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Structural Studies on the Sulfur—Nitrogen Bond. II. The Crystal Structure of Tris(morpholino)sulfonium Tetraphenylborate. A Comparison with the Structure of Tris(morpholino)phosphine

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The structure of the title compound, $[O(CH_2CH_2)_2N]_3S^+ (C_6H_5)_4B^-$, has been determined by X-ray diffraction techniques. The compound is monoclinic, space group $P2_1/c$, with (at −150 °C): $a=9.483(2)$ Å; $b=19.890(3)$ Å; $c=17.350(2)$ Å; $\beta=90.29(1)°$, $Z=4$. Full-matrix least-squares refinement led to a final R-value of 0.054 for 3991 high order reflections ($\sin\theta/\lambda > 0.45$ Å^{-1}).

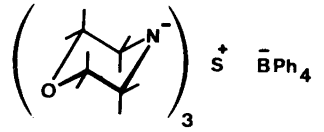
The cation, Mor_3S^+, is highly asymmetric and its structure is in principle quite analogous to that of tris(morpholino)phosphine, Mor_3P: (*i*) Two smaller N–S–N bond angles of 99.0 and 97.3°, respectively, and one larger angle of 117.4°; (*i i*) two shorter S–N bond lengths of 1.620(3) and 1.636(2) Å while the third is significantly longer, 1.683(3) Å; (*i i i*) the nitrogen atom linked to the surfur atom through the long S–N bond is essentially sp^3 hybridized and its lone pair is *anti* with respect to the sulfur lone pair; (*i v*) the remaining two nitrogen atoms are essentially sp^2 hybridized and their lone pair directions are roughly normal to that of the sulfur atom and to each other; (*v*) the two morpholino groups linked through short bonds to the central atom are twisted in opposite directions with torsion angles of ±71.4° about the S–N bond.

The anion, Ph_4B^-, is close to tetrahedral with regard to the BC_4 moiety. The average B–C bond length is 1.645(4) Å. The phenyl groups are significantly distorted from hexagonal symmetry, the internal angles at the carbon atoms linked to the central boron atom being only 115.6(3)°.

In recent studies from these laboratories the crystal and molecular structure of tris(dialkylamino)phosphines, $(R_2N)_3P$, arsines, $(R_2N)_3As$, and phosphine chalcogenides, $(R_2N)_3PSe$ and $(R_2N)_3PTe$, have been described. For a review of references, *cf.* Ref. 1. It was shown that none of these compounds possesses C_3 local symmetry but are highly asymmetric species. The P–X bond in $(R_2N)_3PX$ and the rather diffuse lone pair of the larger arsenic atom in $(R_2N)_3As$ apparently exert the same conformational influence as does the lone pair of the phosphorus atom in $(R_2N)_3P$. It was therefore concluded that the orthogonalization of the nitrogen lone pairs relative to each other is the determining factor with regard to the structure of these compounds.[2]

In an attempt to test the generality of this suggestion we have turned to tris(dialkylamino)-sulfonium salts, $(R_2N)_3S^+X^-$, a class of compounds which only recently has become available.[3–7] Tris(dialkylamino)sulfonium cations are isoelectronic with $(R_2N)_3P$ and some knowledge to their structure and preferred conformation might shed further light upon the factors determining the asymmetric structure of the compounds from the fifth main group. $(R_2N)_3S^+$ cations, contrary to $(R_2N)_3P$, are known to be most stable towards strong nucleophiles and protic solvents.[5] Triazasulfonium cations containing one primary amine, however, are unstable species.[8]

In the present study we want to report on the crystal and molecular structure of tris(morpholino)-



Scheme 1.

0302-4377/82/050407-09$02.50

sulfonium tetraphenylborate, $Mor_3S^+Ph_4B^-$ (Scheme 1). This cation was chosen since previous structural studies of Mor_3P,[9] Mor_3As[2] and Mor_2S[10] allowed a direct comparison to be made. By using the tetraphenylborate anion as counter ion a nicely crystalline and non-hygroscopic salt was obtained.

