege, Babel & Cheney, 1959) a by-product was recently identified (Bombicz, Czugler & Kálmán, 1995) as a sodium salt monohydrate of bis(2-nitro-4-trifluoromethylbenzenesulfonyl)imide (hereinafter NEWONE). It was obtained when the crude product of the reaction between 2-nitro-4-trifluoromethylbenezenesulfonyl chloride and aqueous ammonium hydroxide was treated with 10% sodium hydroxide solution followed by crystallization from water.

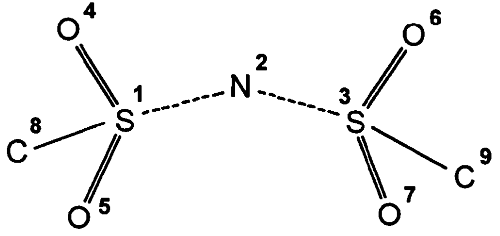
This prompted us to survey the occurrence of compounds possessing either the charged ($Q = e^-$) or neutral form ($Q = H$, C, O, S...) of the $—SO_2—NQ—SO_2—$ moiety. Consequently, all molecules having one or more bis-sulfonylamide or -imide fragments (Fig. 1) were retrieved from the Cambridge Structural Database (CSD, March 1994 release, 120 481 entries). By the use of the 3-D (three-dimensional) retrieval program *QUEST* (Allen & Kennard, 1993) 44 compounds (possessing altogether 57 fragments) were found, which were divided into three groups. Of these, together with NEWONE, 12 structures contain negatively charged nitrogen ($Q = e^-$), while 13 fragments belong to eight compounds containing N-metal bonds. A majority of the fragments (29) possess covalent $N—Q$ bonds. They have been classified in the third group (Table 1):

I: $Q = e^-$ (11 structures + NEWONE);

II: $Q =$ metals (Ag, Hg, In, Sn, Tl; 8 structures, 13 fragments);

III: $Q =$ atoms which form covalent bonds (21 structures, 28 fragments).

Two subgroups can be distinguished in group II and three in group III (see Table 1).



Bond lengths:	Bond angles:	Torsion angles:
*B*1: 1 2	*A*1: 2 1 4	*T*1: 4 1 2 3
*B*2: 1 4	*A*2: 2 1 5	*T*2: 5 1 2 3
*B*3: 1 5	*A*3: 2 1 8	*T*3: 8 1 2 3
*B*4: 1 8	*A*4: 4 1 5	*T*4: 1 2 3 6
*B*5: 2 3	*A*5: 4 1 8	*T*5: 1 2 3 7
*B*6: 3 6	*A*6: 5 1 8	*T*6: 1 2 3 9
*B*7: 3 7	*A*7: 1 2 3	
*B*8: 3 9	*A*8: 2 3 6	
	*A*9: 2 3 7	
	*A*10: 2 3 9	
	*A*11: 6 3 7	
	*A*12: 6 3 9	
	*A*13: 7 3 9	

Fig. 1. The atomic numbering of the CSO_2NSO_2C moieties retrieved from the Cambridge Structural Database.

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Table 1. *Fragments found as a result of CSD retrieval*

Classification: I: $Q = e^-$; II: Q = metals [II*A*: In, Tl; II*B*: Ag, Hg, Sn]; III: N—Q covalent bond [III*A*: H; III*B*: C, Si; III*C*: O, S].

I	II*A*	III*A*	III*C*
1 BIKVIA10	1 SOKLIN	1 BSULFA	1 CAMGAY
2 CUHNUO10	2 SOKLOT	2 DODNUF	2 DODNOZ
3 DEKCAX	3 VIYNEW	3 MSULIM	3 DODNOZ
4 JONSAG	4 VIYNEW	4 SIKYIU	4 DODNOZ
5 KUJYOD	5 VIYNEW	5 VEMKON	5 FADVEL
6 KURJEM	6 VIYNEW		6 JEHXAV
7 KURJOW		III*B*	7 JEHXID
8 NABSUF	II*B*	1 CADCUF	8 JORLOR
9 VASBOG	1 JUWNEU	2 DAYDEM	9 JORLOS
10 VATKEG	2 JUWNIY	3 DUGWEH01	10 KIMFAN
11 VEKMON	3 JUWNOE	4 DUGWEH01	11 KIMFAN
12 NEWONE	4 JUWNOE	5 DUGWIL01	12 KIMFER
	5 VOGJIK	6 JEXREJ	13 KIMFER
	6 VOGJIK	7 LATWEI	14 KIMFER
	7 WAKLUP	8 VOGJUW	15 KIMFER

The crystal lattice of LAGDUS (Blaschette, Hiemisch, Jones & Fischer, 1992) contains one charged and one neutral form of bis-dimesylamide, resulting in a mean of the bond lengths and angles, which could not be listed either in group I or in III and was omitted. Two structures with the S—N—S moiety embedded in a five-membered hetero ring [LAKNOA (group I) and WAKMAW (group II)], resulting in the shortest S—N bond lengths and planar conformations, differ characteristically from the other 44 structures and were omitted. Finally, in the course of studying the S—N bond distribution YABGOX, possessing an Se—N bond, was also omitted from the analysis.

