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FULL PAPER

Bis(*tert*-butyl)sulfurdiimide, S(NBu^t)$_2$, and tris(*tert*-butyl)-sulfurtriimide, S(NBu^t)$_3$: structures by gas electron diffraction, X-ray crystallography and *ab initio* calculations†

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The molecular structures of bis(*tert*-butyl)sulfurdiimide [S(NBu^t)$_2$] and tris(*tert*-butyl)sulfurtriimide [S(NBu^t)$_3$] have been investigated in the gas phase by electron diffraction and *ab initio* calculations, and in the solid phase by low-temperature X-ray diffraction. The structures of each were found to be similar in both phases, and the calculated structures agree well with those in the gas phase. *Ab initio* calculations at levels up to MP2(fc)/cc-pVTZ for S(NBu^t)$_2$ predict that the *E*/*Z* conformer (C_s symmetry) is the preferred arrangement by as much as 36.5 kJ mol^{-1} over the *E*/*E* conformer. Important structural parameters [*ab initio* (r_e)/GED (r_a)/X-ray] for the *E*/*Z* conformer of S(NBu^t)$_2$ are S(1)–N(2) [152.9/153.8(3)/152.8(3) pm], S(1)–N(3) [155.5/156.5(4)/154.4(3) pm], N(2)–C(4) [147.3/146.2(4)/147.7(5) pm], N(3)–C(5) [147.9/147.0(4)/148.9(4) pm], N(2)–S(1)–N(3) [116.9/117.8(6)/117.4(2)°], S(1)–N(2)–C(4) [125.9/125.9(6)/128.1(2)°] and S(1)–N(3)–C(5) [117.1/116.7(7)/118.2(2)°]. One conformer of S(NBu^t)$_3$ with C_{3h} symmetry was located at the MP2(fc)/6-31G* level. The gas and solid-phase studies both returned C_3 structures, with the butyl groups moved a little out of the SN$_3$ plane. Important structural parameters [*ab initio* (r_e)/GED (r_a)/X-ray] for S(NBu^t)$_3$ are S=N [152.8/153.5(3)/151.0(2), 151.0(2), 151.1(2) pm], N–C [148.7/147.2(4)/148.3(3), 148.5(3), 148.3(3) pm], C–C [152.8/150.8(2)/152.4(4), 152.6(4), 153.0(3) pm], S=N–C [123.2/122.9(4)/126.2(2), 125.5(2), 126.0(2)°], C–C–C (mean) [110.4/108.3/110.0°] and N=S=N–C (mean) [180.0/173.0(5)/179.4°]. Theoretical predictions at the MP2(fc)/6-31G* level were used to restrain some of the refining parameters for both structures using the SARACEN method. The lowest energy structure of bis(*tert*-butyl)sulfurdiimide was found to be the *E*/*Z* conformer, and the structure of tris(*tert*-butyl)sulfurtriimide is such that each fragment with two NBu^t ligands has the *E*/*Z* conformation.

Introduction

We have been interested in the coordination behaviour of organyl diimidosulfinate ions [RNS(R′)NR″], R = Bu^t, SiMe$_3$, R′ = Ph, Bu^t, R = Bu^t, SiMe$_3$, c-C$_6$H$_{11}$, towards alkali metals and especially the comparison of solution effects and solid-state structures.[1] Solid-state ^{7}Li MAS spectroscopy in particular has revealed fluxional rearrangements even in the solid state,[2,3] and thus we have also been interested in comparing the gas-phase structures of the sulfur diimides S(NR)$_2$, R = Bu^t and SiMe$_3$, with those of the solid state. Since Goehring and Weis synthesised the first sulfur diimide, S(NBu^n)$_2$,[4] in 1956, many substituted compounds of this type have been prepared and used widely in inorganic and organic chemistry. The structural properties of sulfur diimides have been investigated before. In general, acyclic, symmetrically-substituted sulfur diimides can adopt one of the three possible conformations, *Z*/*Z*, *E*/*E* and *E*/*Z* (*Z* = *syn*, *E* = *anti*). ^{1}H and ^{13}C NMR experiments have been carried out for some alkyl substituted sulfur diimides;[5] based on these, the methyl, ethyl, isopropyl and neopentyl disubstituted compounds exist as *E*/*E* and *E*/*Z* conformers. S(NBu^t)$_2$ shows only two signals in the ^{1}H NMR experiment (−70 °C, C$_7$D$_8$, δ = 1.57, 1.07) and in the ^{15}N NMR experiment [RT, C$_7$D$_8$, δ = −105.9(*Z*), −6.6(*E*)],[6] both corresponding to the *E*/*Z* conformer. Although these solution-state NMR experiments have characterised the S(NBu^t)$_2$ as a single conformation in solution, conformational characteristics of the neat material are as yet unknown.

The first stable three-coordinate sulfur(VI) nitrogen species were also isolated more than 20 years ago.[7] One of the first stable sulfur triimides reported was S(NSiMe$_3$)$_3$, formed by the reaction of NSF$_3$ and LiN(SiMe$_3$)$_2$ in yields of up to 23%.[7] Another route to sulfur triimides is the reaction of sulfur tetrafluoride oxide, O=SF$_4$ with the bis-silylated alkali sodium amide NaN(SiMe$_3$)$_2$.[8] It is worth noting that the stability of the triimides formed varies greatly with the steric bulk of the substituent attached. (Bu^{t}N=)$_2$S=NCF$_3$ was found to decompose within a day whereas (Bu^{t}N=)$_2$S=NSF$_5$ was found to be almost as stable as S(NSiMe$_3$)$_3$. In the (Bu^{t}N=)$_2$S=NSF$_5$ example, S(VI) is also found to exist in its highest and lowest possible coordination numbers of 6 and 3 respectively.

The isolation and characterisation of the more bulky sulfur triimides has been of interest since the first were synthesised. The triimide S(NBu^t)$_3$ was first isolated in 1977 by Glemser and

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† Electronic supplementary information (ESI) available: tables of interatomic distances, amplitudes of vibration and least-squares correlation matrices for S(NBu^t)$_2$ and S(NBu^t)$_3$. See http://www.rsc.org/suppdata/dt/b2/b207193b/

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co-workers,[9] with further characterisation being carried out in 1979.[10] A new effective synthesis with high yields of sulfurtriimides is the oxidation of the triimidosulfite dianion by a halogen.[11] The reactivity of sulfurtriimide is, like that of sulfurdiimide, dominated by the electropositive character of the sulfur atom. Nucleophilic addition of a metal alkyl leads to alkyltriimidosulfonates.[12,13] Of great interest was whether the "Y" framework of the triimide was actually planar, or the sulfur was at the apex of a trigonal based pyramid.[5] Initial crystallographic studies were inconclusive on this issue, although large thermal ellipsoids were observed perpendicular to the SN_3 plane, perhaps indicating that the observed planar structure represents an average of disordered, slightly pyramidal structures.

Our interest in both these sterically crowded molecules was sparked by the remarkable lack of structural investigation carried out since these initial studies. Structural investigations using gas-phase electron diffraction, low-temperature single-crystal X-ray crystallography and *ab initio* calculations have been carried out and the structural characteristics for each compound reported. In addition, *ab initio* calculations on the parent compounds, $S(NH)_2$ and $S(NH)_3$, were performed.

