Is the Molecular Structure of 1,4,7-Trithiacyclononane([9]aneS$_3$) as Symmetrical in the Gas Phase as it is in the Crystal? An Electron Diffraction Study

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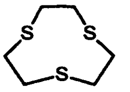
The molecular structure of [9]aneS$_3$ has been studied by gas electron diffraction (GED) and by molecular-mechanics calculations (MM2). Four molecular models have been fitted to the experimental data, one having D_3 symmetry, one C_3 symmetry, one C_2 symmetry and one C_1 symmetry. The D_3 model was incompatible with the GED data and was discarded. The C_1 model gave the lowest R-factor in the GED analysis, and the C_2 model gave only a slightly poorer fit to the data. The C_3 model, which corresponds to the conformation observed in the crystalline state, could not be completely excluded, but the model gave a significantly worse fit to the GED data than the C_2 and C_1 models. MM2 calculations also favoured the C_1 model, but with the C_3 model only 0.13 kJ mol^{-1} higher in strain energy. The C_2 and D_3 models were higher in energy by 8.3 and 9.9 kJ mol^{-1} respectively.

The co-ordination chemistry of macrocyclic sulphide ligands has been the subject of much recent interest.[1,2] Whereas sulphides, R_2S, are often poor donors to transition metal ions,[3] their cyclic analogues have been found to co-ordinate to a wide range of metal ions to form stable complexes.[1] The trithia macrocycle [9]aneS$_3$ (1,4,7-trithiacyclononane), in particular, usually binds facially to metal ions and therefore parallels the co-ordination of cyclopentadienyl, aryl, tripyrazolylborate and triphos ligands.[1] The single-crystal X-ray structure of metal-free 1,4,7-trithiacyclononane ([9]aneS$_3$) shows it to adopt a [333][4] *endo* conformation with C_3 symmetry.[5] Approximate C_3 symmetry of the ligand is retained in most metal complexes, although C_2 symmetry has been observed in some cases, particularly with d^8 metal ions.[6] If the ligand symmetry found in the crystal is maintained in solution, the *S*-donors in the metal-free ligand are pre-organised[7] for facial co-ordination to metal ions. In contrast, the solid-state structures of other polysulphides S_4-, S_5- and S_6-donor crowns show that they tend to adopt *exo* conformations in which the donor atoms point out of the macrocyclic cavities.[8,9] Rearrangement from an *exo* to an *endo* conformation is therefore a common feature of the co-ordination chemistry of these latter ligands,[8,10] but not for [9]aneS$_3$.



[9]aneS$_3$
1,4,7-trithiacyclononane

Conformational analysis of [9]aneS$_3$ using photoelectron spectroscopy has suggested that the [333] conformation is retained in the gas phase.[11] We wished to probe the conformation of metal-free [9]aneS$_3$ further, particularly with respect to pre-organisation effects. We report here a gas-phase electron-diffraction study and the results of molecular-mechanics (MM2) calculations on uncoordinated [9]aneS$_3$.

Experimental

Synthesis.—[9]aneS$_3$ was synthesised according to the template method of Sellmann and Zapf[12] or purchased directly from the Aldrich Chemical Co.

Electron Diffraction.—Electron diffraction scattering intensities were recorded photographically on Kodak Electron Image plates using the Edinburgh gas diffraction apparatus,[13] operating at *ca.* 44.5 kV. During the measurements the sample was maintained at 473 K and the nozzle at 493 K. Three plates were exposed with the distance between nozzle and plate set at 258 mm and three at 95 mm. Data for benzene were recorded to provide calibration of the camera distances and electron wavelength (Table 1). The ranges of the data sets and weighting points used in setting up the off-diagonal weight matrix, scale factors and correlation parameters are also listed in Table 1. Absorbance data were obtained using a Joyce–Loebl MDM6 microdensitometer at the SERC Laboratory, Daresbury. The scanning program[14] and programs used subsequently for data reduction[15] and least-squares refinements are those described previously. The scattering factors used were those reported by Fink *et al.*[16] The experimental molecular scattering intensity curves are shown in Fig. 2.