During its preparation it was noted that tris(dialkylamino)sulfonium bromides may easily be prepared from $(R_2N)_2S$ and a secondary amine in the presence of bromine in dichloromethane,[11] eqn. (1).

$$(R_2N)_2S + 2R_2NH + Br_2 \xrightarrow{CH_2Cl_2} (R_2N)_3SBr + R_2NH \cdot HBr \quad (1)$$

The two products are fairly easily separated from each other owing to their greatly different solubility in dry acetone. The sulfonium bromides are converted into their corresponding tetraphenylborates in nearly quantitative yield with a slight excess of $NaBPh_4$ in aqueous solution.

EXPERIMENTAL

Material. A dichloromethane solution of freshly prepared bis(morpholino)sulfide, Mor_2S[10] (1M), dry morpholine (2M) and bromine (1M) was stirred for 48 h at room temperature. The solvent together with traces of unreacted morpholine and bromine were removed in vacuum while unreacted Mor_2S was removed with diethyl ether. Tris(morpholino)-sulfonium bromide, $Mor_3S^+Br^-$, was then extracted from the remaining solid with cold acetone in which the other product, morpholinium hydrobromide, is rather insoluble. In order to remove traces of the latter compound the acetone solution was twice evaporated to dryness, the residue treated with acetone and the least soluble part discarded. The very soluble sulfonium bromide was finally precipitated with a large volume of diethyl ether.

Since suitable crystals of the apparently hygroscopic bromide could not be obtained, the corresponding tetraphenylborate, $Mor_3S\ BPh_4$, was prepared by precipitation in aqueous solution with $NaBPh_4$. After azeotropic drying from an acetonitrile–benzene solution the product was crystallized from an acetone–diethyl ether mixture from which satisfactory crystals for the X-ray study were obtained.

M.p.215–217 °C (210–211 °C[5]); NMR (CH_2Cl_2): [δ 2.78–2.96 (m,12,NCH_2), 3.50–3.67 (m,12,OCH_2), 6.80–7.40 (m,20,BPh_4)]; IR (KBr-disc):710 cm^{-1} (S–N).

Table 1. Atomic coordinates for non-hydrogen atoms.

Atom	*x*	*y*	*z*
S	.22569(7)	.59362(3)	.78075(3)
O1	−.0835(3)	.4675(1)	.9104(2)
O2	.1456(4)	.7977(1)	.7357(2)
O3	.1742(3)	.5267(1)	.5393(1)
N1	.0895(3)	.5522(1)	.8201(1)
N2	.1818(3)	.6696(1)	.8043(1)
N3	.1978(2)	.5705(1)	.6914(1)
C11	.0948(4)	.4780(1)	.8108(2)
C12	−.0496(5)	.4509(2)	.8327(2)
C13	−.0816(4)	.5384(2)	.9210(2)
C14	.0619(3)	.5678(1)	.9025(1)
C21	.0402(3)	.6994(1)	.7957(2)
C22	.0363(4)	.7492(2)	.7289(2)
C23	.2794(5)	.7655(2)	.7347(2)
C24	.2970(3)	.7196(2)	.8041(2)
C31	.3185(3)	.5780(2)	.6390(2)
C32	.3060(3)	.5227(2)	.5786(2)
C33	.0605(4)	.5181(2)	.5919(2)
C34	.0603(3)	.5735(2)	.6523(2)
C41	.6079(3)	.7096(1)	1.0138(2)
C42	.5037(3)	.6934(1)	1.0676(2)
C43	.4264(3)	.6335(2)	1.0645(2)
C44	.4498(3)	.5875(2)	1.0062(2)
C45	.5520(4)	.6021(2)	.9515(2)
C46	.6289(3)	.6616(2)	.9551(2)
C51	.6326(3)	.8221(1)	.9366(1)
C52	.4989(3)	.8518(1)	.9407(2)
C53	.4368(4)	.8858(2)	.8784(2)
C54	.5082(4)	.8906(2)	.8091(2)
C55	.6399(4)	.8600(2)	.8018(2)
C56	.7005(4)	.8264(1)	.8649(2)
C61	.8671(3)	.7678(1)	1.0053(1)
C62	.9579(3)	.8200(1)	.9823(2)
C63	1.1040(3)	.8130(2)	.9811(2)
C64	1.1659(3)	.7528(2)	1.0043(2)
C65	1.0793(3)	.7005(1)	1.0289(2)
C66	.9328(3)	.7081(1)	1.0284(2)
C71	.6829(3)	.8258(1)	1.0904(1)
C72	.6855(3)	.8964(1)	1.0895(2)
C73	.6867(3)	.9347(2)	1.1576(2)
C74	.6818(3)	.9035(2)	1.2295(2)
C75	.6805(4)	.8337(2)	1.2323(2)
C76	.6836(4)	.7962(2)	1.1649(2)
B	.6966(3)	.7807(1)	1.0114(2)