Experimental

Synthesis

Bis(*tert*-butyl)sulfurdiimide. $S(NBu^t)_2$ was prepared by the literature method.[14] For the crystallographic studies 2 cm^3 $S(NBu^t)_2$ were dissolved in 8 cm^3 *n*-hexane and crystallised at −100 °C. The colourless plates (melting point −28 °C) were selected under the microscope and transferred to the diffractometer at −80 °C.[15]

Tris(*tert*-butyl)sulfurtriimide. $S(NBu^t)_3$ was prepared by the literature method.[12] For the crystallographic studies $S(NBu^t)_3$ was freshly sublimed in vacuum. The colourless cubes were selected under the microscope and transferred to the diffractometer at −30 °C.[15]

Theoretical methods

All calculations were performed on a DEC Alpha workstation using the Gaussian 94[16a] and Gaussian 98[16b] programs.

Geometry optimisations. An extensive search of the torsional potential of $S(NBu^t)_2$ and $S(NBu^t)_3$ was undertaken at the HF/3-21G*[17–19] level in order to locate all minima. For $S(NBu^t)_2$, two conformers, *E*/*Z* and *E*/*E* with C_1 and C_s symmetry respectively, were located and further geometry optimisations were undertaken at the HF and MP2(fc) levels using the standard 6-31G*[20–22] basis set. Finally, the structure of *E*/*Z* $S(NBu^t)_2$ was reoptimised at the MP2/cc-pVTZ″ level (*i.e.* employing cc-pVTZ basis on S, N, and the nearest-neighbour C atoms, and cc-pVDZ on the Me groups).[23] For $S(NBu^t)_3$, one conformer of C_{3h} symmetry was located and further geometry optimisations were undertaken at the HF and MP2(fc) levels using the standard 6-31G* basis set. The structures of $S(NBu^t)_2$ and $S(NBu^t)_3$ with the atom numbering schemes are shown in Figs. 1(a) and 1(b).

Frequency calculations. Analytic second derivatives of the energy with respect to nuclear coordinates calculated at the HF/6-31G* level for both conformers of $S(NBu^t)_2$ and the single conformer of $S(NBu^t)_3$ gave the force fields, which were used to provide estimates of the amplitudes of vibration (u) for use in the gas electron diffraction (GED) refinements. The force fields were also used to calculate the frequencies, which in turn provided information about the nature of stationary points. Calculating the force field at the MP2(fc) level of theory would make little difference to the vibrational quantities and for this size of molecule was deemed unnecessary.

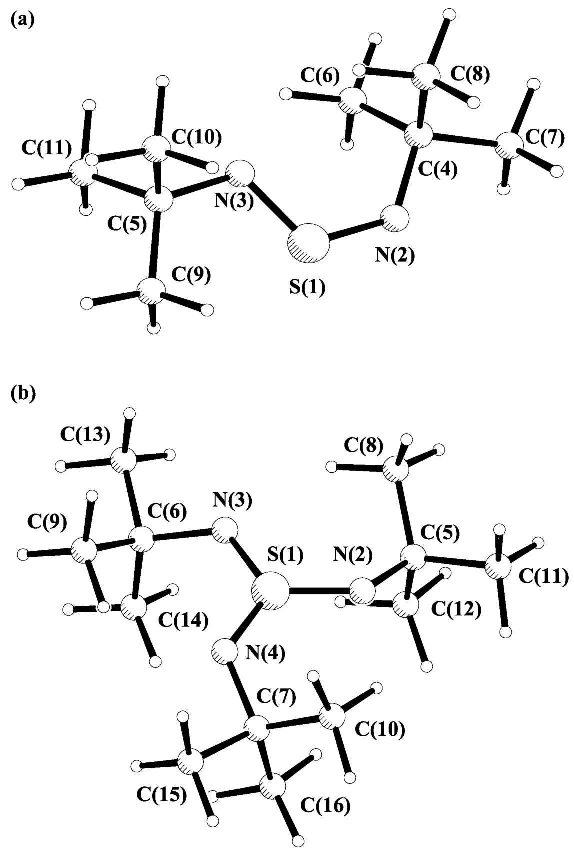

Fig. 1 Experimentally determined molecular structures of (a) $S(NBu^t)_2$ and (b) $S(NBu^t)_3$ in the gas phase.

S=N bond length convergence. During optimisation of the structures of $S(NBu^t)_2$ and $S(NBu^t)_3$ the S=N distances varied with both basis set and level of theory, and it was clear that convergence had not been reached. Further calculations on the parent molecules $S(NH)_2$ and $S(NH)_3$ in C_1 symmetry were therefore undertaken at much higher levels of theory and with larger basis sets. For each parent, a series of geometry optimisations was performed at the MP2 level employing Dunning's correlation-consistent basis sets,[23] namely cc-pVDZ, cc-pVTZ, cc-pVQZ′ (*i.e.* cc-pVQZ on S and N, cc-pVTZ on H), and cc-pV5Z′ (*i.e.* cc-pV5Z on S and N, cc-pVQZ on H). Optimised S=N bond lengths and relative energies of the *E*/*Z* and *E*/*E* isomers for $S(NH)_2$ and the single conformer of $S(NH)_3$ are collected in Table 1.

Inverse exponential functions were subsequently fitted to a plot of the MP2/cc-pVxZ S=N bond lengths, which proved to be very sensitive to changes in the basis set, and extrapolated to the basis-set limit (*i.e.* to $x = \infty$). It turned out that inverse quadratic functions can be fitted equally well to the data in the range from $x = 2$ to 5. Such functions converge much more slowly, affording significantly smaller extrapolated values. It was therefore decided to regard the corresponding extrapolated distances as upper and lower limits (thereby marking "theoretical error bars") and to take their mean values as final MP2 estimates.

For $S(NH)_2$, effects of higher theoretical levels were assessed by optimisations of the S=N bond lengths at the CCSD(T) level (*i.e.* coupled cluster with single, double, and perturbatively included connected triple excitations),[24] employing cc-pVTZ′ basis (*i.e.* cc-pVTZ on S and N, and cc-pVDZ on H) and correlating all electrons. In these CCSD(T) partial optimisations, all other parameters were fixed at the MP2/cc-pVTZ values.

For $S(NBu^t)_2$, using the results obtained for $S(NH)_2$, final bond length estimates were made for the Bu^t derivative according to the following incremental procedure:

Table 1 Optimised and extrapolated S=N bond lengths (pm) and relative energies (kJ mol^{-1}) for the *E*/*Z* and *E*/*E* conformers of $S(NH)_2$ and for $S(NH)_3$