NMR Spectra.—In an attempt to ascertain which conformation was preferentially adopted, or whether there was an equilibrium mixture of co-existing conformers, ^{13}C NMR spectra were recorded at low temperatures. Using a Bruker WH360 spectrometer, only a single peak was observed in the ^{13}C spectrum of a solution in toluene, from room temperature down to 190 K. This was the lowest temperature that could be attained using solvents in which an appreciable amount of [9]aneS$_3$ could be dissolved.

Structure Refinements.—Four different molecular models were considered in the structural analysis of [9]aneS$_3$ based on electron-diffraction data. The four models had D_3, C_3, C_2 and C_1 symmetry and are shown in Fig. 1. For all four models all C–H bond lengths were assumed to be equal, the HCH angles were fixed at 110° and the CH$_2$ groups were placed so that the plane defined by the atoms of each group bisected the SCC angle at the corresponding carbon atom. Each model is described in detail below.

The D$_3$ *Model.*—This represents one of two possible conformers described as [333] when using Dale's nomenclature[4] and is shown in Fig. 1(*a*). The ring geometry can be described by four independent parameters: the distance between the sulphur atoms, $r(S\cdots S)$, the sulphur–carbon bond length, r(S–C), the carbon–carbon bond length, r(C–C), and one valence angle, chosen as CSC. Together with r(C–H) and the

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Table 1 Camera heights, electron wavelengths, weighting functions, correlation parameters and scale factors for the ED data[a]

Camera height/ mm	λ/pm	Δs	$s_{\min}$	sw_1	sw_2	$s_{\max}$	Correlation parameter	Scale factor
		nm^{-1}						
256.46	5.670	2	20	40	140	164	0.4511	0.807(8)
94.17	5.671	4	100	140	300	352	0.3725	0.801(26)

[a] The correlation parameters and scale factors are in principle different for the models presented in this paper. The differences are, however, very small, and only the data for the C_2 model are listed here.

