

differ significantly from the normal double bond length. Electrophilic reagents are known to attack the molecule at N(3) (Olsen, 1969); this is in accordance with a significant contribution of a resonance structure which has the double bond between N(1) and N(2) and a negative charge at N(3).

The remaining bond lengths agree with the values given in *International Tables for X-Ray Crystallography* (1962). The C-H distances are in the range 0.82–1.08 Å with a standard deviation of 0.04 Å. Bond angles which involve hydrogen are also quite normal (98–119°, e.s.d. 2–3°).

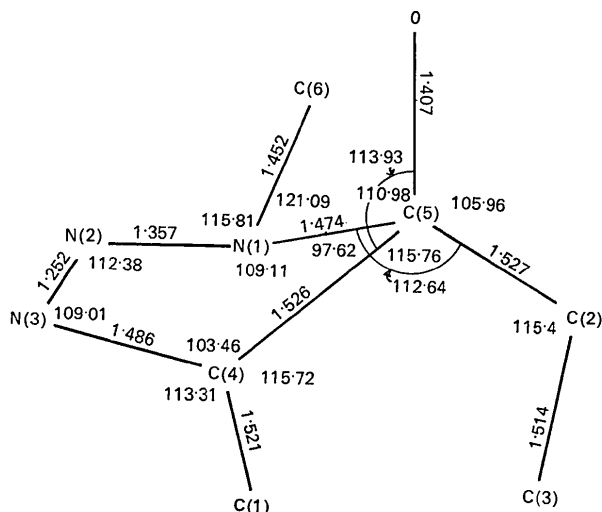


Fig. 5. Bond distances (Å) and angles (°).

### The hydrogen bond

The hydrogen bond O-H(1)···N'(3) is approximately linear. The O-N distance is 2.879 (3) Å, the O-H distance 0.88 (4) Å and the N···H distance 2.01 (4) Å. The N'-H-O angle is 173 (3)°. The hydrogen bond makes an angle of 30.6° with the planar part of the ring containing the hydrogen bonded nitrogen. The C(4)-N(3)···H' angle is 136.5 (9)°, and the N(2)-N(3)···H' angle is 111.5 (9)°.

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## The Crystal Structure of Sodium Tetrasulphide, Na<sub>2</sub>S<sub>4</sub>

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Sodium tetrasulphide, Na<sub>2</sub>S<sub>4</sub>, is tetragonal and crystallizes in space group  $I\bar{4}2d$  with cell dimensions  $a = 9.5965(3)$  and  $c = 11.7885(5)$  Å, and with  $Z = 8$ . Three-dimensional intensity data were collected with a linear diffractometer (PAILRED) using Mo  $K\alpha$  radiation. Positional and anisotropic temperature-factor parameters for all atoms were refined by a full-matrix least-squares method to  $R(F) = 0.030$  based on 1749 independent reflexions with  $I_o > 4I$ . The crystal structure is built up of unbranched S<sub>4</sub><sup>2-</sup> ions surrounded by Na<sup>+</sup> ions. The distance between different S<sub>4</sub><sup>2-</sup> ions is about 3.60 Å. The S<sub>4</sub><sup>2-</sup> ions lie on a twofold axis and the sulphur-sulphur bond distances are 2.074(1) Å (end) and 2.061(1) Å (middle). The sulphur-sulphur bond angle is 109.76(2)° and the dihedral angle is 97.81°. The sodium-sulphur coordination polyhedra consists of two types: a distorted tetrahedron with two pairs of distances of 2.826(1) and 2.842(1) Å and a distorted octahedron with three pairs of distances of 2.887(1), 3.043(1) and 3.081(1) Å.

### Introduction

Our current work attempts to establish conditions for the formation of Na polysulphides and to determine

their structures in the solid and liquid states (Rosén & Tegman, 1972; Tegman, 1972). The structure of Na<sub>2</sub>S<sub>4</sub> was studied as a part of this programme. Crystal structure determinations of sodium polysulphides can give

valuable information as regards, for example, coordination numbers and bond distances, which are difficult to obtain by the indirect methods available for 'structure' determinations of salt melts.