2. Discussion

2.1. *Comparison of the conformation and bonding of BSULFA, NABSUF and NEWONE*

Of the 40 compounds retained, BSULFA and NABSUF [dibenzenesulfonamide and sodium dibenzenesulfonimide (Cotton & Stockely, 1970)] are closely related to NEWONE. Thus, NABSUF - without the second and third substituents of the phenyl rings - is the 'skeleton' of NEWONE, while BSULFA is the protonated form of NABSUF (Fig. 2). Consequently, they together gave a genuine possibility to measure the influence of the substituents and salt formation on the molecular structures.

The almost perfectly 'folded' conformation of NEWONE (Fig. 2) is similar to that of NABSUF, but substantially different from the open (elongated) form of BSULFA. The conformational similarities and differences assumed by the three related structures are depicted by the Newman projections (Fig. 3). In the salts; the rotations around the S—N bonds are approximately mirror-related, the mean difference in their absolute rotations is only $\Delta\varphi_{SN} = 6.6[3]$ and 8.1 [16]°,* respectively. Accordingly, the highest (C_{2v}) symmetry of the S—N—S bridge is reduced to C_s if the terminal benzene rings are neglected. In contrast, they differ significantly in BSULFA. Apart from the rotational difference of $\Delta\varphi_{SN} = 29.5[12]°$, they are related by a *pseudo*-twofold axis. Thus, the highest group symmetry of this fragment is approximately C_2. The relative position of the S^{VI}[O,O′,N,C] tetrahedra (hereinafter *A* and *B*), bound by the common N atom, can be expressed directly by the non-bonded torsion angles of the C—S···S′—C′ type, which is synperiplanar (folded shape) for NEWONE and NABSUF [−7.8 (3) and −7.6 (3)°, respectively] and antiperiplanar (open shape) for BSULFA [158.7 (3)°]. In each N-arylsulfonyl moiety the best plane of the phenyl ring is eclipsed with one of the S=O bonds. Simultaneously, this S=O bond in both NSO_2R groups of NEWONE is synclinal with the N—S′ bond. These two bonds are synperiplanar in group *A* and antiperiplanar in group *B* of NABSUF, whereas they are, respectively, synclinal and anticlinal in BSULFA. In addition, the dihedral angle of the phenyl rings for NEWONE is only 14.1 (3)° *versus* 42.0 (3) and 46.5 (3)° observed in NABSUF and BSULFA, respectively.

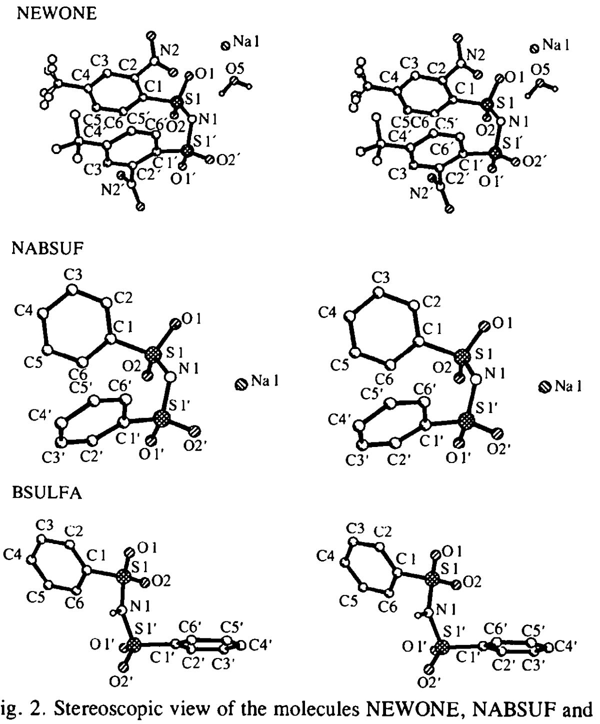

Fig. 2. Stereoscopic view of the molecules NEWONE, NABSUF and BSULFA. NABSUF is the 'skeleton' of NEWONE - with no substituents on the phenyl ring - while BSULFA is the N-protonated derivative of NABSUF.

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* To distinguish between e.s.d. and r.m.s. error estimates, the former are given hereinafter in parentheses, while the latter in square brackets.

The deformation of the terminal rings in BSULFA and NABSUF is determined by the sulfonyl group. The mean bond angle 122.2 [7]° at the *ipso*-C atoms is close to the prediction of Domenicano & Murray-Rust (1979) for mono-substituted benzene derivatives. It is accompanied by narrower bond angles in *ortho*-positions (mean value 118.7 [7]°). In NEWONE the superposition of the electronic effects of *ortho*-nitro and *para*-trifluoromethyl substituents (nitro group $-M$ and $-$I; F atoms $+M$ and $-$I) give rise to a contracted angle (117.9 [3]°) at the *ipso*-C counterbalanced by equally increased bond angles at the *ortho*-C atoms (mean value: 121.5 [6]°).