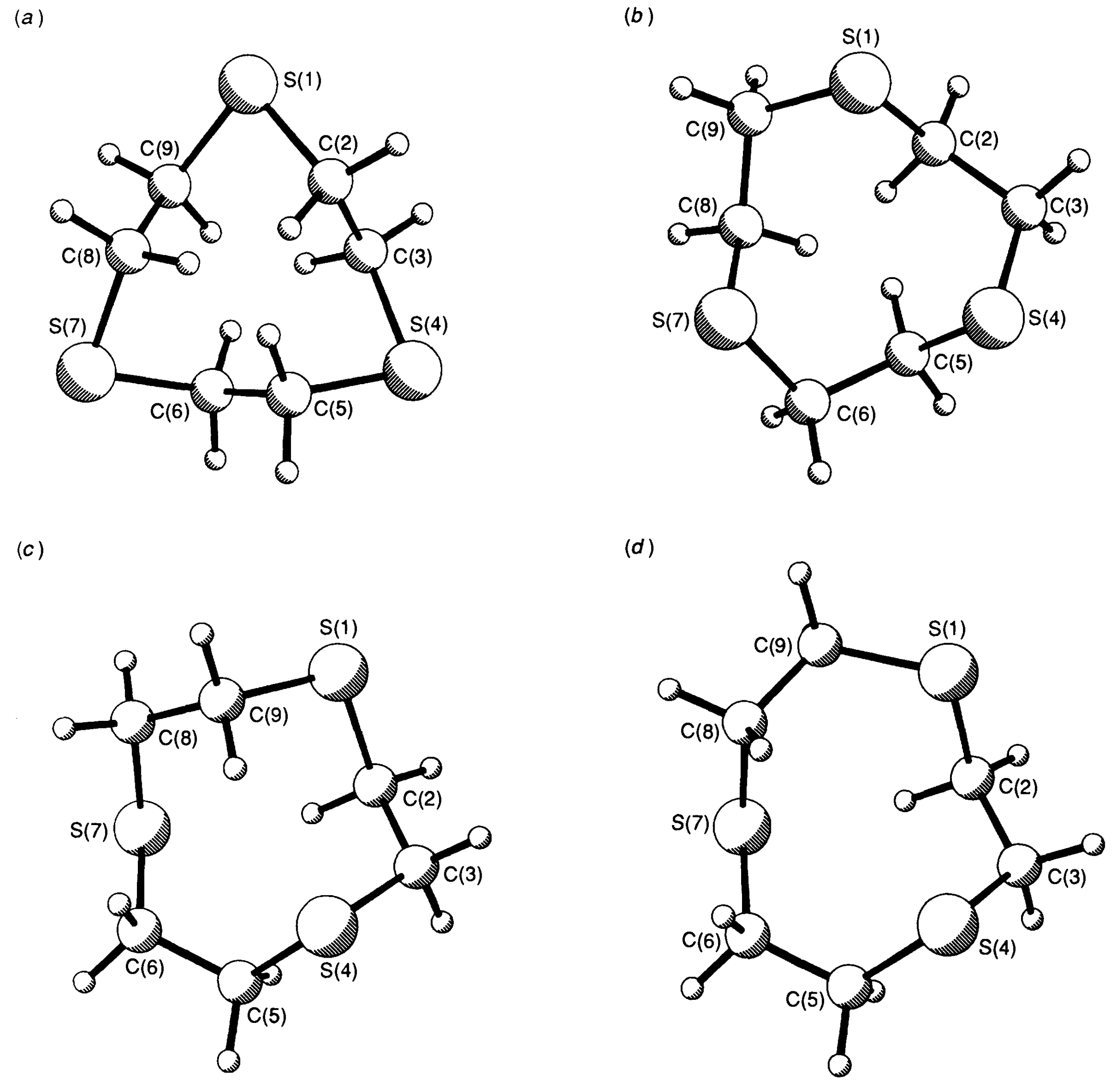

Fig. 1 The molecular models considered in the gas electron-diffraction study of [9]aneS_3 (*a*) D_3 model, (*b*) C_3 model, (*c*) C_2 model and (*d*) C_1 model. Numbering of the atoms is shown.

angle HCH this makes six independent parameters which together describe the whole molecular structure. The D_3 model was found to be incompatible with the electron-diffraction data. The curves labelled (*b*) in Figs. 2 and 3 are the differences between experimental and theoretical curves for a reasonable molecular model of D_3 symmetry. The reason for the great discrepancy between the theoretical and observed molecular scattering intensity curves obtained is mainly a consequence of the very long S $\cdots$ S distance, which is inevitable for this model if the valence angles are sensible. It is reasonable to assign the peak at approximately 360 pm in the radial distribution curve [Fig. 3(*a*)] to the S $\cdots$ S distances. This is much shorter than the S $\cdots$ S distance of 440 pm expected for the D_3 model (see Table 4).

The C_3 *Model*.—This conformer is the second [333] conformer, and is shown in Fig. 1(*b*). The ring geometry can be described by seven independent parameters. By fixing the S_3 triangle in the *xy* plane the six carbon atoms will form two triangles which must be parallel to the S_3 plane. One such plane is defined by the atoms 2, 5 and 8 and the other by the atoms 3, 6 and 9. One of the parameters was chosen as the distance between the sulphur atoms, $r(S \cdots S)$, and three parameters were then needed to define each C_3 plane. They were chosen to be the C $\cdots$ C distances of the two C_3 triangles, $d(2,5,8)$ and $d(3,6,9)$, the perpendicular distances between the S_3 plane and the two C_3 planes, $z(2,5,8)$ and $z(3,6,9)$, and the rotations about the *z*-axis of the two C_3 triangles relative to the fixed S_3 triangle, $\tau(2,5,8)$ and $\tau(3,6,9)$, defined as positive for clockwise