X-Ray data. Data for the measurement of cell dimensions and intensity data were collected on a SYNTEX $P\bar{1}$ diffractometer using graphite crystal monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å). The temperature at the crystal site was -150 °C, crystal dimensions were approximately $0.4 \times 0.4 \times 0.4$ mm. Cell parameters were determined by a least-squares fit to the diffractometer settings of 15 general reflections with $2\theta > 35°$. The θ-2θ scan technique was used for the collection of intensity data with a scan speed of $3-6°$ min^{-1} and a scan range of $\pm 1°$. The background counts were taken for 0.35 times the scan time at each of the scan limits. Out of the 6959 unique reflections recorded within $\sin\theta/\lambda = 0.7$ Å^{-1}, 6188 with $I > 2.5\sigma(I)$ were retained for the structure analysis. The standard deviations for the intensities were calculated as $\sigma(I) = [C_T + (0.02\ C_N)^2]^{\frac{1}{2}}$, where C_T is the total number of counts and C_N is the scan count minus background count. The intensities were corrected for Lorentz and polarization effects but not for absorption.

For description of computer programs and references to atomic form factors, *cf.* Ref. 10.

CRYSTAL DATA

Tris(morpholino)sulfonium tetraphenylborate, $C_{36}H_{44}BN_3O_3S$, m.p. 216–217 °C. Monoclinic, $a = 9.483(2)$ Å; $b = 19.890(3)$ Å; $c = 17.350(2)$ Å; $\beta = 90.29(1)°$; $V = 3272.5(8)$ Å^3; ($t = -150$ °C); $M = 609.63$; $Z = 4$; $F(000) = 1304$; $D_x = 1.237$ g cm^{-3}. Absent reflections: ($h0l$) for l odd, ($0k0$) for k odd. Space group $P2_1/c$ (No. 14).

STRUCTURE DETERMINATION

The structure was determined by direct methods and refined in the way described in Ref. 9. In order to avoid the influence of bonding electrons, the final cycles of least-squares refinement were performed with only high angle data included ($\sin\theta/\lambda > 0.45$ Å^{-1}, 3991 reflections). The refinements converged to the following figures of merit: R (All data, 6188 reflections): 0.069; R (high angle data, 3991 reflections): 0.054; $R_w = 0.068$; $S = 2.13$.

Final positional parameters for non-hydrogen atoms are listed in Table 1. Thermal parameters, hydrogen atomic parameters and tables of observed and calculated structure factors are available from the authors.

ORTEP drawings of the ions are shown in Fig. 1 where the numbering of the atoms is also indicated.

RESULTS AND DISCUSSION

In Table 2 are summarized the various structural data determined in the present study. Estimated standard deviations in bond lengths and angles are calculated from the variance–covariance matrix.

The compound consists of discrete cations and anions in the crystal lattice with no exceptionally short contacts. Between, as well as within the ions, the contacts are of the van der Waals' type, mainly between hydrogen atoms.