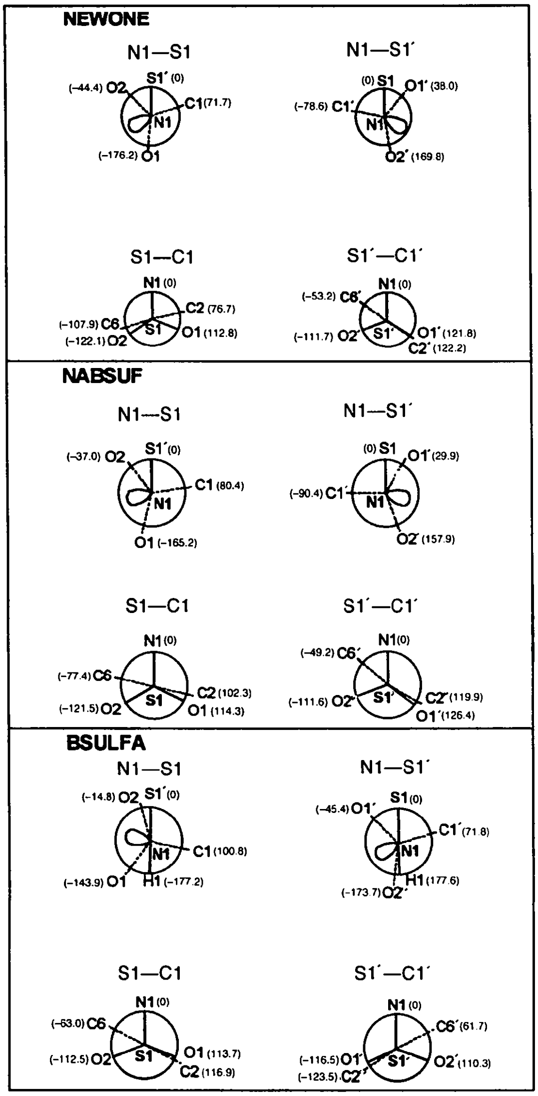

Fig. 3. The conformational similarities and differences in disulfonylamide/-imide moieties as observed in NEWONE, NABSUF and BSULFA, shown by the Newman projections perpendicular to the N—S and S—C bonds.

In both Na^+ salts the S—N bond lengths are significantly shorter [1.590 (1) and 1.585 (1) Å for NEWONE and 1.598 (5) and 1.571 (5) Å for NABSUF] than in the neutral BSULFA molecule [1.644 (5) and 1.657 (5) Å]. The shorter S—N distances and the pronounced inequalities of the O—S—N angles (Kálmán, Czugler & Argay, 1981) in both NSO_2R groups *A* and *B* summarized in Table 2 refer to the delocalization of the negative charge, increasing the multiplicity of the S—N bonds. This seems to account for a slight increase of the mean S=O distance (1.441 [9] Å) and a more pronounced increase of the mean S—C bond distance (1.789 [17] Å) with respect to those observed in BSULFA (1.419 [20] and 1.755 [4] Å). Similarly, the longest S—N bonds [mean 1.651 (5) Å] - in accordance with Gillespie's (1963) rules - give rise to the largest O—S—O angles [mean 120.7 (4)°] in BSULFA and *vice versa*.

2.2. *Database analysis*

The dependence of the S=O and S—C bond lengths and O—S—O angles on the characteristically different S—N distances observed between BSULFA, NABSUF and NEWONE, together with the N—S—O bond angle inequalities and the substantial difference between the conformation of the C—SO_2—N*Q*—SO_2—C fragments in the neutral (BSULFA) and ionized molecules (NABSUF and NEWONE), encouraged us:

(i) to characterize the S—N bonds against the differences in the nitrogen environment (charged N, N-metal and N-covalent bonds);

(ii) to prove the applicability of the *bond order conversation principle* (Johnston, 1961) and the *VSEPR* rules (Gillespie, 1963) on the S^{VI}[O,O′,N,C] tetrahedra;

(iii) to describe the intra- and intermolecular conditions of the folded conformation *versus* the energetically favourable open form of the C—SO_2—N*Q*—SO_2—C fragments;

(iv) to substantiate the observation (Kálmán *et al.*, 1981) on the difference between the O—S—N angles which was attributed to the synclinal position of one of the S=O bonds with the N lone pair;

by the analysis of the retrieved parameters (histograms and scattergrams) of the 41 structures (and NEWONE) listed in Table 1. This work could not have been done much earlier without the new accurate experimental data. A quick glance at the list of these structures reveals that, except for BSULFA, NABSUF (Cotton & Stockely, 1970) and MSULIN (Attig & Mootz, 1975), the others have been published since 1983 (among them 28 published since 1990), 2 years after our paper (Kálmán *et al.*, 1981), dealing with the properties of the S^{VI}[O,O′,N,C] tetrahedra. Our present work is supported also by the fact that the novel compounds classified in subgroups III*B* and III*C* extend

Table 2. *Relevant bond angles (°) and torsion angles (°) around the coupled N-arylsulfonyl groups*

		O1—S1—N1—S1′	O1—S1—N1		O1′—S1′—N1	O1′—S1′—N1—S1	S1′—N1—S1—C1
NEWONE	(*A*)	−44.4 (2)	114.3 (1)	≫	106.1 (1)	−176.2 (2)	71.5 (2)
	(*B*)	38.0 (2)	114.7 (1)	≫	106.1 (1)	169.8 (1)	−78.6 (1)
NABSUF	(*A*)	−37.0 (2)	112.8 (1)	≫	106.6 (1)	−165.2 (1)	80.4 (1)
	(*B*)	29.9 (2)	116.0 (1)	≫	104.3 (1)	157.9 (1)	−90.4 (1)
BSULFA	(*A*)	−14.9 (5)	104.8 (4)	≈	106.4 (4)	−144.1 (7)	100.8 (7)
	(*B*)	−45.5 (6)	108.6 (4)	>	103.1 (4)	−173.7 (7)	71.8 (6)

substantially the range of the S—N bond lengths observed in the $—O_2S—NQ—SO_2—$ moieties.