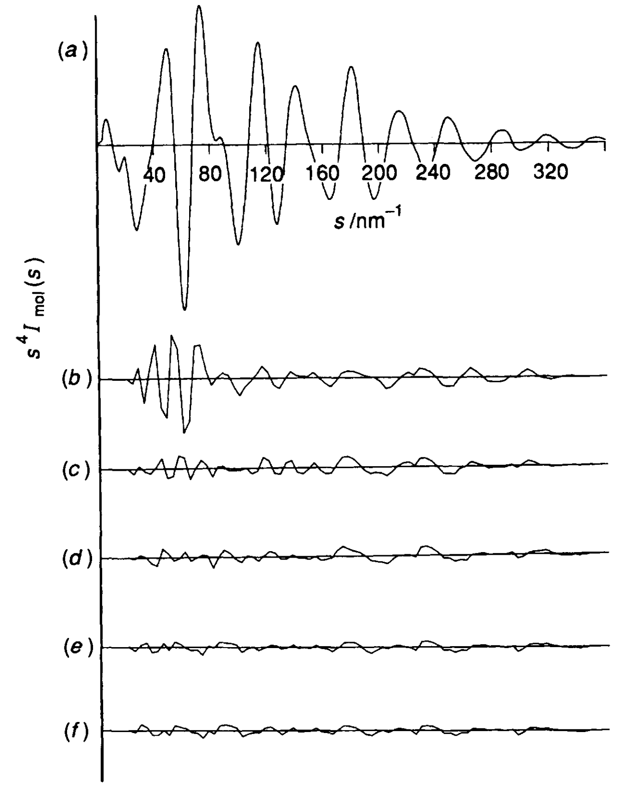

Fig. 2 (*a*) The combined experimental molecular scattering intensity curve for [9]aneS$_3$. The lower part of the figure shows the difference curves (experimental–theoretical) for (*b*) D_3 model, (*c*) constrained C_3 model (see the text), (*d*) non-constrained C_3 model, (*e*) C_2 model and (*f*) C_1 model.

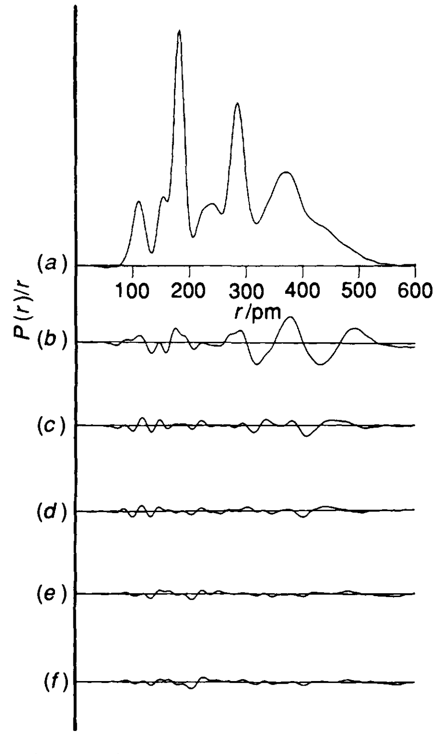

Fig. 3 (*a*) The experimental radial distribution curve, *P*(*r*)/*r*, for [9]aneS$_3$. The lower part of the figure shows the difference between experimental and theoretical curves for (*b*) the D_3 model, (*c*) the constrained C_3 model, (*d*) the non-constrained C_3 model, (*e*) the C_2 model and (*f*) the C_1 model. Before Fourier inversion the data were multiplied by $s \exp(-0.000\,02s^2)/(Z_C - f_C)(Z_S - f_S)$.

rotations. Together with *r*(C–H) and the angle HCH there are thus nine independent parameters. Eight of these could be refined, together with six RMS amplitudes of vibration (*u*-values). The values of the parameters obtained are presented in Table 2, and the corresponding bond lengths and angles and amplitudes of vibration are listed in Table 3. Refinements in which CSC was loosely constrained to 103(1)°, SC(2) to 112.5(5)° and CC(3)S to 116.3(5)°, values close to those measured in the crystalline phase, gave a poorer fit to the experimental intensity curves than the unconstrained C_3 model. The *R*-factors obtained for the constrained C_3 model for the two sets of data were 0.16 and 0.18, respectively. In Figs. 2 and 3 differences between experimental and theoretical intensity and radial distribution curves for the constrained C_3 model (*c*) and the unconstrained C_3 model (*d*) are shown.