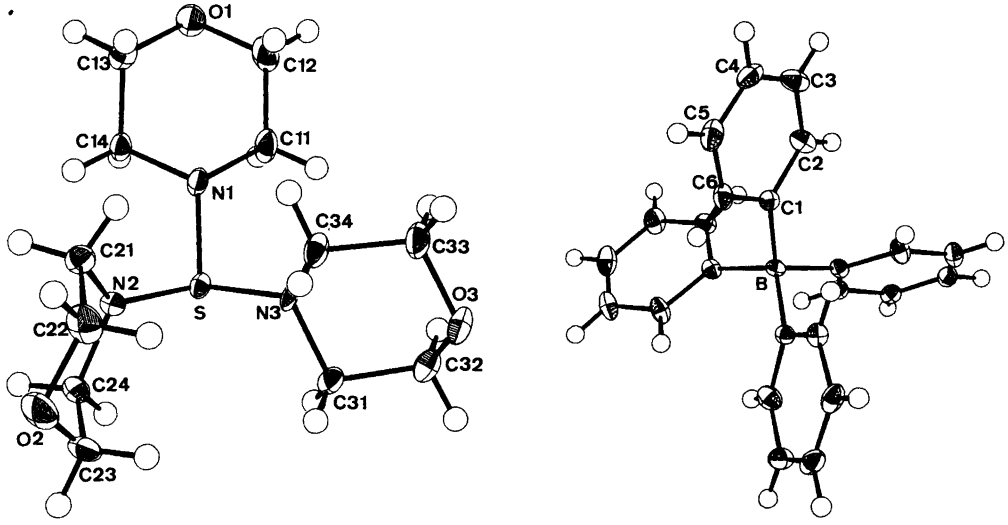


Fig. 1. ORTEP plots of the tris(morpholino)sulfonium ion and the tetraphenylborate ion.

Table 2. Structural data.

Bond lengths (Å)

S	N1	1.680(3)
S	N2	1.620(3)
S	N3	1.636(2)
N1	C11	1.486(4)
C11	C12	1.522(6)
C12	O1	1.426(4)
O1	C13	1.423(4)
C13	C14	1.516(4)
C14	N1	1.488(3)
N2	C21	1.472(4)
C21	C22	1.526(4)
C22	O2	1.421(5)
O2	C23	1.421(6)
C23	C24	1.520(5)
C24	N2	1.477(4)
N3	C31	1.473(3)
C31	C32	1.524(4)
C32	O3	1.423(4)
O3	C33	1.426(4)
C33	C34	1.521(4)
C34	N3	1.469(3)
B	C41	1.647(4)
B	C51	1.649(4)
B	C61	1.640(4)
B	C71	1.645(4)

Bond angles (°)

N1	S	N2	99.0(1)
N2	S	N3	117.4(1)
N1	S	N3	97.3(1)
S	N1	C11	114.7(2)
S	N1	C14	115.3(2)
S	N2	C21	125.8(2)
S	N2	C24	115.9(2)
S	N3	C31	115.8(2)
S	N3	C34	124.4(2)
N1	C11	C12	107.1(3)
C11	C12	O1	111.2(3)
C12	O1	C13	110.5(2)
O1	C13	C14	111.5(3)
C13	C14	N1	106.6(2)
C14	N1	C11	108.5(2)
N2	C21	C22	110.9(3)
C21	C22	O2	111.2(3)
C22	O2	C23	110.1(3)
O2	C23	C24	110.9(3)
C23	C24	N2	109.1(3)
C24	N2	C21	113.7(3)
N3	C31	C32	107.1(2)
C31	C32	O3	110.8(2)
C32	O3	C33	110.6(2)
O3	C33	C34	111.0(3)
C33	C23	N3	106.6(3)
C34	N3	C31	113.6(2)
C41	B	C51	105.2(2)
C41	B	C61	111.8(2)
C41	B	C71	113.9(2)
C51	B	C61	112.7(2)
C51	B	C71	110.7(2)
C61	B	C71	102.8(2)

Torsion angles (°)

N3	S	N1	C11	61.6(2)
N3	S	N1	C14	−171.3(2)
N3	S	N2	C21	56.9(3)
N3	S	N2	C24	−97.4(3)
N2	S	N3	C31	94.5(2)
N2	S	N3	C34	−56.0(3)
N1	S	N3	C31	−161.4(2)
N1	S	N3	C34	48.1(2)

Various averaged and derived data

N_x	N1	N2	N3
$\overline{N-C}$ (Å)	1.487	1.475	1.471
$\overline{C-C}$ (Å)	1.519	1.523	1.523
$\overline{C-O}$	1.425	1.421	1.425
Sum of N bond angles (°)	338.5	355.4	353.8
Torsion angle about $S-N_x$	−175.2	−71.8	71.3

Tetraphenylborate ion

$\overline{B-C1}$ (Å)	1.645(4)	$\overline{C6-C1-C2}$ (°)	115.6(3)
$\overline{C1-C2}$ (Å)	1.406(8)	$\overline{C1-C2-C3}$ (°)	122.5(3)
$\overline{C2-C3}$ (Å)	1.398(6)	$\overline{C2-C3-C4}$ (°)	120.4(4)
$\overline{C3-C4}$ (Å)	1.394(6)	$\overline{C3-C4-C5}$ (°)	118.4(4)