	$S(NH)_2$					
	E/*Z* (C_s)			*E*/*E* (C_{2v})		
Level/basis set	r_1(S=N)	r_2(S=N)	$r_2 - r_1$	r(S=N)	E_{rel}[a]	$S(NH)_3$
RHF/6-31G*	150.1	151.3	1.2	150.7	23.3	149.3
MP2/6-31G*	155.9	157.7	1.8	157.2	21.2	154.1
MP2/cc-pVDZ	157.8	159.5	1.7	159.1	18.3	155.7
MP2/cc-pVTZ	154.7	156.5	1.8	155.9	12.7	153.0
MP2/cc-pVQZ′[b]	153.5	155.4	1.9	154.7	11.3	152.0
MP2/cc-pV5Z′[c]	152.8	154.7	1.9	154.0	10.4	151.3
MP2 extrapolation [e^{-x}][d]	152.7	154.6	1.9	154.0	10.0	151.2
MP2 extrapolation [x^{-2}][e]	152.0	153.9	1.9	153.3	8.8	150.6
MP2 extrapolation [av.][f]	152.3 ± 0.4	154.3 ± 0.4	2.0 ± 0.6	153.6 ± 0.4	9.4	—
CCSD(T)/cc-pVTZ′ [g]	154.1	155.8	1.7	155.3	14.5	—
B3LYP/6-31G*	—	—	—	—	—	154.0
B3LYP/6-311G*	—	—	—	—	—	153.3
B3LYP/GEN[h]	—	—	—	—	—	153.5
B3LYP/6-311+G(3df,p)	—	—	—	—	—	151.4
B3PW91/6-31G*	—	—	—	—	—	153.4
B3PW91/6-311G*	—	—	—	—	—	152.7
B3PW91/GEN[h]	—	—	—	—	—	152.8
B3PW91/6-311+G(3df,p)	—	—	—	—	—	151.0
1_4GGA/TZ2P						151.6

[a] Relative to *E*/*Z* isomer. [b] cc-pVQZ on S and N, cc-pVTZ on H. [c] cc-pV5Z on S and N, cc-pVQZ on H. [d] Extrapolated using inverse exponential fit. [e] Extrapolated using inverse quadratic fit. [f] Average of inverse exponential and inverse quadratic fit. [g] Only S=N bond lengths were optimised. [h] 6-311+G* on S and N, 6-31G* on H.

$$(\mathrm{Bu}^t,\mathrm{estim.}) = r(\mathrm{H,MP2\ estim.}) + [r(\mathrm{H,CCSD(T)}) - r(\mathrm{H,MP2})] + [r(\mathrm{Bu}^t,\mathrm{MP2}) - r(\mathrm{H,MP2})]$$

where *r*(H,MP2 estim.) is an extrapolated value from Table 1 and the *r*(R,level) in the square brackets are distances optimised using a basis of pVTZ quality.

In the case of $S(NH)_2$, CCSD(T)/cc-pVTZ′ calculations gave S=N bond lengths 0.6–0.7 pm shorter than at the MP2(fc)/cc-pVTZ level, so, for $S(NH)_3$, we estimate the distance at CCSD(T)/extrapolated basis set to be 150.2(3) pm. Using these results, the final S=N bond length estimate was made for the Bu^t derivative according to the following incremental procedure:

$$(\mathrm{Bu}^t,\mathrm{estim.}) = r(\mathrm{H,MP2(fc)\ estim.}) + \{-0.7\ \mathrm{pm\ [from\ S(NH)_2\ calculation]}\} + [r(\mathrm{Bu}^t,\mathrm{MP2(fc)}) - r(\mathrm{H,MP2(fc)})]$$

where *r*(H,MP2(fc) estim.) is an extrapolated value from Table 1 and the values *r*(R,level) in square brackets are distances optimised using a basis of 6-31G* quality. S=N bond lengths in $S(NH)_3$ are 2.4 pm shorter than the average length in $S(NH)_2$. Therefore, we expect the S=N bond length to be 152.8 pm in $S(NBu^t)_3$. DFT calculations were carried out on $S(NH)_3$ using the standard 6-31G* and 6-311G* basis sets, as well as with the 6-311+G* basis set on S and N and 6-31G* on H, and 6-311+G(3df,p) on all atoms.

Electron diffraction measurements

Data were collected for both compounds using the Edinburgh gas diffraction apparatus.[25] An accelerating voltage of *ca.* 44.5 kV (electron wavelength *ca.* 5.7 pm) was used, whilst maintaining the sample and nozzle temperatures at 343 and 383 K respectively for $S(NBu^t)_2$, and 383 K for $S(NBu^t)_3$. Scattering intensities were recorded at nozzle-to-plate distances of 94 and 260 mm for $S(NBu^t)_2$ and 93 and 258 mm for $S(NBu^t)_3$ on Kodak Electron Image plates. The weighting points for the off-diagonal weight matrices, correlation parameters and scale factors for the two camera distances are given in Table 2, together with electron wavelengths, which were determined from the scattering patterns of benzene vapour, recorded immediately after the compound patterns and analysed in exactly the same way to minimise systematic errors in wavelengths and camera distances. A Joyce–Loebl MDM6 microdensitometer[26] was used to convert the intensity patterns into digital form. Data reduction and least-squares refinements were carried out using standard programs,[26,27] employing the scattering factors of Ross *et al.*[28]

X-Ray diffraction measurements

Details of data collection for $S(NBu^t)_2$ and $S(NBu^t)_3$ are shown in Table 3.

CCDC reference numbers 191359 and 191360.

See http://www.rsc.org/suppdata/dt/b2/b207193b/ for crystallographic data in CIF or other electronic format.

Results

Ab initio calculations

Bis(*tert*-butyl)sulfurdiimide. Optimisations converged to two different isomers, namely *E*/*Z* and *E*/*E*, in C_s and C_{2v} symmetry, respectively. The latter was found to be much higher in energy than the former [36.6 kJ mol^{-1} at the MP2(fc)/6-31G* level], implying 99.9% of the *E*/*Z* conformer at 298 K and consistent with the lack of evidence for detectable amounts of the *E*/*E* isomer in ^1H and ^{15}N NMR studies.[4]

Since electron correlation is usually important for the description of multiple bonds,[29] a further geometry optimisation was undertaken on the *E*/*Z* conformer at the MP2/cc-pVTZ′ level. In general, geometric parameters proved to be rather insensitive to improvements in the basis set and level of theory, with the exception of the S=N bond lengths, which were predicted to be 149.7 and 151.0 pm at the HF/6-31G* level but increased to 157.2 and 159.7 pm at MP2/6-31G* and 155.7 and 158.3 pm at MP2/cc-pVTZ′.

In view of the large variation in the predicted values of the S=N bond lengths in $S(NBu^t)_2$, a series of further computations was carried out for the parent, $S(NH)_2$, in an attempt to

Table 2 Nozzle-to-plate distances (mm), weighting functions (nm^{-1}), correlation parameters, scale factors and electron wavelengths (pm) used in the electron-diffraction study

	$\mathrm{S(NBu^t)_2}$		$\mathrm{S(NBu^t)_3}$	
Nozzle-to-plate distance[a]	93.51	260.03	92.5	258.05
Δs	4	2	4	2
$s_{\min}$	100	20	92	20
sw_1	120	40	112	40
sw_2	304	140	256	128
$s_{\max}$	356	164	300	150
Correlation parameter	0.428	−0.053	0.400	0.325
Scale factor[b]	0.720(5)	0.774(5)	0.684(17)	0.945(7)
Electron wavelength	5.684	5.687	6.016	6.016

[a] Determined by reference to the scattering pattern of benzene vapour. [b] Values in parentheses are the estimated standard deviations.