The alkali metals form polysulphides with the general formula  $M_2S_n$ , containing  $S_n^{2-}$  anions. The many analogous  $M_2S_n$  compounds form an interesting area for systematic studies of sulphur-sulphur bonds in structures with different M and  $S_n$  species. Of about fifteen polysulphides described in the literature the crystal structures have been determined for only  $Na_2S_2$ ,  $K_2S_2$  (obtained from powder data) by Föppl, Busmann & Frorath (1962) and  $Cs_2S_6$  (obtained from single-crystal data) by Abrahams & Grison (1953) and Hordvik & Sletten (1968). The surprisingly few structure determinations that have been performed probably reflect the difficulties in single-crystal preparations of polysulphides. This paper presents the structure of  $Na_2S_4$  with accurate dimensions for the S-S and Na-S distances and includes some comments on the sulphur-sulphur bond characters.

### Experimental

#### Crystal preparation

Polycrystalline  $Na_2S_4$ , prepared by the reaction between  $Na_2S$  and S at  $300^\circ C$ , was used as starting material in the single-crystal preparations (Rosén & Tegman, 1971). The polycrystalline  $Na_2S_4$  was suspended in absolute ethanol. The suspension was placed in one arm of a very clean U-shaped Pyrex tube with one end closed. The U-tube was carefully cooled in ice water to reduce the vapour pressure of alcohol and then evacuated and sealed. After equilibrating the solution with solid  $Na_2S_4$  for some hours at  $25^\circ C$  the

U-tube was inverted with approximately equal amounts of solid and solution in the two arms. One arm was then placed in a Dewar flask with melting ice and the other was held in air at room temperature. After a few hours, small crystals appeared in the liquid film on the wetted glass wall about 10–20 mm above the surface of the warmer solution. Slow evaporation of the solution from the warm part to the cold part of the U-tube caused the crystals to grow. After a week the tube was broken and the most regular crystals were collected and mounted in Lindemann glass capillaries.  $Na_2S_4$  is extremely hygroscopic and sensitive to humid air oxidation. All handling operations of the open  $Na_2S_4$  system were therefore performed in a glove-box filled with purified and dried nitrogen.

#### Crystal data

Chemical formula	$Na_2S_4$
F.W.	174.24
Melting point	$295^\circ C$
Habit	Dipyramidal
Crystal system	Tetragonal
Unit-cell dimensions at $23^\circ C$	
<i>a</i>	9.5965 (3) Å
<i>c</i>	11.7885 (5) Å
<i>V</i>	1085.6 (1) Å <sup>3</sup>
<i>Z</i>	8
$D_{calc}$	2.13 g cm <sup>-3</sup>
$D_{meas}$	2.12 g cm <sup>-3</sup>
$\mu(Mo K\alpha)$	17.65 cm <sup>-1</sup>
$F(000)$	688
$\lambda(Mo K\alpha)$	0.710688 Å
Space group	$I4_2d$ (No. 122)

Table 1. Computer programs used for crystallographic calculations

<i>PIRUM</i>	Indexing and refinement of cell parameters from powder data	P.-E. Werner, Stockholm, Sweden
<i>SOSYT</i>	Primary reduction of diffractometer data	G. Ivarsson & B. Lundberg; modified by R. Tegman, Umeå, Sweden
<i>DATA P2</i>	Lp and absorption corrections. Preparative calculations for extinction corrections according to Zachariasen	P. Coppens, L. Leiserowitz & D. Rabinovich, Rehovoth, Israel; modified by O. Olofsson & M. Elfström, Uppsala, Sweden. Inclusion of calculations for extinction corrections by B. C. Brandt & S. Åsbrink, Stockholm, Sweden B. G. Brandt, Stockholm, Sweden
<i>EXDATA</i>	Applies extinction corrections according to Zachariasen	
<i>DRF</i>	Fourier summations and structure factor calculations	A. Zalkin, Berkeley, U.S.A.; modified by R. Liminga & J.-O. Lundgren, Uppsala, Sweden
<i>LALS</i>	Full-matrix least-squares refinement of positional and thermal parameters and of scale factors	P. K. Gantzel, R. A. Sparks & K. N. Trueblood, Los Angeles, U.S.A.; modified by A. Zalkin, Berkeley, U.S.A., & J.-O. Lundgren, R. Liminga and C.-I. Brändén, Uppsala, Sweden C. K. Johnson, Oak Ridge, U.S.A.
<i>ORTEP</i>	Thermal ellipsoid plot program for crystal structure illustrations	
<i>DISTAN</i>	Calculates distances and angles with standard deviations	A. Zalkin, Berkeley, U.S.A.; modified by J.-O. Lundgren & R. Liminga, Uppsala, Sweden
<i>LAYOUT</i>	Editing of structure factor tables	O. Mårtensson, Umeå, Sweden