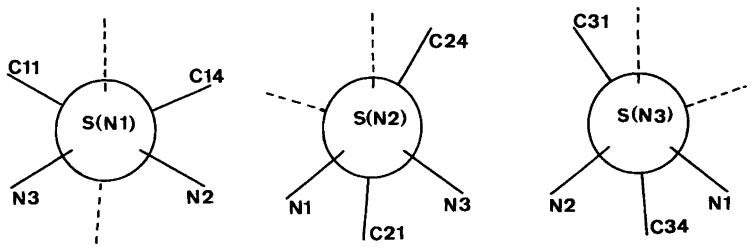


Fig. 2. Newman diagram of the S–N bonds. Broken lines indicate lone pair directions.

The tris(morpholino)sulfonium cation. In the cation there are two short S–N bonds, 1.620(3) and 1.636(2) Å, the third bond being significantly longer, 1.680(3) Å. The nitrogen atom linked to the central sulfur atom through a long bond is essentially sp^3 hybridized, the bond angle sum, $\Sigma\angle$N, being 338.5°. The lone pair of this nitrogen atom is *anti* to the sulfur atom lone pair, the torsion angle about the S–N bond is 175.2°. The two other nitrogen atoms are mainly sp^2 hybridized and their lone pair directions are nearly orthogonal to the sulfur lone pair and to each other. For these atoms $\Sigma\angle$N is 353.8 and 355.4°, the morpholino groups being twisted in opposite directions with torsion angles about the S–N bonds of 71.3 and −71.8°, respectively. In Fig. 2 are shown the Newman projections of the S–N bonds; the torsion angles are defined as outlined in Ref. 9.

The cation is highly asymmetric with regard to the N–S–N bond angles; two of these bond angles are fairly small, 97.3(1) and 99.0(1)°, while the third, the one between bonds to sp^2 hybridized nitrogen atoms, is 117.4°. The sum of the N–S–N angles is 313.7°.

The morpholino groups are all in the expected chair conformation. The N–S bond directions correspond approximately to that of an equatorial bond of the morpholino rings. In the morpholino groups the bond lengths and the bond angles are, with one possible exception, of the expected magnitude; the N–C bond length in the morpholino group linked to the central sulfur atom through an sp^3 hybridized nitrogen atom, and thus a long S–N bond, is 1.487 Å which is about 3 times the e.s.d. longer than the average N–C bond lengths in the two remaining morpholino groups.

Fundamentally, the structure of Mor_3S^+ in $Mor_3S\ BPh_4$ is most similar to that of the

Table 3. Comparison of some structural parameters in the tris(morpholino)sulfonium cation, in bis(morpholino)sulfid and in tris(morpholino)phosphine.

	[a]	Mor_3S^+		Mor_2S[b]		[a]	Mor_3P[c]	
∠NSN°, ∠NPN°	117.4	97.3	99.0	113.2		110.7	97.7	98.0
Σ∠NSN°, Σ∠NPN°		313.7					306.6	
Σ∠N°	338.5	355.4	353.8	349.5		337.6	353.2	350.5
S–N, P–N (Å)	1.680	1.620	1.636	1.680		1.726	1.691	1.696
$S^+-N_{sp^3}$, $P^{III}-N_{sp^3}$ (Å)		1.71[d]					1.74[d]	
$S^+-N_{sp^2}$, $P^{III}-N_{sp^2}$ (Å)		1.61[d]					1.68[d]	
∠SNC°, ∠PNC°	114.7	124.4	125.8	118.5	118.9	114.4	125.9	124.3
	115.3	115.8	115.9	119.1	119.3	115.0	116.7	115.6
S–N, P–N								
torsion angles (°)[e]	−175.2	−71.8	71.3			170.6	−70.9	73.2
N–C (Å)	1.487	1.475	1.471	1.470		1.470	1.463	1.460
C–C (Å)	1.519	1.523	1.523	1.512		1.498	1.497	1.505
C–O (Å)	1.425	1.421	1.425	1.429		1.421	1.423	1.417