Prior to the analysis we must realise that the search fragment (Fig. 1) has C_{2v} topological symmetry, which yields an atomic permutational symmetry group of the order 8 and results in topological, but not necessarily numerical, equivalences between various parameters, *e.g.* *B*1 and *B*5, *A*1, *A*2, *A*8 and A9 *etc.* These parameters are only numerically equivalent if the 3-D symmetry exhibited by the fragment is identical to the 2-D (topological) symmetry. Thus, in a number of cases, we must analyse groups of parameters together as indicated in the subsequent text.

2.3. *Distribution of the S—N bonds and S—N—S angles in the retrieved fragments*

The high regression coefficient (0.986) of the plot (Fig. 4) of the S—N distances (*B*5) against their counterparts (*B*1) indicates a good internal consistency of the S—N bond pairs belonging to the same $O_2S—N—SO_2$ moiety. Naturally, with the decreasing multiple bond character, discrepancies within the S—N bond pairs are increased and the strict C_{2v} group symmetry of the SNS moiety is violated. Nevertheless, this plot enabled us to partition the numerical distribution of the S—N bond distances (*B*1 and *B*5), which are continuous in the range 1.57-1.76 Å, firstly into the three groups (I-III), defined above.

The shortest S—N distances form a sharp Gaussian peak at 1.591 [6] Å (Fig. 5). They belong to the compounds possessing charged (N^-) N atoms (group I). The subsequent wide and flat range 1.59-1.66 Å is occupied by the S—N bonds to which *metal* atoms are linked through the (partly charged) nitrogen (group II). A detailed analysis of the flat distribution reveals that the metal atoms coordinated to the nitrogen can be assigned to two subgroups (II*A* and II*B*) in terms of their coordination number to the nitrogen. The first flat peak about 1.614 [13] Å is formed by In and Tl complexes (SOKLIN, SOKLOT, VIYNEW) coordinated to only one $N(SO_2R)_2$ moiety. The second small but Gaussian peak around 1.651 [11] Å is built up of Ag, Hg and Sn complexes in which the metal atoms are coordinated simultaneously to two $N(SO_2R)_2$ fragments. The wide distribution of the S—N distances (1.63-1.76 Å) observed in neutral molecules with $Q = H$, C and hetero atoms, and classified in group III, divides into three subgroups. The first peak (III*A*) is formed around 1.641 [9] Å by five compounds (MSULIN, BSULFA, DODNUF, SIKYIU, VEMKON), where $Q = H$. This peak substantially overlaps that for subgroup II*B*. The second subgroup III*B* accommodates compounds where $Q = C$ and Si. They form a flat Gaussian distribution around 1.675 [10] Å. Finally, there is a third well shaped Gaussian distribution (subgroup III*C*) around 1.717 [15] Å in which the hetero atom is either O or S with electronegativity $\varepsilon \geq 2.5$. It is formed by 15 fragments, including CAMGAY which has *Q* with a group electronegativity greater than 2.5. In contrast, YABGOX with $Q = Se$, but possessing ε less than 2.5, was deliberately omitted from the plots formed between the parameters of the $S^{VI}[O,O',N,C]$ tetrahedra.

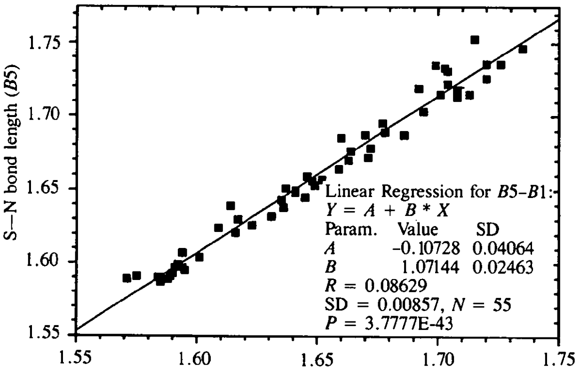

Fig. 4. Scattergram of the S—N distances *versus* their counterparts forming by pairs the same O_2SNSO_2 moieties.

The numerical distribution of S—N—S angles is more Lorentzian than Gaussian (Fig. 6) with a peak at ~120°, but there is no correlation between them and the S—N bonds. Interestingly, the S—N—S bond angles exhibited by NEWONE, NABSUF and BSULFA [125.5 (1), 127.5 (3) and 127.7 (3)°, respectively] fall into the upper range of the distribution.

2.4. *Distribution of the S=O and S—C bonds and their dependence on the S—N bond*

Following the direct comparison of NABSUF, NEWONE and BSULFA with further NSO_2C pairs taken from Table 1, with extremely different S—N distances, the interdependence of the S—*X* bonds is established (Table 3). Of course, the pairs selected at random exhibit different degrees of S—*X* dependence upon each other. Consequently, it is advisable to rationalize this analysis in terms of the S—N bond types defined in Fig. 5. First, the mean ⟨S=O⟩ values were calculated separately for each main group. The mean values for groups I and II are practically the same (1.441 [9] *versus* 1.439 [10] Å), but differ from those calculated for the neutral molecules listed in group III (1.422 [8] Å). Indeed, according to the double-bond order (p) estimates for the S—N and S=O bonds derived by the use of Coulson's (1939) formula, as modified by Liquori & Vaciago (1956)

$$B = S - (S - D)/[1 + 0.6625(1 - p)/p]$$

(B is an observed S—X bond length, S is the pure single-bond and D the pure double-bond distance), for the S—N bonds between 1.59 (group I) and 1.75 Å (subgroup III*C*), Δp is ~0.4, but it is attenuated asymmetrically on the S=O 'double' and S—C 'single' bonds. Consequently, the $\Delta p'$ response from each S—X bond gives rise to shortenings or lengthenings of only a few hundredths of an Ångström. Thus, their significance is guaranteed only by the newly published accurate data. Fortunately, the dependence of the S—X bonds on the S—N distances is sharpened by the charge of the N atoms.