The C_2 *Model.*—In Dale's nomenclature this is a [12222] conformer: it is illustrated in Fig. 1(*c*). By assuming that the two S–C bonds which are, in principle, different, are actually of equal length and that the two different types of C–C bond are also of equal length, the ring geometry can be described by eight independent parameters. The S(1) atom was fixed at the origin and the three atoms S(1), C(5) and C(6) were fixed in the *xy* plane. Two dummy atoms, A at (0,1,0) and B at (1,1,0), were used when calculating the atomic co-ordinates from the bond distances *r*(S–C), *r*(C–C) and *r*(C–H), the four valence angles CS(1)C, SC(2)C, CC(3)S and HCH, and the three torsional angles τ[ABS(1)C(2)], τ[AS(1)C(2)C(3)] and τ[S(1)C(2)C(3)C(4)]. Nine of the independent parameters could be refined together with six RMS amplitudes of vibration.

There are two possible C_2 conformers. One can be made from the D_3 conformer by twisting one of the C–C torsions from $+g$ to $-g$. However, MM2 calculations indicate that the S···S distances of this C_2 conformer are of the same magnitude as the S···S distance in the D_3 conformer (approximately 420 pm), which is not compatible with the peak in the experimental radial distribution curve at about 360 pm assigned to the S···S distances [Fig. 3(*a*)]. The calculations also give 13.8 kJ mol^{-1} higher strain energy for this C_2 conformer compared with that shown in Fig. 1(*c*). For these reasons only the low-energy C_2 conformer shown in Fig. 1(*c*) was considered in the structural analysis based on electron diffraction data. The final values of the refined parameters obtained for this conformer are given in Table 2, and the corresponding geometrical and vibrational parameters are listed in Table 3. The curves labelled (*e*) in Figs. 2 and 3 are the differences between experimental and theoretical curves obtained for the best C_2 model.

The C_1 *Model.*—The molecular model is shown in Fig. 1(*d*). By assuming that the lengths of all the S–C bonds are equal, that the three C–C bond lengths are equal, that the three CSC angles are equal, and that the six SCC angles are equal to within 1.0(8)° (loosely constrained), 13 independent parameters are needed to describe the molecular structure. These parameters were chosen as the three bond distances *r*(S–C), *r*(C–C) and *r*(C–H), the four angles CS(1)C, SC(2)C, CC(3)S and <HCH, and six torsional angles τ[SC(2)C(3)S], τ[CC(3)S(4)C], τ[CS(4)C(5)C], τ[SC(5)C(6)S], τ[CC(6)S(7)C] and τ[CS(7)C(8)C].

There are several reasonable C_1 conformers, and in a structural analysis based on electron diffraction alone we cannot distinguish properly between them. In this case we have chosen to rely on the results from the MM2 calculations and only do structural refinements on the best C_1 model from these calculations, using the calculated parameters as starting values in the electron diffraction analysis. Three different C_1 conformers were obtained, starting from the C_3 and two C_2 conformers, by twisting one C–C torsion in each case. The conformers obtained correspond roughly to [234], [12222] and [234] in Dale's nomenclature.[4] The two different [234]

Table 2 The independent geometrical parameters used to describe the C_3, C_2 and C_1 models for [9]aneS$_3$

	C_3 model		C_2 model		C_1 model	
p_1	r(S···S)	353.0(10)	r(S–C)	181.9(1)	r(S–C)	182.0(1)
p_2	d(2,5,8)[b]	287.5(16)	r(C–C)	153.6(4)	r(C–C)	153.3(4)
p_3	z(2,5,8)[c]	−132.7(7)	r(C–H)	110.6(4)	r(C–H)	110.9(4)
p_4	τ(2,5,8)[d]	37.6(2)	<CS(1)C	104.5(12)	<CSC	103.8(7)
p_5	d(3,6,9)[b]	395.7(14)	<SC(2)C	118.2(42)	<SC(2)C	115.0(5)
p_6	z(3,6,9)[c]	−95.2(14)	<CC(3)S	115.8(21)	<CC(3)S	115.7(5)[e]
p_7	τ(3,6,9)[d]	78.4(1)	τ[BAS(1)C(2)][f]	145.4(29)	<HCH	110.0[g]
p_8	r(C–H)	108.6(5)	τ[AS(1)C(2)C][f]	−71.6(11)	τ[SC(2)C(3)S]	59.5(18)
p_9	<HCH	110.0[e]	τ[SC(2)C(3)S]	−113.5(37)	τ[CC(3)S(4)C]	74.6(14)
p_{10}	—		<HCH	110.0[g]	τ[CS(4)C(5)C]	−102.9(14)
p_{11}	—		—		τ[SC(5)C(6)S]	74.3(10)
p_{12}	—		—		τ[CC(6)S(7)C]	−104.2(13)
p_{13}	—		—		[CS(7)C(8)C]	129.6(14)
R_1[h]		0.095		0.080		0.088
R_2[h]		0.149		0.115		0.103