[a] The nitrogen atom with its lone pair *anti* to the lone pair of the hetero atom. [b] From Ref. 10, average values. [c] Ref. 9. [d] Extrapolated values, *cf.* Fig. 3. [e] Torsion angles as defined in Ref. 9.

isoelectronic species Mor_3P.[9] In Table 3 a comparison is made between the most important structural parameters in the sulfonium cation and in the aminophosphine. Also are included some relevant structural parameters of bis-(morpholino)sulfide obtained in a recent structural study.[10] From Table 3 it is apparent that the only parameter significantly different in Mor_3S^+ and in Mor_3P, apart from the S–N and P–N bond lengths, is the one N–X–N bond angle between bonds to sp^2 hybridized nitrogen atoms. In the sulfonium cation this bond angle is 117.4° as compared to 110.7° in the aminophosphine. As a result, the sum of the N–S–N bond angles is greater than the sum of the N–P–N angles, 313.7 and 306.6°, respectively.

The introduction of a third morpholino group around the sulfur atom forming Mor_3S^+ from Mor_2S results in only minor structural and conformational changes in two of the substituents. The torsion angles remain essentially unaltered while the N–S–N bond angle is increased from 113.0 to 117.4°. A slight increase of the *s*-character of the nitrogen atoms is also observed; the sum of the nitrogen bond angles being 353.8 and 355.4° in Mor_3S^+ while being 350° in Mor_2S. The S–N bond lengths, however, are different; 1.680(3) Å in the sulfide while only 1.620(3) and 1.636(3) Å in the sulfonium cation. The third morpholino group being linked through an essentially sp^3 hybridized nitrogen atom to the central sulfur atom is bonded with an S–N bond of 1.680(3) Å, which is comparable to that in the parent sulfide. As in Mor_3P[9] the lone pair of this third nitrogen atom is essentially *anti* to the hetero atom lone pair.

In Fig. 3 is plotted the sum of the nitrogen bond angles *vs.* the corresponding S–N bond lengths in Mor_3S^+, and, similarly, the P–N bond lengths in Mor_3P from Ref. 9. A fairly linear dependence is apparent and the least-squares straight lines are indicated. By extrapolation $S^{II+}-N_{sp^2}$ and $S^{II+}-N_{sp^3}$ bond lengths of 1.61(1) and 1.71(1) Å, respectively, are obtained compared with $P^{III}-N_{sp^2}$ and $P^{III}-N_{sp^3}$ bond lengths of 1.68(1) and 1.74(1) Å, respectively.[9] As may be seen from Fig. 3 the slope of the two least-squares lines are quite different; the S^+-N bond length being apparently more dependent upon the hybridization of the nitrogen atom than is the $P^{III}-N$ bond lengths. As a result, the difference between the two extrapolated S^+-N bond lengths is 0.10 Å as compared to 0.06 Å for the corresponding P–N bond lengths. This observation may suggest that the orbitals at the sulfur atom are better suited for overlap with the nitrogen orbitals than are the phosphorus orbitals, especially when some positive charge is residing on the central atoms. The S–N bond length in uncharged species is known to range from 1.416 to 1.90 Å [10,13] while in the $|NS|^+$-cation the S^+-N bond length is estimated to be as short as 1.25 Å.[14] A similar extensive range for P–N bond lengths has so far not been observed.[9,13,15,16]

In Fig. 3 are also indicated the S–N bond length in bis(morpholino)sulfide[10] and the P–N bond length in 4-nitrobenzyl tris(morpholino)phosphonium perchlorate, abbreviated Mor_3P^+R.[15] (In these compounds only one S–N and one P–N bond length together with essentially only one type of nitrogen hybridization are observed.[10,15]) From Fig. 3 it is apparent that the positive charge causes a decrease of the S–N bond length of about 0.04 Å and of the P–N bond length of about 0.05 Å when the hybridization on the nitrogen atom is retained as viewed by the sum of the nitrogen bond angles. If