Table 3 X-Ray crystal structure data collection, processing, solution and refinement for $\mathrm{S(NBu^t)_2}$ and $\mathrm{S(NBu^t)_3}$

Compound	$\mathrm{S(NBu^t)_2}$	$\mathrm{S(NBu^t)_3}$
Empirical formula	$\mathrm{C_8H_{18}N_2S}$	$\mathrm{C_{12}H_{27}N_3S}$
Formula weight	175.31	245.43
Temperature/K	100(2)	100(2)
Wavelength/pm	71.073	71.073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/pm	596.99(3)	932.28(3)
b/pm	928.77(4)	934.55(3)
c/pm	993.38(4)	1066.75(3)
α/°	72.5050(10)	70.5150(10)
β/°	88.3380(10)	77.5710(10)
γ/°	84.6610(10)	60.5540(10)
Volume/nm^3	0.52304(4)	0.76152(4)
Z	2	2
Absorption coefficient/mm^{-1}	0.258	0.196
F(000)	194	272
Crystal size/mm	0.4 × 0.4 × 0.4	0.48 × 0.45 × 0.30
Reflections collected	12299 (low ∠ batch), 25532 (high ∠ batch)	17996 (low ∠ batch), 44864 (high ∠ batch)
Independent reflections	11808 [R(int) = 0.0546 (low ∠ batch), R(int) = 0.0666 (high ∠ batch)]	18250 [R(int) = 0.0287 (low ∠ batch), R(int) = 0.0307 (high ∠ batch]
Absorption correction	Empirical	Empirical
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	11808/0/155	18250/0/227
Final R indices [I>2σ(I)]	$R_1 = 0.0324$, $wR_2 = 0.0775$	$R_1 = 0.0280$, $wR_2 = 0.0730$
R indices (all data)	$R_1 = 0.0509$, $wR_2 = 0.0820$	$R_1 = 0.0343$, $wR_2 = 0.0750$

quantify how further improvements in the calculations might affect bond lengths in $\mathrm{S(NBu^t)_2}$. These involved larger basis sets and higher theoretical levels than are currently possible for $\mathrm{S(NBu^t)_2}$. From the corresponding results in Table 1, it is clear that the optimised S=N bond lengths in $\mathrm{S(NH)_2}$ are very sensitive to the basis set employed. At the MP2 level, a very large basis is required for convergence of the results. For instance, between MP2/cc-pVQZ′ and MP2/cc-pV5Z′, the S=N bond distances vary by as much as 0.7 pm. The series of correlation-consistent basis sets employed has been specifically designed for extrapolation to the basis-set limit. According to our extrapolation scheme (see Theoretical methods), the MP2/6-31G* distances are larger by more than 3 pm than the final MP2 estimates. Effects of higher levels of electron correlation appear to be less important, and are of the order of 1 pm [compare MP2/cc-pVTZ and CCSD(T)/cc-pVTZ′ entries in Table 1].

When applying the higher-level corrections obtained for $\mathrm{S(NH)_2}$ to the $\mathrm{Bu^t}$ derivative (see Theoretical methods), one arrives at the final extrapolated theoretical estimates of 152.9 and 155.5 (±0.4) pm for the S=N bond lengths, compared to the MP2/cc-pVTZ″ estimates of 155.7 and 158.3 pm. The molecular geometry of $\mathrm{S(NBu^t)_2}$ for the MP2/cc-pVTZ″ calculation is presented in Table 4.

Tris(*tert*-butyl)sulfurtriimide. Most parameters remained insensitive to changes in basis set and level of theory used. However, the large jump in S=N bond length from HF/6-31G* to MP2/6-31G* levels observed in $\mathrm{S(NBu^t)_2}$ was also observed in $\mathrm{S(NBu^t)_3}$ and can be attributed to the effects of electron correlation. Further geometry optimisations at higher levels were not undertaken because of the size of the molecule. However, the extrapolation of S=N bond length applied to $\mathrm{S(NBu^t)_2}$ from the calculations on the parent compound $\mathrm{S(NH)_2}$ (see above) can also be applied in this case, with a slight modification to allow for the highest level calculation being MP2/6-31G* instead of MP2/cc-pVTZ. First, the change in S=N distance going from MP2/6-31G* to MP2/cc-pVTZ found for $\mathrm{S(NBu^t)_2}$ was applied to $\mathrm{S(NBu^t)_3}$. Then corrections based on $\mathrm{S(NH)_2}$ were applied as before. The best estimate of r(S=N) in $\mathrm{S(NBu^t)_3}$ was thus 153.9 pm.

Density functional theory calculations were also carried out on the parent $\mathrm{S(NH)_3}$ compound using Becke's three-parameter hybrid functional[30a] with both the correlation of Lee, Yang and Parr[30b,c] (B3LYP), and Perdew and Wang (B3PW91).[30d–f] Several basis sets of increasing size were used, 6-31G*, 6-311G*, 6-311+G* on S and N and 6-31G* on H (GEN), and 6-311+G(3df,p). Both B3LYP/GEN and B3PW91/6-31G* give estimates of the S=N bond length (153.5 and 153.4 pm) that compare extremely well with the experimentally determined S=N bond length of 153.5(3) pm. However, larger basis sets gave extremely poor results, as did other functionals, including newer ones such as 1_4GGA.[31] In this case, the 1_4GGA/TZ2P gave an S=N bond length of 151.6 pm. The success of the B3LYP and B3PW91 calculations with the smaller basis sets must be regarded as fortuitous. At this time, we do not

Table 4 Refined and calculated geometric parameters for $\mathrm{S(NBu^t)_2}$ (distances in pm, angles in degrees) from the GED study[a],[b]

No.	Parameter	GED (r_a)	MP2/cc-pVTZ″	Restraint
p_1	[C–C + S(1)–N(2) + S(1)–N(3) + C(4)–N(2) + C(5)–N(3)]/5	151.2(1)	151.4[c]	—
p_2	C(5)–N(3) − C(4)–N(2)	0.7(5)	0.7[c]	0.7(5)
p_3	S(1)–N(3) − S(1)–N(2)	2.6(5)	2.6	2.7(5)
p_4	[C–C] − [{C(5)–N(3) + C(4)–N(2)}/2]	6.0(4)	5.6	5.6(5)
p_5	[C–C] − [{S(1)–N(3) + S(1)–N(2)}/2]	−0.2(4)	−1.0	−0.4(5)
p_6	C–H	111.8(1)	110.3	—
p_7	[N(3)–C(5)–C(9) + N(2)–C(4)–C(6)]/2	110.1(3)	108.8	—
p_8	[N(3)–C(5)–C(9) − N(2)–C(4)–C(6)]/2	–0.2(4)	0.4	—
p_9	[S(1)–N(2)–C(4) + S(1)–N(3)–C(5)]/2	121.3(6)	121.6	—
p_{10}	[S(1)–N(2)–C(4) − S(1)–N(3)–C(5)]/2	−9.3(4)	−8.9	−8.9(5)
p_{11}	N(2)–S(1)–N(3)	117.8(6)	116.9	—
p_{12}	C–C–H	109.6(4)	110.0	—
p_{13}	*tert*-butyl tilt(1)	−6.7(5)	—	—
p_{14}	*tert*-butyl tilt(2)	−4.9(5)	—	—
Dependent parameters				
p_{15}	N(3)–C(5)–C(9)	115.6(6)	116.2	116.2(10)
p_{16}	N(3)–C(5)–C(10/11)	105.4(5)	105.4	105.4(10)
p_{17}	N(2)–C(4)–C(6/8)	111.1(4)	110.3	110.3(10)
p_{18}	N(2)–C(4)–C(7)	103.8(6)	105.1	105.1(10)
p_{19}	C(6)–C(4)–C(7)	110.2(3)	110.0	—
p_{20}	C(9)–C(5)–C(10)	110.0(3)	109.8	—
p_{21}	S(1)–N(2)–C(4)	125.9(6)	126.0	—
p_{22}	S(1)–N(3)–C(5)	116.7(7)	117.1	—
p_{23}	S(1)–N(2)	153.8(3)	152.9	—
p_{24}	S(1)–N(3)	156.5(4)	155.5	—
p_{25}	N(2)–C(4)	146.2(4)	147.3	—
p_{26}	N(3)–C(5)	147.0(4)	147.9	—
p_{27}	C(5)–C(9)	152.6(2)	153.1	—
p_{28}	C(4)–C(6)	152.6(2)	153.3	—

[a] Figures in parentheses are the estimated standard deviations of the last digits. [b] See text for parameter definitions. [c] Values for S(1)–N(2) and S(1)–N(3) are based on extrapolated values (see Theoretical methods).