Table 3. *Direct comparison of the S—X bonds (Å) of* NSO_2C *moieties taken at random by pairs from group I and subgroup IIIC listed in Table 1*

Compounds	S—N	S=O	S=O′	S—C
BIKVIA	1.585	1.449	1.434	1.779
JEHXID	1.735	1.420	1.418	1.757
ΔR	0.150 (+)	0.029 (−)	0.016 (−)	0.022 (−)
CUHNUO10	1.584	1.444	1.427	1.787
FADVEL	1.753	1.422	1.420	1.737
ΔR	0.169 (+)	0.022 (−)	0.007 (−)	0.050 (−)
KUJYOD	1.591	1.443	1.442	1.757
JORLOR	1.699	1.425	1.424	1.744
ΔR	0.108 (+)	0.018 (−)	0.018 (−)	0.013 (−)

This recognition discouraged us from the use of narrow Δ(S—N) intervals on the abscissa of the ⟨S=O⟩ plot. Therefore, group II (Q = metal) was not partitioned into the two small subgroups distinguished in terms of the coordination number of the metal atoms to nitrogen. Similarly, the subgroups Q = H (III*A*) and Q = C, SI (III*B*) are amalgamated and characterized by a grand mean of the S—N bond lengths. Accordingly, the S—N bonds are divided into four subsets: groups I and II, subgroups III*A*/*B* and III*C*. The plot of the mean ⟨S=O⟩ values against the ⟨S—N⟩ distances calculated for the four subsets (Fig. 7), as expected, shows their interdependence in a narrow range with a sharp ridge between group II and subgroup III*A*/*B*.

The numerical distribution of the S—C bonds collected from the 41 structures is wide but Gaussian with a centre of gravity around 1.756 Å

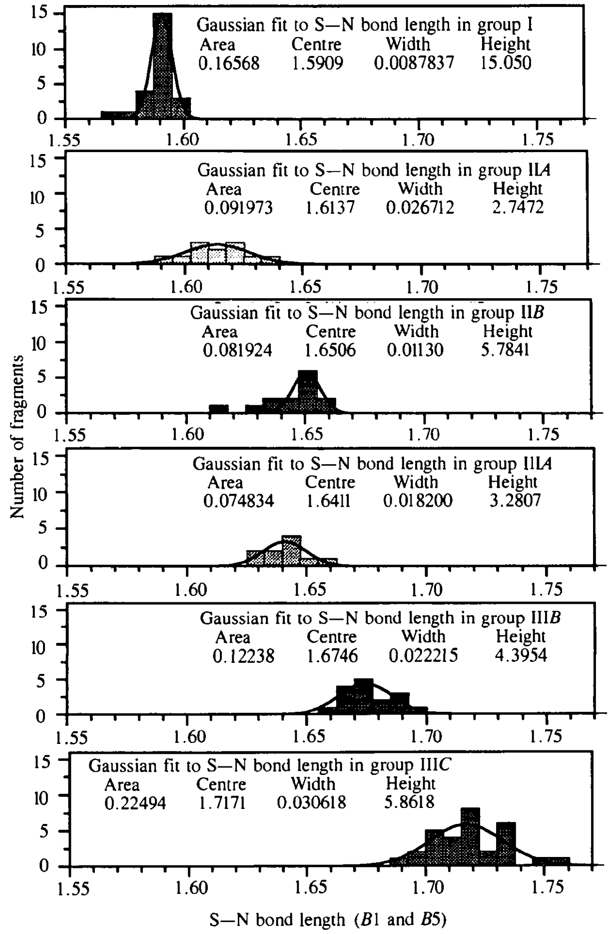

Fig. 5. Numerical distribution of the S—N bond lengths.

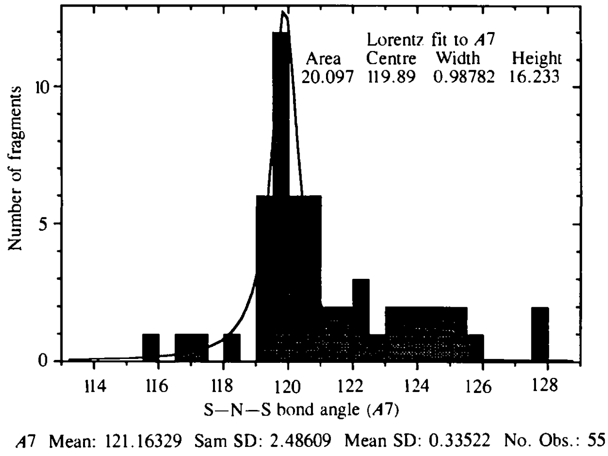

Fig. 6. Numerical distribution of the S—N—S bond angles. The peak of the nearly Lorentz distribution is around 120°.

and similar to the scattergram published earlier (*cf.* Fig. 4 in Kálmán *et al.*, 1981). However, partitioning this wide distribution into the four subsets defined above it can be seen (Fig. 8) that the longest S—C bonds fall in group I, while the shortest S—C bonds occur in group III. This means that not only the S=O but the S—C bond lengths, also in a narrow range of ~0.05 Å, are also dependent on the character of the S—N and S=O bonds.