[a] Distances in pm, angles in degrees. [b] d(a,b,c) is the length of the sides of the equilateral triangle a,b,c, where a, b and c are the atom reference numbers. [c] z(a,b,c) is the distance between the plane defined by the three sulphur atoms and the parallel plane defined by the three atoms a, b and c. [d] τ(a,b,c) is the clockwise rotation of the triangle (a,b,c) relative to the triangle defined by the three sulphur atoms. [e] Constrained to be 1.0(8)° larger than SC(2)C. [f] In order to describe the molecular model two dummy atoms A and B at (0,1,0) and (1,1,0) were used. [g] Fixed value. [h] R_n for data set number n of Table 1. R = **D**′**WD**/**I**′**WI**, where **I** is the vector of observed intensities, **D** the vector of residuals and **W** the weight matrix.

Table 3 Structural parameters obtained for the C_3, C_2 and C_1 models of [9]aneS$_3$ by analysis of gas electron-diffraction data[a]

	C_3 model		C_2 model		C_1 model	
	r_a	u	r_a	u	r_a	u
r(S–C)	182.0(1)	5.9(2)	181.9(1)	5.8(2)	182.0(1)	5.7(2)
r(C–C)	154.2(4)	5.6(5)	153.6(4)	5.5(4)	153.3(4)	5.7(4)
r(C–H)	108.6(5)	7.6(6)	110.6(4)	7.3(4)	110.9(4)	7.2(4)
r(S···S)	352(1)	23.0(8)	365(1)	21(1)	350(2)	19(1)
	—	—	368(3)	21[b]	367(1)	19[b]
	—	—	—	—	369(2)	19[b]
r(S···C)	290(1)	6.4(7)	288(6)	8.1(17)	283(1)	9.1(2)
	280(1)	6.4[c]	285(3)	8.1[c]	284(1)	9.1[c]
	—	—	278(2)	8.1[c]	284(1)	9.1[c]
	—	—	—	—	283(1)	9.1[c]
	—	—	—	—	284(1)	9.1[c]
	—	—	—	—	283(1)	9.1[c]
<CS(1)C	90.6(7)	—	104.5(12)	—	103.8(7)	—
<SC(2)C	119.1(4)	—	118.2(2)	—	115.0(5)	—
<CC(3)S	111.8(3)	—	115.8(21)	—	115.7[d]	—
<CS(4)C	—	—	103.8(14)	—	103.8[e]	—
<SC(5)C	—	—	111.5(11)	—	115.0[f]	—
<CC(6)S	—	—	—	—	115.7[g]	—
<CS(7)C	—	—	—	—	103.8[e]	—
<SC(8)C	—	—	—	—	115.0[f]	—
<CC(9)S	—	—	—	—	116.1[h]	—
τ[CS(1)C(2)C]	−141.5(5)	—	−71.6(11)	—	−127.1(15)	—
τ[SC(2)C(3)S]	61.7(9)	—	66.5(37)	—	59.5(18)	—
τ[CC(3)S(4)C]	56.1(8)	—	66.1(46)	—	74.6(14)	—
τ[CS(4)C(5)C]	—	—	−110.5(29)	—	−102.9(14)	—
τ[SC(5)C(6)S]	—	—	85.9(17)	—	74.3(10)	—
τ[CC(6)S(7)C]	—	—	—	—	−104.2(13)	—
τ[CS(7)C(8)C]	—	—	—	—	129.6(14)	—
τ[SC(8)C(9)S]	—	—	—	—	−74.9(18)	—
τ[CC(9)S(1)C]	—	—	—	—	63.9(16)	—