Table 5 Refined and calculated geometric parameters for $\mathrm{S(NBu^t)_3}$ (distances in pm, angles in degrees) from the GED study[a]

No.	Parameter	GED (r_a)	MP2(fc)/6-31G*	Restraint
p_1	C–H	112.9(3)	109.4	—
p_2	(S=N + C–C + 0.4N–C)/2.4	151.3(1)	153.2	153.2(10)
p_3	S=N − [C–C + C–N)/2]	4.9(5)	4.6	4.6(5)
p_4	C–C − C–N	2.7(4)	4.1	4.1(5)
p_5	C–C–H	107.1(5)	108.8	108.8(10)
p_6	N–C–C average	108.4(3)	108.4	—
p_7	N–C–C difference	10.5(5)	7.4	—
p_8	C–C–C difference	0.5(7)	1.3	1.3(8)
p_9	S=N–C	122.9(4)	123.2	—
p_{10}	N=S=N–C	173.0(5)	180.0	—
p_{11}	Methyl twist	53.4(23)	54.9	54.9(30)
p_{12}	Butyl twist	188.5(7)	180.0	180.0(10)

[a] Figures in parentheses are the estimated standard deviations of the last digits. See text for parameter definitions.

believe that the problems associated with the S=N bond length convergence can be resolved with the use of standard DFT procedures alone, and a user-defined model would need to be generated, using the gas-phase results as a guide.

The molecular geometry of $\mathrm{S(NBu^t)_3}$ for the MP2/6-31G* calculation is presented in Table 5.

Gas-phase electron diffraction refinement

Bis(*tert*-butyl)sulfurdiimide. On the basis of the *ab initio* calculations, the molecular model for $\mathrm{S(NBu^t)_2}$ was defined assuming overall C_s symmetry, that all methyl substituents were equivalent and maintained local C_{3v} symmetry, and that *tert*-butyl substituents had local C_3 symmetry. Within levels of experimental uncertainty all six of the C–C bond lengths were predicted to be indistinguishable and were therefore treated as equivalent.

Altogether 14 independent geometrical parameters were used to define the structure of the $\mathrm{S(NBu^t)_2}$ in C_s symmetry, as listed in Table 4 using the atom-numbering scheme in Fig. 1. These parameters define a total of six bond length, six bond angle, and two tilt parameters. The bond length parameters are the average of C–C, C(5)–N(3), C(4)–N(2), S(1)–N(2), and S(1)–N(3), p_1; the difference between C(5)–N(3) and C(4)–N(2) bond lengths, p_2; the difference between S(1)–N(2) and S(1)–N(3) bond lengths, p_3; difference between the average C–N and the C–C bond lengths, p_4; difference between the average S–N bond length and the C–C bond length, p_5; and the C–H bond length, p_6. The bond angle parameters are the average and difference of the C–C–C angles for each of the two *tert*-butyl groups, p_7 and p_8, the average and difference of S(1)–N(2)–C(4) and S(1)–N(3)–C(5), p_9 and p_{10}, the N(2)–S(1)–N(3) bond angle, p_{11}, and C–C–H, p_{12}. The two tilt parameters, p_{13} and p_{14}, allow the two *tert*-butyl substituents to tilt in the mirror plane of the molecule. For p_{13}, a negative value tilts the *tert*-butyl group toward the central sulfur atom and a positive value tilts away from the sulfur; p_{14}, tilts in an inverse manner to p_{13}. Deviations of the *tert*-butyl groups from the plane of the molecule are possible but it would be difficult to distinguish them and so a *tert*-butyl group torsion was not included.

The radial-distribution curve for $S(NBu^t)_2$ [Fig. 2(a)] contains three distinct peaks below 300 pm, at distances of *ca.* 110, 150, and 250 pm. The peak at 110 pm corresponds to C–H scattering while the intense peak at 150 pm corresponds to scattering from C–C, C–N, and N–S bonds. The peak at 250 pm corresponds to scattering from a number of non-bonded atom pairs such as C(6–8) ⋯ N(2), C(9–11) ⋯ N(3), S(1) ⋯ C(4,5) and N(2) ⋯ N(3). The associated shoulder at 215 pm arises from non-bonded interactions of the methyl hydrogens with their central *tert*-butyl carbon. Above 300 pm the two well-defined peaks at 320 and 390 pm result from scattering by S ⋯ C(methyl) atom pairs.

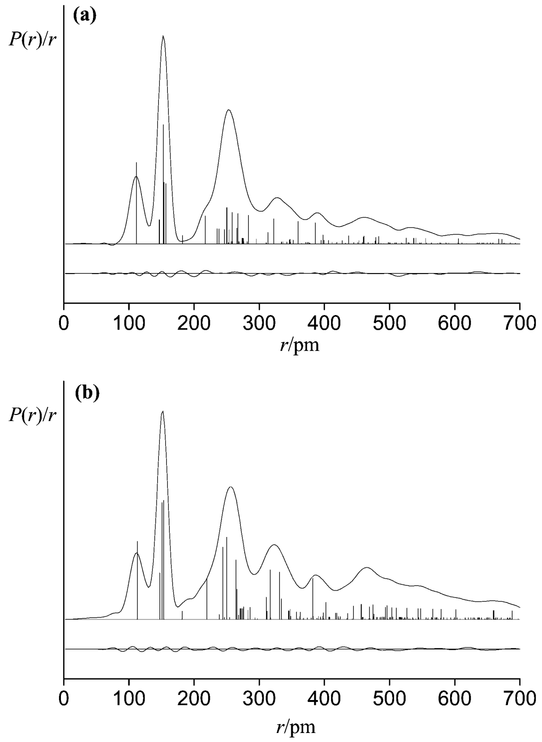

Fig. 2 Experimental and difference (experimental − theoretical) radial-distribution curves, $P(r)/r$, for (a) $S(NBu^t)_2$ and (b) $S(NBu^t)_3$. Before Fourier inversion the data for both compounds were multiplied by $s{\cdot}\exp(-0.00002s^2)/(Z_N - f_N)/(Z_C - f_C)$.

Initial parameter values for the r_a structure refinement were taken from the geometry optimisation at the MP2/cc-pVTZ level, except for parameters involving the S=N bonds for which the extrapolated values were employed. The theoretical HF/6-31G* Cartesian force field was converted into symmetry coordinates using the ASYM 40[32] program and scaled to obtain amplitudes of vibration (u). In the absence of an assignment of the experimental frequencies scaling factors were chosen empirically to be 0.90, 0.85 and 0.80 for bond stretches, angle bends and torsions, respectively. The presence of a number of low-frequency modes led to overestimated predictions for perpendicular amplitudes of vibration. Since these values were considered to be unreliable, corrections for shrinkage effects were not incorporated.