2.5. *Correlation between the X—S—X′ bond angles and the corresponding S—X(X′) bonds*

As shown by the plot (solid square) depicted in Fig. 9, the ⟨O—S—O⟩ bond angles are dependent on the ⟨S—N⟩ distances. The mean value of 119.4 [8]° calculated for the neutral molecules (subgroups III*A*/*B* and III*C*) is significantly contracted (115.8 [8]°) for the ionized molecules (group I), indicating the repulsion exerted by the S—N multiple bonds on the S=O bonds (Gillespie, 1963).

Similarly, as shown by the plots of the mean ⟨O—S—C⟩ (solid triangle) and ⟨N—S—C⟩ (solid circle) bond angles against the corresponding ⟨S—N⟩ mean values which have a decreasing (charged⟶neutral) double-bond character of the S—N bonds, the ⟨O—S—C⟩ angles, in accordance with the VSEPR rules, are increasing, while the ⟨N—S—C⟩ angles are decreasing (Fig. 9). Of course, the mean of the six bond angles around S^{VI} remains as close to 109.5° as possible (*e.g.* 109.4 [46]° for NABSUF *versus* 109.3 [55]° for BSULFA). Finally, the plot of the mean ⟨O—S—O⟩ angles against the corresponding mean ⟨S=O⟩ distances (Fig. 10)* underscores once again the difference between the structures with charged N atoms and N-metal bonds (groups I and II), and those where the nitrogens bear covalently bonded substituents (group III).

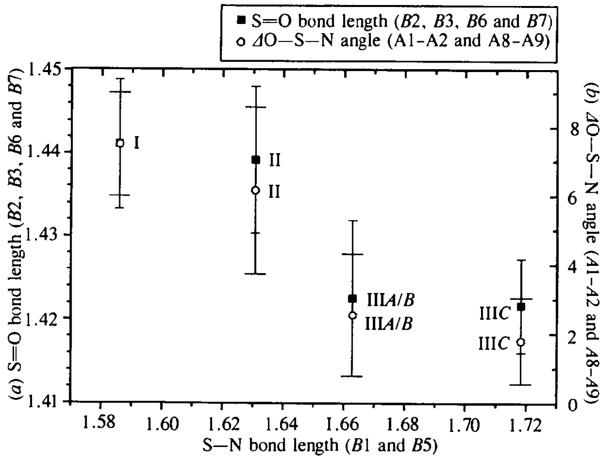

Fig. 7. (*a*) Plot *A* of the mean ⟨S=O⟩ bond lengths (scale on the left side) and (*b*) plot *B* of the mean ⟨O—S—N⟩ angle differences ⟨Δ_{OSN}⟩ (scale on the right side) *versus* the corresponding mean ⟨S—N⟩ bond lengths for groups I-III*C*. Each mean value is given with its Pearson's correlation coefficient calculated from the e.s.d.'s.

2.6. *Rotation about the S—N bonds*

Fig. 11 shows the scattergram of the C—S—N—S torsion angles. It differentiates those molecules possessing *R* = C(alkyl) moieties with an open circle, whereas the C(aryl)—S—N—S torsion angles are distinguished with a full triangle. The same sign for the *T*3/*T*6 pair of torsion angles indicates the open (elongated) conformation, different signs indicate the folded conformation. Of course, we must keep in mind that the four groups having *T*3/*T*6 with (*a*) −/+, (*b*) +/−, (*c*) +/− and (*d*) −/+ torsional sign combinations depicted in Fig. 11 derive simply from different 3-D enantiomorphs of the fragments as stored in the CSD: a true treatment of the topological symmetry problem would assign these pairs of torsional sign combinations to a single peak in each

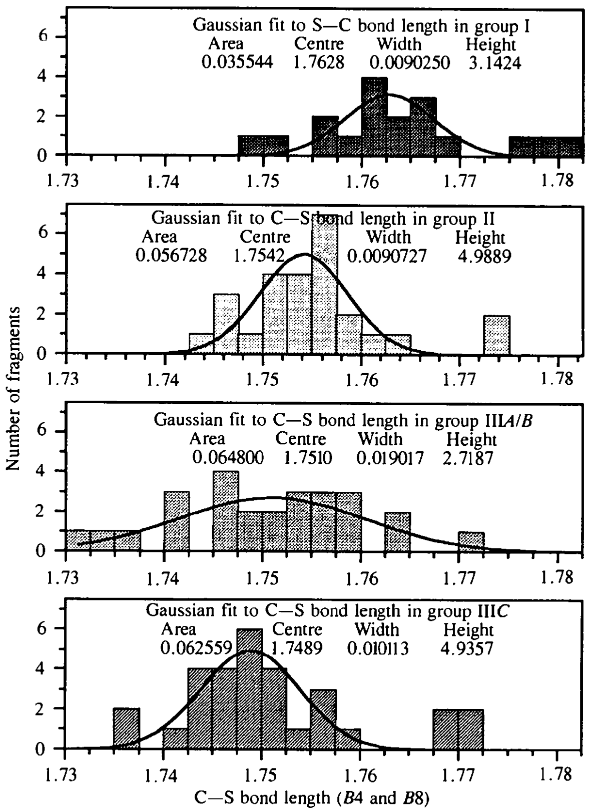

Fig. 8. Numerical distribution of the S—C distances partitioned in terms of groups I and II and subgroups III*A*/*B* and III*C*.