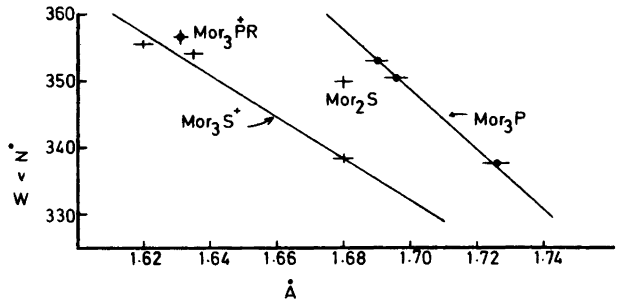


Fig. 3. Plot of the sum of nitrogen bond angles *vs.* the corresponding S–N bond lengths in Mor_3S^+ and Mor_2S and the P–N bond lengths in Mor_3P and Mor_3P^+R.

one assumes a similar dependence of the S–N bond length in uncharged species upon the hybridization of the nitrogen atom as observed for the S^+–N bond length in the sulfonium cation, *cf.* Fig. 3, one obtains an $S^{II}-N_{sp^3}$ bond length of about 1.75 Å. The extrapolated value is in excellent agreement with the Schomaker-Stevenson estimate, 1.74 Å.[17] In comparison, the Schomaker-Stevenson value for the P^{III}–N single bond is 1.76 Å[17] and it has been suggested that the S–N and P–N single bonds are of comparable length.[18]

However, the present and admittedly fairly crude estimate of 1.75 Å for an $S^{II}-N_{sp^3}$ single bond may be hard to verify experimentally. Actually, owing to the apparent facility by which the sulfur and nitrogen orbitals on adjacent atoms interact, *cf.* Ref. 10, causing a decrease in both the S–N bond length and the *p*-character of the nitrogen atom, it is highly doubtful whether uncharged sulfur–nitrogen compounds with sulfur in oxidation state II and with sp^3 hybridized nitrogen atoms exist. An interesting comparison may be made with the S–N bond length of 1.76 Å as observed in sulfamic acid, $^-O_3SNH_3^+$.[19] This compound is known to exist in the crystalline state as the zwitterion and thus leaving no electrons on the nitrogen atom available for π bonding. The S–N bond in this compound should thus be a classical single bond. However, the single bond in sulfamic acid is an $S^{IV}-N_{sp^3}$ single bond. From previous structural studies on phosphorus–nitrogen compounds it is well known that when discussing bond lengths in this class of compounds it is necessary to consider not only the hybridization of the nitrogen atom but also the oxidation state of the central atom.[1,2] For bond lengths in S–N compounds the same care should apparently also be exercised. Fortunately, since S^{II}–N and S^{VI}–N single bonds appear to be of comparable length,[20,21] the excellent agreement between our extrapolated value for an $S^{II}-N_{sp^3}$ single bond length and the $S^{VI}-N_{sp^3}$ single bond length as observed in sulfamic acid[19] may be more than fortutious.

The preference of S–N bonds to attain a bond order slightly but significantly greater than unity[10,22] is reflected by the considerable rotational energy for rotation about the S–N bond as observed in numerous sulfur–nitrogen compounds.[23] In the case of an aminosulfonium cation, $(Me_2N)_3S^+$, the barrier to S–N rotation is 61.4 kJ mol^{-1},[6] even though one of the nitrogen atoms in this cation is presumably sp^3 hybridized as observed in Mor_3S^+ in the present study. In comparison, the P–N rotational barrier for the isoelectronic tris(dialkylamino)phosphines, $(R_2N)_3P$, is usually too small to be detected by the NMR technique. With bulky substituents the P–N torsional barrier in this class of compounds may be raised to 35–40 kJ mol^{-1}.[24] Presumably, the positive charge on the sulfur atom in the triazasulfonium ion causes a contraction of the sulfur *d*-orbitals which make these orbitals more suitable for overlap with the lone pair on the nitrogen atoms. In sulfur compounds in which the atoms linked to the central sulfur atom have no lone pairs, the charge on the sulfur atom is of negligible influence upon the S–X bond lengths, *cf.* Refs. 25 and 26 for S–C bond lengths in Me_2S and in Me_3S^+.

The tetraphenylborate ion, Ph_4B^-. In Table 2 are listed the average values of bond lengths and angles; the standard deviations from the mean (in parenthesis) are small and indicate the similarity in the structural parameters in the four phenyl groups and the B–C bond lengths.