In all 11 restraints were applied in accordance with the SARACEN[33] method; these consisted of nine geometric and two amplitude restraints. The use of these restraints allowed the refinement of all geometric parameters, together with all amplitudes of vibration for pairs of heavy atoms and for those pairs involving hydrogen that contribute intensity greater than 10% of the predominant scattering pair. Fig. 1 shows a diagram of the final refined structure of $S(NBu^t)_2$, for which $R_G = 0.033$ ($R_D = 0.039$). The interatomic distances, mean amplitudes of vibration and most significant elements of the correlation matrix for $S(NBu^t)_2$ are provided as ESI (Tables S1 and S2). The success of the final refinement may be assessed on the basis of the difference between the experimental and the calculated radial-distribution curves in Fig. 2(a). Fig. 3(a) offers a similar comparison between the experimental and calculated molecular scattering curves.

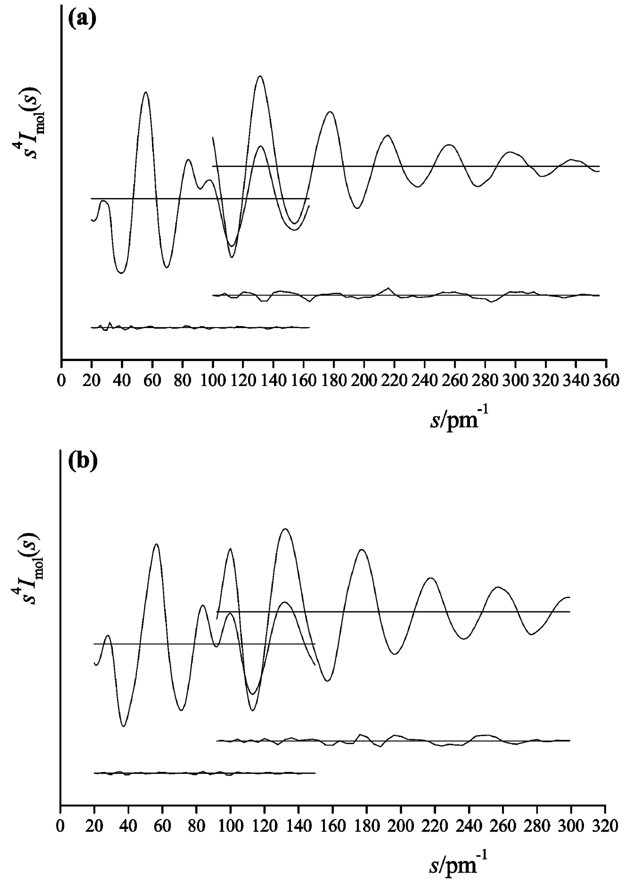

Fig. 3 Experimental and final weighted difference (experimental − theoretical) molecular-scattering intensities for (a) $S(NBu^t)_2$ and (b) $S(NBu^t)_3$.

Tris(*tert*-butyl)sulfurtriimide. On the basis of the *ab initio* calculations described above, electron-diffraction refinements were carried out using a model of C_3 symmetry to describe the vapour. The large number of geometric parameters needed to define the model made it necessary to make some assumptions, including local C_{3v} symmetry for all methyl groups. The structure of $S(NBu^t)_3$ was finally defined in terms of twelve independent geometric parameters, comprising four bond lengths, five bond angles and three torsion parameters [Table 5; atom numbering shown in Fig. 1(b)].

The independent distance parameters are the C–H bond length (p_1) and the weighted average of the C–C, S=N and 0.4 × C–N distances (p_2), with two differences, [(S=N + C–C)/2 − C–N] (p_3) and [S=N − C–C] (p_4). All C–C–H bond angles (p_5) were assumed to be identical, but the calculated large asymmetry in the butyl groups was allowed for by introducing an average N–C–C bond angle (p_6) (which therefore defines the mean C–C–C angle), with difference angles p_7 [N–C–C(4) − N–C–C(5/6)] and p_8 [C(5)–C(3)–C(6) − C(4)–C(3)–C(5/6)]. These three together define the six angles at the central carbon

Table 6 Comparison of experimental and theoretical geometrical parameters for S(NBu^t)$_2$.[a] (Parameter numbering X-ray/GED, *ab initio*)

Parameter	X-Ray	GED	*Ab initio* (MP2/cc-pVTZ″)
S(1)–N(2)/S(1)–N(2)	152.8(3)	153.8(3)	152.9[b]
S(1)–N(1)/S(1)–N(3)	154.4(3)	156.5(4)	158.3[b]
N(2)–C(2)/N(2)–C(4)	147.7(5)	146.2(4)	147.3
N(1)–C(1)/N(3)–C(5)	148.9(4)	147.0(4)	147.9
C–C (mean)	152.2(3)	152.6(2)	153.2
C–H (mean)	96.8(13)	111.8(1)	110.3
N(2)–S(1)–N(1)/N(2)–S(1)–N(3)	117.4(2)	117.8(6)	116.9
S(1)–N(2)–C(2)/S(1)–N(2)–C(4)	128.1(2)	125.9(6)	125.9
S(1)–N(1)–C(1)/S(1)–N(3)–C(5)	118.2(2)	116.7(7)	117.1
C–C–C (mean)	110.1	110.2(3)	109.6
C–C–H (mean)	109.5	109.6(4)	110.3
N(2)–S(1)–N(1)–C(1)/N(2)–S(1)–N(3)–C(5)	2.0	0.0(fixed)	0.0
N(1)–S(1)–N(2)–C(2)/N(3)–S(1)–N(2)–C(4)	179.2(1)	180.0(fixed)	180.0

[a] See Fig. 1 for atom numbering. [b] Extrapolated values (see Theoretical methods).

atom with local C_s symmetry as calculated *ab initio* and the S=N–C angle was also included (p_9). If the N=S=N–C dihedral angle (p_{10}) was 180°, the molecule would have perfect planarity of the S(NC)$_3$ core and C_{3h} symmetry. This parameter allows for possible deviation from this planarity, which would lead to C_3 symmetry for the molecule.

The remaining two parameters represent the torsions of the methyl and butyl groups. These groups were generated initially by placing a methyl group carbon atom at the origin, with its three H atoms arranged with local C_{3v} symmetry about the x-axis and one H in the xy plane in the positive x and y directions. The methyl torsion parameter (p_{11}) is a rotation about the local x axis. The methyl group is then translated along the positive x axis by the C–C bond length and the central carbon of the *tert*-butyl group is placed at the origin. The correct C–C–C bond angles are generated by rotating the methyl group about the z axis, moving the methyl carbon atom in the positive y direction, and then generating the other methyl groups by rotation of the first group about the local x axis. The *tert*-butyl torsion angle is a rotation of the group about the local x axis (p_{12}).

The *tert*-butyl group is then translated along the positive x axis by the N–C bond length and the butyl group rotated into position by the S=N–C angle. The other NBu^t groups are then generated by 120 and 240° rotations of the first group about the z axis of the central S atom. Finally, the N=S=N–C torsion angle describes the deviation of the NBu^t groups from the C_{3h} axis of the molecule.