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* One of the oxygen coordinates of DAYDEM [O21, $x = 0.0052(3)$] was transcribed with an error (0.0552) to the CSD files, therefore, the corresponding NSO_2 moiety is skipped from the analysis.

case, yielding a two-peak asymmetric unit of $T3/T6$ space. At any rate, the scattergram substantiates the hindered rotation of the S^{VI}[O,O′,N,C] tetrahedra around the S—N bonds as reported earlier by Kálmán *et al.* (1981). In accordance with the energy calculation of Mezey & Kucsman (1972), synperiplanar torsion angles are missing and forbidden. From this it follows that the C_{2v} symmetry of a S—N—S triangle, if retained at all, is necessarily degraded in the 52 investigated fragments. Compounds such as bis-mesylamide, which occurs in different molecular associates (*e.g.* monohydrate MSULIN, moreover VATKEG) and also in imido form (VEKMON), may retain from C_{2v} not more than a C_2 axis. In MSULIN it corresponds to the crystallographic twofold axis in space group $C2/c$, while in DUGWIL01, VATKEG and VEKMON it is slightly distorted. At any rate, all compounds possessing an R = C(alkyl) group (except DODNOZ) assume the open form with a more or less approximate C_2 axis, as shown by a dense group close to the scattergram-diagonal from the lower-left to the upper-right corner. DODNOZ is formed by three SO_2Et moieties joined by a common N atom, therefore, three relative Et—S—N—S—Et conformations are shown, one of which must be folded.

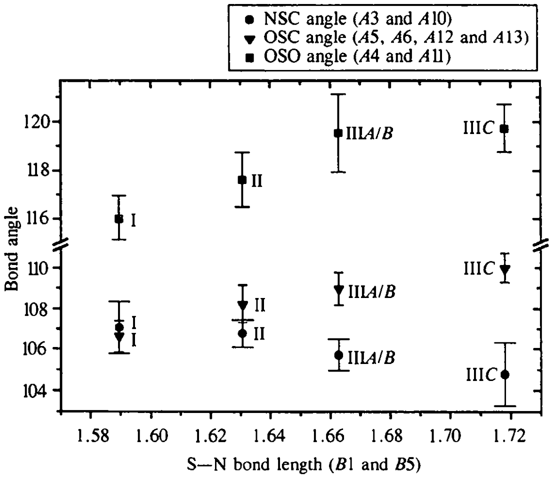

Fig. 9. Plots of the mean ⟨O—S—O⟩ (solid square), ⟨O—S—C⟩ (solid triangle) and ⟨N—S—C⟩ (solid circle) angles (°) *versus* the corresponding mean ⟨S—N⟩ bond lengths (Å) for groups I-IIIC. Each mean value is given with its Pearson's correlation coefficient calculated from the e.s.d.'s.

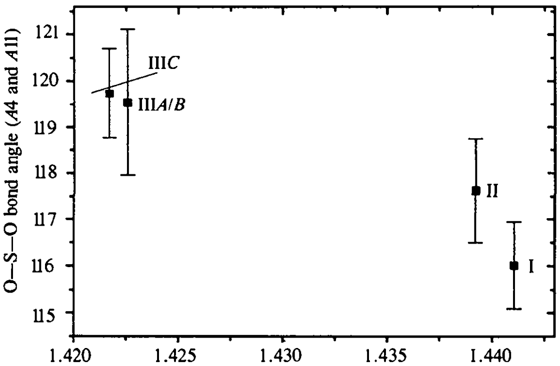

Fig. 10. A plot of the mean ⟨O—S—O⟩ bond angles (°) *versus* the mean ⟨S=O⟩ bond lengths (Å) for groups I-IIIC. Each mean value is given with its Pearson's correlation coefficient calculated from the e.s.d.'s.

Of the 11 compounds, including NEWONE represented by the scattergram, the folded (hairpin-like) conformation is assumed only by those in which the nitrogen is charged and balanced by a small cation (Na^+ or H_3O^+) or bears a hetero atom such as oxygen (JEHXAV and JEHXID). In the folded structures (BIKVIA10, DEKCAX, NABSUF, JEHXAV and JEHXID) the general conformation approaches C_s symmetry with σ_v perpendicular to the S—N—S triangle, but only NEWONE comes close to it (see above).

Within the Gaussian distribution of the S—N—S angles, the folded conformations of BIKVIA10, DEKCAX, JEHXAV, JEHXID, NABSUF and NEWONE seem to account for the values that are somewhat greater than 120°. In contrast, the open form of BSULFA cannot explain the largest S—N—S angle observed. This anomaly can presumably be attributed to the repulsion between the synperiplanar oxygen and sulfur atoms forming the torsion angle, $T2 = -14.9(3)°$ (see below).