[a] Distances and u-values in pm, angles in degrees. [b] The S···S u-values were constrained to be equal. [c] The u-values of these similar S···C distances were constrained to be equal. [d] Loosely constrained to be 1.0(8)° larger than <SC(2)C. [e] Assumed equal to <CS(1)C. [f] Assumed equal to <SC(2)C. [g] Assumed equal to <CC(3)S. [h] Constrained to be 0.1(8)° smaller than <CC(3)S.

conformers were both about 9.6 kJ mol^{-1} higher in strain energy than the [12222] conformer so only the latter was considered in the electron diffraction analysis. The C_1 [12222] conformer shown in Fig. 1(*d*) is made by twisting the S(2)C(3)S torsion of the C_2 model shown in Fig. 1(*c*) from +*g* to −*g*. The final refined parameters obtained for this C_1 conformer are given in Table 2 and the corresponding set of bond lengths and angles and vibrational parameters is given in Table 3. The differences between experimental and theoretical intensity data and radial distribution curves obtained for the C_1 [12222] model are shown labelled (*f*) in Figs. 2 and 3, respectively.

Table 4 Structural parameters obtained from MM2 calculations for the D_3, C_3, C_2 and C_1 models of [9]aneS_3[a]

	D_3 model	C_3 model	C_2 model	C_1 model
r[S(1)–C(2)]	182.6	182.1	181.8	182.2
r[C(2)–C(3)]	154.1	154.2	153.7	153.9
r[C(3)–S(4)]	—	182.5	181.7	182.3
r[S(4)–C(5)]	—	—	181.9	182.1
r[C(5)–C(6)]	—	—	154.9	154.0
r[C(6)–S(7)]	—	—	—	182.0
r[S(7)–C(8)]	—	—	—	182.1
r[C(8)–C(9)]	—	—	—	154.1
r[C(9)–S(1)]	—	—	—	182.2
r(C–H)	111.0, 111.5	111.1–111.5	110.8–111.5	111.1–111.5
r[S(1) ··· S(4)]	432.9	330.9	361.6	336.0
r[S(4) ··· S(7)]	—	—	377.9	362.4
r[S(7) ··· S(1)]	—	—	—	383.4
<CS(1)C	102.8	101.4	106.3	101.8
<SC(2)C	112.5	111.5	114.9	110.6
<CC(3)S	—	114.4	115.4	112.4
<CS(4)C	—	—	102.8	100.8
<SC(5)C	—	—	111.5	111.2
<CC(6)S	—	—	—	111.1
<CS(7)C	—	—	—	101.2
<SC(8)C	—	—	—	110.8
<CC(9)S	—	—	—	112.3
τ[CS(1)C(2)C]	61.1	−133.9	−73.7	−124.8
τ[SC(2)C(3)S]	−140.9	52.1	70.2	61.8
τ[CC(3)S(4)C]	—	62.4	58.6	74.2
τ[CS(4)C(5)C]	—	—	−111.3	−122.1
τ[SC(5)C(6)S]	—	—	92.8	82.2
τ[CC(6)S(7)C]	—	—	—	−93.0
τ[CS(7)C(8)C]	—	—	—	134.1
τ[SC(8)C(9)S]	—	—	—	−96.7
τ[CC(9)S(1)C]	—	—	—	75.0
Strain energy (E_s/kJ mol^{-1})	87.74	77.95	86.11	77.82
Dipole moment-(μ/Debye)	0.0	4.3	1.3	1.5

[a] Distances and angles in degrees.

MM2 Calculations.—In order to estimate the energy differences between the conformers, molecular-mechanics calculations on [9]aneS_3 were carried out using the MM2 program.[17] A number of energy minimisations were performed from different starting parameters and using different symmetry constraints. The structural parameters and final strain energies obtained for the four lowest-energy conformers are shown in Table 4. Study of a model of the molecule indicates that the energy minima are separated by significant barriers, and there can be no doubt that they do represent genuine minima on the calculated energy surface.