The six C–B–C bond angles in the anion are less similar and range from 102.8(3)° to 113.9(2)°. The boron atom is thus in principle tetrahedrally surrounded by the *ipso* carbon atoms which has also been observed in numerous structural studies on various tetraphenylborates, *cf.* Refs. 27–32. The average B–C bond length of 1.645(4) Å is as observed in previous studies; *cf.* Ref. 33 for a survey of B–C bond lengths and their dependence upon the refinement procedure. In Ph_3B and in $[(Ph_3B)_2CN]^-$ the B–C bonds are significantly shorter, ranging from 1.571(3) Å to 1.589(5) Å in Ph_3B[34] and being 1.603(11) Å in the anion.[35]

As is apparent from the data in Table 2 significant deviations from perfect D_{6h} symmetry in the phenyl rings occur in the tetraphenylborate anion which also has been encountered in previous structural studies.[36] The internal C–C–C bond angles at the *ipso* carbon atom are only 115.6(3)° while the bond angles at the neighbouring carbon atom are significantly larger than 120°, the average value being 122.5(3)°. The bond angle at the *ipso* carbon atom is known to range from 115 to 125° depending upon the electronegativity of the substituent linked to the phenyl group, Ph_3B^- and $N\equiv N^+$ causing the extreme values.[36] For substituents of low electronegativity 117.5–118° is the expected bond angle and not 120° as observed in tetraphenylmetane,[37] and in tri-,[38] tetra-[39] and pentaphenylethane.[40]

It has been argued that significantly smaller C–C–C bond angles at the *ipso* carbon atom in substituted phenyl compounds than about 118° is due to the small X–C bond length and are thus sterically induced.[28,31] However, the significantly larger C–C–C bond angle in Ph_4C[37] than in Ph_4B^-, the former being even more crowded owing to the shorter $C-C_{ipso}$ bond, points against an explanation based upon steric crowding. Sheldrick[41] several years ago from a structural study on Ph_4Si suggested that the distortion of the phenyl rings could not be rationalized by short contacts involving *ortho* carbon and hydrogen atoms. Furthermore, small C–C–C bond angles are observed in several transition metal aryls in which the metal–carbon bond lengths are significantly longer than the B–C bond length in Ph_4B^-.[42]

It thus seems conceivable that the cause for the distortion in the phenyl rings in Ph_4B^- has its origin in the inherently low electronegativity of boron which is further lowered by the negative charge of the anion. Even in $PhBX_2$, X being electronegative halides, is the BX_2 substituent an electron donor to the phenyl groups.[43] The central part of the anion may thus be formulated as $B^{\delta+}-C^{\delta-}$, indicating that some negative charge is residing on the *ipso* carbon atoms, a suggestion for which there is some chemical evidence. The carbanionic nature of the carbon atoms linked to the boron atom in Ph_4B^- is the probable cause for the instability of this anion in the presence of mineral acids forming Ph_3B and benzene.[44] Furthermore, salts of Ph_4B^- appear to have some synthetic potential as arylating agents toward powerful Lewis acids; *cf.* the facile formation of $Ph_3Te^+Ph_4B^-$ from $TeCl_4$ and $NaBPh_4$ and related reactions.[45]

CONCLUSIONS

The tris(dialkylamino)sulfonium cations are not symmetrical and are structurally most similar to the isoelectronic species tris(dialkylamino)phosphine. The cause for the asymmetric structure of these compounds may thus be of the same origin, presumably the desire of the nitrogen lone pairs to be orthogonal. For a recent review of references, *cf.* Ref. 46.

The similarity in the structures of $(R_2N)_3S^+$ and $(R_2N)_3P$ offers a possible explanation for the exceptional chemical stability of triazasulfonium ions.[5] $(R_2N)_3P$ are known to be very poor electrophilic species and their chemistry is nearly entirely governed by the nucleophilicity of the phosphorus atom and, in some few instances, the nitrogen atoms.[9,47] The positive charge on the central sulfur atom in $(R_2N)_3S^+$ will obviously subdue any nucleophilicity of the sulfur atom and presumably also of the neighbouring nitrogen atoms, even though one of these atoms is essentially sp^3 hybridized. However, strong mineral acids may interact with this latter nitrogen atom and initiate decomposition of the cation.

The available structural data on S–N compounds suggest that great care should be exercised when comparing S–N bond lengths without taking into account both the oxidation state and the charge of the sulfur atom as well as the hybridization of the nitrogen atom.

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