From the scattergram depicted in Fig. 11 it follows that the O—S—N—S torsion angles ($T1/T2$, $T4/T5$) should also fall into relatively narrow ranges. Indeed, apart from DODNOZ and one half of both BSULFA and LATWEI, respectively (Fig. 12), one of the O—S—N—S torsion angles for each S—NSO_2R

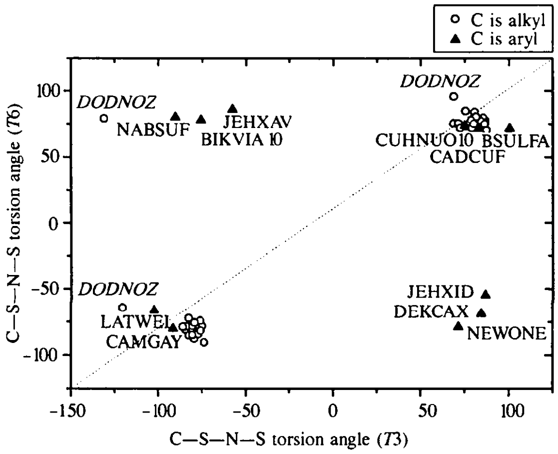

Fig. 11. Scattergram of the C—S—N—S angles (°); $T6$ *versus* $T3$. The C = *alkyl* and *aryl* groups are labelled with open circles and solid triangles, respectively. Where the *signs* of the torsion angles by pairs are the same, the compound assumes an open conformation and *vice versa*. The structure $(EtSO_2)_3N$ (DODNOZ) is represented by three conformers. One is folded (*sign*$T6$ is opposite to *sign*$T3$).

moiety is antiperiplanar (> 150°), while the other is predominantly synclinal (30-50°). There are a few synperiplanar angles in subgroups III*A*/*B* (one half of BSULFA, CAMGAY, DODNUF and LATWEI) and III*C* (DODNOZ and DUGWEH01, one half of both FADVEL and JORLOR). In groups I and II the synclinal O—S—N—S torsion angle is always accompanied by the larger O—S—N angle. For these two groups the deviations (Δ_{OSN}) between the two O—S—N angles are also substantial. Their mean is even somewhat larger for group I than for group II. In contrast, as shown by the scattergram (*b*) in Fig. 7 of the four $\langle\Delta_{OSN}\rangle$ mean values plotted against the ⟨S—N⟩ distances of subgroup III*C*, $\langle\Delta_{OSN}\rangle$ is close to zero (for 8 out of 36 NSO_2 groups Δ_{OSN} were negative) and somewhat larger for subgroup III*A*/*B*, in accordance with the covalent environment of their bridging N atoms with respect to those listed in groups I and II where the ionic character is predominant.

3. Concluding remarks

Tha analysis of the 41 structures (including NEWONE) possessing $O_2S—NQ—SO_2$ moieties retrieved from the Cambridge Structural Database enabled us to distinguish between the *covalent* and the *charged* environments of the nitrogen atoms. By the use of the scattergram of the averaged differences between the O—S—N pairs plotted *versus* the corresponding mean values of the S—N distances, the two main forms can be recognized. The anionic forms (group I) are characterized by the shortest S—N bonds accompanied by reduced O—S—O angles (Gilliespie, 1963), pronounced inequalities of the O—S—N angles and elongated (weakened) S=O and S—C bonds. At the other extreme (group III*C*) there are the covalent bonds formed between the bridging nitrogen and atoms with high electronegativities ($\varepsilon \geq 2.5$) which govern the distribution of the longest S—N distances counterbalanced by shortened S=O and S—C bond lengths, respectively.

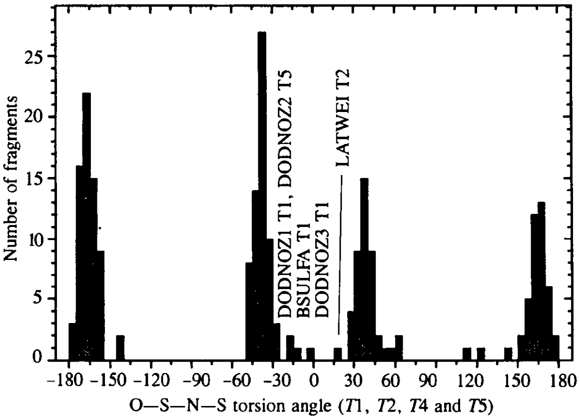

Fig. 12. Numerical distribution of the O—S—N—S torsion angles.

Accordingly, the present work is the first which, by the use of the symmetrical $—O_2S—NQ—SO_2—$ moieties, substantiates the interdependence of the bonds and angles forming $S^{VI}[O,O',N,C]$ tetrahedra, in accordance with Johnston's *Bond Order Conservation Principle* (1960) and the *VSEPR* rules (Gillespie, 1963). We note that such work could only be done earlier for the tetrahedral oxyanions XO_4^{n-} and the simpler trigonal pyramidal $S^{IV}N_3$ moieties possessing homogeneous *X*—O or S—N bonds. The interdependence of the *X*—O bonds (through the whole periodic system of elements), proved by mean bond-length calculations for the XO_4^{n-} anions using the equation $d(X—O) = kn^2 + d_o$ introduced by Kálmán (1971) and by bond-order calculations for the S—N bonds of trigonal pyramidal $S^{IV}N_3$ moieties (Kálmán, Argay, Fischer & Rembarz, 1979), have suggested that interdependence might also exist among the heterogeneous S=O, S—N and S—C bonds pertaining to $S^{VI}[O,O',N,C]$ tetrahedra. However, the interdependence of S=O, S—C and S—N distances in *N*-sulfonylsulfilimines reported earlier (Kálmán, Párkányi & Kucsman, 1980, and references therein) and the related *N*-substituted arylsulfonamides (Kálmán *et al.*, 1981) has been noticeable only at the level of the bond length e.s.d.'s.

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