Results and Discussion

The aim of this study was to investigate the conformation of [9]aneS_3 as a free molecule in the gas phase. We have used molecular-mechanics calculations (MM2) as a tool and electron diffraction (ED) as the experimental method. Because it is necessary to derive the three-dimensional molecular structure from one-dimensional ED data, it is possible to fit more than one molecular model to the experimental data. This means that any conclusion concerning the conformation of such a complex molecule as [9]aneS_3 has to be drawn with care. As is seen in Table 4, the strain energies of the conformers studied do not differ enormously, so the MM2 calculations do not allow us to reach absolutely unequivocal conclusions about the conformation(s) present. Nevertheless, these calculations do give information about the likely values of the various structural parameters of the different conformers, as well as giving an indication of the relative stability (and hence abundance) of the various forms. In this way the structures from the MM2 calculations can be used to decide whether or not a structure deduced from the experimental data is reasonable.

Previous conformational studies of medium to large non-co-ordinated cyclic sulphides ($\geqslant 12$ ring atoms) in the crystalline state indicate that most of these compounds adopt the *exo* conformation with the sulphur atoms pointing out of the macrocyclic cavity. This has been explained as a consequence of the tendency of the CCSC linkages to adopt *gauche* conformations.[8,9] A maximum number of such *gauche* arrangements is attained when the sulphur atoms have positions in the 'corners' of the macrocycle. This is in contrast with what is observed for the analogous crown oxyethers, in which the oxygen atoms are not positioned in the corners and the *anti* conformation is preferred for the CCOC linkages. As the ring size becomes smaller ($\leqslant 11$ ring atoms) the flexibility of the ring becomes less and one would expect other effects such as 1,4 and 1,5 interactions across the ring to be significant in determining the conformation of the ring.

For [9]aneS_3, the D_3 conformer is the only one in which all the CCSC groups have the *gauche* conformation. This conformer is, however, not present, either in the gas or in the crystalline phase. [9]aneS_3 has been found to adopt the C_3 conformation in the crystal, and a C_3 conformer can also be fitted to the ED data, but some of the structural parameters obtained are not reasonable (Table 3). In particular, the refined CSC angle of 90.6(7)° is much too small compared with the CSC angle of 99° in SMe_2,[18] whereas one would expect it to be somewhat larger than in SMe_2, owing to steric effects. The constrained C_3 model, in which the CSC and SCC angles were restricted to values close to those measured in the crystal, gave an unsatisfactory fit to the experimental data. From these refinements we can therefore conclude that [9]aneS_3 does not exclusively adopt the C_3 conformation in the gas phase, although we cannot exclude the possibility that it is present as a minor component of a mixture of forms.

The C_2 and C_1 conformers [Figs. 1(*c*) and 1(*d*)] can both be fitted satisfactorily to the experimental data. The structural parameters refine easily to reasonable values that are in good agreement with those obtained from the MM2 calculations. Both the C_2 and C_1 structure models have two possible 1,5 S $\cdots$ H interactions which may stabilise them. Such 1,5 interactions were invoked to account for the conformation of [9]aneO_3,[19] which has been shown to adopt a C_1 conformation very similar to the C_1 conformation of [9]aneS_3 in the present study, but S $\cdots$ H contacts would not be expected to be so significant energetically as the O $\cdots$ H interacts. The MM2 calculations favour the C_1 relative to the C_2 conformer by 8.3 kJ mol^{-1}, which is not enough to indicate definitely that one form is strongly preferred over the other. In addition, we cannot rule out the possibility that the C_2 and C_1 conformers are present in a mixture, with or without small amounts of the C_3 form. Nevertheless, we must note that the C_1 model gives both the lowest *R*-factor in the ED analysis and the lowest strain energy in the MM2 calculations, and consequently it is highly probable that this conformer is the major constituent of gaseous [9]aneS_3 at about 500 K.

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