The starting parameters for the r_a refinement were taken from the theoretical geometry optimised at the MP2/6-31G* level. The r_α structure was not refined because the rectilinear vibrational corrections (*i.e.* parallel and perpendicular correction terms) are known to be unreliable for a molecule this size with many low-lying vibrational modes. Theoretical (HF/6-31G*) Cartesian force fields were obtained and converted into force fields described by a set of symmetry coordinates using ASYM 40.[32] All geometric parameters were then refined.

Altogether twelve geometric parameters and eighteen groups of vibrational amplitudes were refined. Flexible restraints were employed during the refinement using the SARACEN method.[33] In total, seven geometric and five amplitude restraints were employed. These are listed in Tables 5 and S3 (ESI).

The success of the final refinement, for which R_G = 0.039 (R_D = 0.030), can be assessed on the basis of the radial distribution curve [Fig. 2(b)] and the molecular scattering intensity curves [Fig. 3(b)]. Final refined parameters are listed in Table 5. Interatomic distances with their corresponding amplitudes of vibration and the least-squares correlation matrix are provided as ESI (Tables S3 and S4). In the SARACEN analysis, because all parameters are refining, the error estimates are realistic. We therefore quote the estimated standard deviations, σ, and do not need to add any further allowance for correlation with fixed parameters.

Fig. 1(b) shows a perspective view of S(NBu^t)$_3$ in the optimum refinement of the GED data.

Crystal structure determination

Solid-state structural analysis of S(NBu^t)$_2$ and S(NBu^t)$_3$ in the solid phase was carried out using low-temperature single-crystal X-ray diffraction at 153 and 100 K respectively. Both were found to possess the triclinic space group $P\bar{1}$ with two asymmetric units per unit cell. The structures were solved by direct methods[34] and all non-hydrogen atoms were treated as anisotropic. In the solid state, S(NBu^t)$_2$ adopts the *E*/*Z* conformation [Fig. 4(a)], while S(NBu^t)$_3$ adopts a structure with a planar SN$_3$ skeleton [Fig. 4(b)]. Tables 6 and 7 show relevant

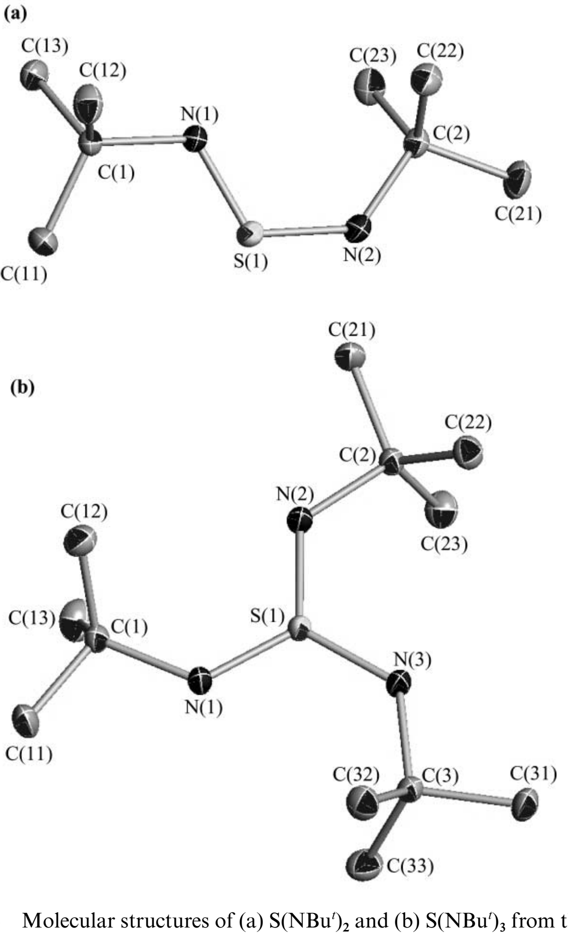

Fig. 4 Molecular structures of (a) S(NBu^t)$_2$ and (b) S(NBu^t)$_3$ from the low-temperature X-ray crystallographic studies.

Table 7 Comparison of experimental and theoretical geometrical parameters for $S(NBu^t)_3$[a]

Parameter	X-Ray	GED	*Ab initio* [MP2(fc)/6-31G*]
S=N	151.0	153.5(3)	152.8[b]
N–C	148.3	147.3(5)	148.7
C–C (mean)	153.1	150.8(2)	152.8
C–H (mean)	98.0	112.9(3)	109.3
S=N–C	125.9	122.9(4)	123.2
C–C–C (mean)	110.0	109.9(3)	110.4
H–C–H (mean)	109.5	107.1(5)	108.8
N=S=N–C	179.4	173.0(5)	180.0

[a] See Fig. 1 for atom numbering. [b] Extrapolated value (see Theoretical methods).

bond distances and angles of the crystal structure results as well as comparable information obtained from GED refinements and *ab initio* calculations for both molecules. Although crystal structures for both molecules have been reported,[10,35a] the new data are markedly superior and yield much greater precision.

Discussion

The structural properties of $S(NBu^t)_2$ and $S(NBu^t)_3$ have been investigated in the gas phase by GED, in the solid state by low temperature X-ray crystallography, and by *ab initio* calculations. The solid-phase structure of $S(NBu^t)_2$ reveals that all the atoms of the C_2N_2S backbone are almost coplanar, with a deviation from the mean plane of 0.51 pm. The methyl carbon C(11) lies in the plane, whereas C(23) is 28 pm out of the plane. The mean S–N distance [153.6 pm] is slightly longer than that found for $S(NSiMe_3)_2$[35] from an X-ray crystallographic study [151.9(1) pm] and in the normal range found for S=N double bonds in a range of solid-state structures including $S[NP(S)Bu^t{}_2]_2$[36] and $Me_3SiNSNSC_6H_4$-4-NO_2.[37] In alkali-metal derivatives of the chelating anionic ligands of the type $[(RN)_2S(R')]$, the mean SN distance is 160–163 pm and the N(1)–S(1)–N(2) angles are in the range of 105 to 110°.[1] It is worth noting that in the solid state, the crystal packing exhibits relatively short intermolecular S ··· S interactions of 359.9 pm, which are 10 pm shorter than the sum of the van der Waals radii.[38] These intermolecular interactions may account for the slight deviations from molecular C_s symmetry observed. Similar Te–Te intermolecular interactions of this type have previously been observed for $Te[N(SiMe_3)_2]_2$, which has an analogous arrangement of the molecules.[39]

In the gas phase, $S(NBu^t)_2$ is predicted from *ab initio* calculations to adopt an *E*/*Z* conformation (C_s symmetry), in agreement with earlier NMR studies. Of the other possible conformers, *E*/*E* and *Z*/*Z*, only the *E*/*E* structure is predicted to represent a local minimum on the potential energy surface, but is substantially higher in energy than the *E*/*Z* arrangement. GED studies were undertaken assuming the presence of the *E*/*Z* conformation only. On that basis an excellent fit to the experimental data was obtained (R_G = 0.033). Furthermore, impressive agreement between the theoretical and experimental structures was achieved. For example, the S=N bond lengths refined to 153.8(3) and 156.5(4) pm, compared to the extrapolated theoretical estimates of 152.9 and 155.5 pm for these distances, while the C–N bond distances refined to 146.2(4) and 147.0(4) pm, compared to 147.3 and 147.9 pm at the MP2/cc-pVTZ′ level. Bond angles also agreed quite well: N(2)–S(1)–N(3) refined to 117.8(6)° compared to 116.9° (MP2/cc-pVTZ′), S(1)–N(2)–C(4) refined to 125.9(6)° compared to to 125.9° (MP2/cc-pVTZ′), and S(1)–N(3)–C(5) refined to 116.7(7)° compared to to 117.1° (MP2/cc-pVTZ′).

Comparison of the structure of $S(NBu^t)_2$ in the gas and solid phases reveals surprisingly good agreement for all parameters, except those involving hydrogen, suggesting that this molecule can be regarded as forming a molecular solid. The largest discrepancies occur in the bond lengths of the C_2N_2S backbone. S=N bond lengths refined to 153.8(3) and 156.5(4) pm and are longer than the distances determined in the solid state [152.8(3) and 154.4(3) pm]. The gas-phase C–N bond lengths [146.2(4) and 147.0(4) pm] are slightly shorter than the solid-state distances [147.7(5) and 148.9(4) pm].

The refined structure of $S(NBu^t)_2$ is in good agreement with that previously obtained for $S(NMe)_2$ using GED.[40] All bond length and bond angles for both the structures are found within a range of 2 pm and 2°, with the exception of the N(2)–S(1)–N(3) bond angle of 113.6(9)° for $S(NMe)_2$ and 117.8(6)° for $S(NBu^t)_2$. This change in the N(2)–S(1)–N(3) bond angle for $S(NBu^t)_2$ may be attributed to the increased steric bulk of the *tert*-butyl substituents over the smaller methyl groups in $S(NMe)_2$. Many other structural features found in sulfur diimides are also observed for $S(NBu^t)_2$, for example a widening of the S–N–C angle of the *Z* substituent [125.9(6)°] over the corresponding angle of the *E* substituent [116.7(7)°]. Widening of this S–N–C angle on the *Z* substituent may be explained by the close interaction of the *tert*-butyl substituent with the further nitrogen atom.

High level *ab initio* calculations for the parent compound H–N=S=N–H suggest that the *E*/*Z* conformer is also preferred for this compound. The relative energies for the *E*/*Z*, *E*/*E* and *Z*/*Z* forms are 0.0, 13.8 and 2.9 kJ mol^{-1} respectively at the CCSD/TZP+//MP2/TZP+ level.[41] While the *Z*/*Z* conformer of the parent sulfur diimide is only slightly above the *E*/*Z* global minimum in this case, the *Z*/*Z* form of $S(NBu^t)_2$ is expected to be strongly destabilised as a result of severe steric repulsions between the adjacent *tert*-butyl groups.

Previous GED studies of $S(NSiMe_3)_2$[42] show the *Z*/*Z* conformer in the gas phase, which conflicts with the previously determined solid-state structure of the *E*/*Z* conformer.[35] The intermolecular hydrogen ··· hydrogen interactions of 210.7 pm are only slightly beyond their van der Waals radii.[38] The refined GED structure of $S(NSiMe_3)_2$ was refined in the absence of *ab initio* calculations, which may account for its implausible geometry with extremely distorted bond angles. In light of this investigation of the preferred conformations of sulfur diimides, re-evaluation of the gas phase $S(NSiMe_3)_2$ structure seems prudent.

The solid-phase structure of $S(NBu^t)_3$ was found to be very close to molecular C_{3h} symmetry. The S=N distance (151.0 pm) is appreciably shorter than both those in $S(NBu^t)_2$ and most other compounds, except for $S(NSiMe_3)_2$ [151.9(1) pm].[42]

In the gas phase, all three $=S(NBu^t)_2$ fragments are *E*/*Z* with a third NBu^t group attached, an arrangement very similar to that adopted by the $S(NBu^t)_2$ molecule. This is the only possible conformation for the triimide that avoids the steric crowding associated with the *Z*/*Z* conformation which was found not to exist for $S(NBu^t)_2$. GED studies were undertaken assuming the presence of this one conformation. On the basis of this assumption an excellent fit to the experimental data was obtained [R_G = 0.039]. The theoretical and experimental structures were also in good agreement. For example, the S=N bond length refined to 153.5(3) pm, compared to the extrapolated theoretical estimate of 152.9 pm and the DFT value of 153.5 pm. This is close to one of the S=N bond distances calculated for $S(NBu^t)_2$ [153.8(3) pm] but the second distance in that compound is 156.5(4) pm. The C–N bond distance refined to 147.2(4) pm, compared to 148.7 pm at the MP2(fc)/6-31G* level, and 146.2(4) and 147.0(4) pm for $S(NBu^t)_2$. Bond angles in $S(NBu^t)_3$ also agreed well with theoretical values; for example, the S=N–C angle refined to 122.9(4)° compared to 123.2° [MP2(fc)/6-31G*]. As the molecule has C_3 symmetry, there is just one S=N–C angle, slightly wider than the average of the *Z* and *E* angles observed in $S(NBu^t)_2$. The shorter S=N bond length in $S(NBu^t)_2$ [153.8(3) pm] is associated with the much wider S=N–C angle [125.9(6)°], while the longer bond length is associated with the narrower bond angle [156.5(4) pm and 116.7(7)°]. It can be concluded that in $S(NBu^t)_2$, the angles and bond lengths can adjust to a greater extent to reduce the steric interaction between the two *tert*-butyl groups, whereas in $S(NBu^t)_3$, the presence of the extra *tert*-butyl group reduces this effect and leads to a more strained structure overall.

$S(NBu^t)_3$ was calculated to have C_{3h} symmetry. However, the observed GED structure has C_3 symmetry, with the butyl groups twisted out of the plane by ~7° [ϕ(NSNC]: MP2(fc)/6-31G* 180.0°, experimental 173.0(5)°]. An r_a refinement was carried out rather than r_α, because, as for $S(NBu^t)_2$, the calculation of perpendicular amplitudes is known to be unreliable for molecules of this size, with many low-frequency torsional vibrations. Therefore there are shrinkage effects leading to the apparent non-planarity of the refined structure of the molecule.

The main difference between the solid and gas-phase structures of $S(NBu^t)_3$ occurs in the NSNC torsion angle. Other parameters generally agree well, although there are differences between the structures. For example, the mean C–C distance refined to 150.8(2) pm in the GED study, whereas it was observed to be 153.1 pm in the crystal. Another significant difference is in the S=N–C bond angles, 122.9(4)° in the gas-phase structure, 125.9° in the solid structure. This could be an effect of the packing constraints imposed on the molecules in the crystal. The bulky butyl groups are not able to deviate from the C_{3h} plane, so instead the S=N–C angles increase to accommodate them. The internal CCC angles are consistent with each other and with calculated values, and deviate very little from 109.5°. This indicates that there is very little distortion actually within the butyl groups themselves, and the widening at the S=N–C angles provides all of the release of steric strain.

The refined structure of $S(NBu^t)_3$ appears to differ slightly from that calculated for $S(NMe)_3$ at the B3PW91/cc-pVDZ level.[23,30] The calculated S=N and N–C bond lengths were 155.2 and 146.0 pm compared to 153.5(3) and 147.3(5) pm for the experimental structure of $S(NBu^t)_3$. The difference in the S=N bond lengths cannot be analysed quantitatively because of the uncertainties in the calculated values. However, the lengthening of the N–C bond in $S(NBu^t)_3$ can be attributed to the inductive effect of the butyl groups. Another observation is the marked widening of the S=N–C angle to 122.9(4)° in $S(NBu^t)_3$; this may be attributed to the bulk of the butyl groups.

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