Rotation photographs around the  $b$  and  $c$  axes and corresponding Weissenberg photographs taken with  $\text{Cu } K\alpha$  radiation showed tetragonal symmetry. Conditions limiting the possible reflexions were  $hkl:h+k+l=2n$  and  $hhl:2h+l=4n$ , which are characteristic for the space groups ( $I\bar{4}md$ ) No. 109 and ( $I\bar{4}2d$ ) No. 122. Accurate unit-cell parameters were obtained from an X-ray powder photograph taken with a Guinier-Hägg focusing camera using  $\text{Cu } K\alpha_1$  radiation ( $\lambda=1.54051 \text{ \AA}$ ) with  $\text{Pb}(\text{NO}_3)_2$  as an internal standard ( $a=7.8570 \text{ \AA}$ ). The lattice parameters were refined by a least-squares treatment of 58 different  $\sin^2 \theta$  values using a program developed by Werner (1970). The composition of the single crystals prepared was assumed to be  $\text{Na}_2\text{S}_4$ , since the powder pattern from single crystals and that from the congruently melting  $\text{Na}_2\text{S}_4$  phase found in the  $\text{Na}_2\text{S-S}$  system gave the same unit-cell parameters (Rosén & Tegman, 1972). To check the cell parameters of the single crystal, new measurements were performed with a diffractometer using  $\text{Mo } K\alpha$  radiation ( $\lambda=0.71069 \text{ \AA}$ ). These measurements gave  $a=9.598$ ,  $c=11.786 \text{ \AA}$  at  $25^\circ\text{C}$ . The density was measured with the flotation method using a mixture of carbon tetrachloride and bromoform for the liquid medium. The melting point was measured by high-temperature microscopy with crystals in sealed capillaries.

#### Collection and reduction of the intensity data

The habit of the crystal was that of an incompletely grown dipyramid with dimensions  $0.35 \times 0.35 \times 0.40 \text{ mm}$  along the crystallographic  $a$ ,  $b$  and  $c$  axes and a crystal volume of  $1.33 \cdot 10^{-2} \text{ mm}^3$ . To protect the crystal from moisture it was mounted in a sealed Lindemann glass capillary with a diameter of  $0.5 \text{ mm}$ .

Intensity data were collected with a linear automatic diffractometer (PAILRED) using  $\text{Mo } K\alpha$  radiation

monochromated by a  $\text{LiF}$  crystal. The collimator diameter was  $0.95 \text{ mm}$  and the detector aperture was  $2.0^\circ$ .

Diffracted intensities were measured about the  $b$  axis for the layers  $k=0-12$  and with  $2\theta$  up to  $90^\circ$ , giving a maximum  $h=17$  and  $l=21$  with  $k=0$ . Owing to the reflexion condition  $hkl:h+k+l=2n$ , only reflexions satisfying  $h+k+l=2n$  were measured. For constructional reasons both  $hkl$  and  $hk\bar{l}$  reflexions were measured by the diffractometer.

All reflexions were measured with a half  $\omega$ -scan interval of  $1.2^\circ$  for  $\theta > 20^\circ$  and  $1.6^\circ$  for  $\theta < 20^\circ$  and with a scan speed of  $0.5^\circ/\text{min}$ . The scanning procedure was automatically repeated for weak reflexions (up to three times) until the number of total counts reached 4000. The background counts were measured during a 100 sec period at both ends of the scan interval.

The basic intensity data for about 3800 reflections, punched on a paper tape, was processed by the program *SOSYT*, where the net intensity  $I_o$  and the statistical error  $\Delta I$  were calculated. Reflexions with  $I_o < \Delta I$  were omitted as unobserved thus giving 3266 accepted reflexions. Lorentz, polarization and absorption corrections were applied to the intensities with the program *DATA P2*. The absorption corrections were calculated by a numerical integration procedure over 512 volume elements of the crystal using a linear absorption coefficient of  $17.65 \text{ cm}^{-1}$ . The calculated transmission factors varied between 0.70 and 0.75 for different reflexions. After correction the mean intensities for  $hkl$  and  $hk\bar{l}$  reflexions were calculated giving 1749 independent reflexions for use in structure calculations. All the programs used in the different stages of the calculations are summarized in Table 1. They are written in Fortran IV for a CD 3200 computer.

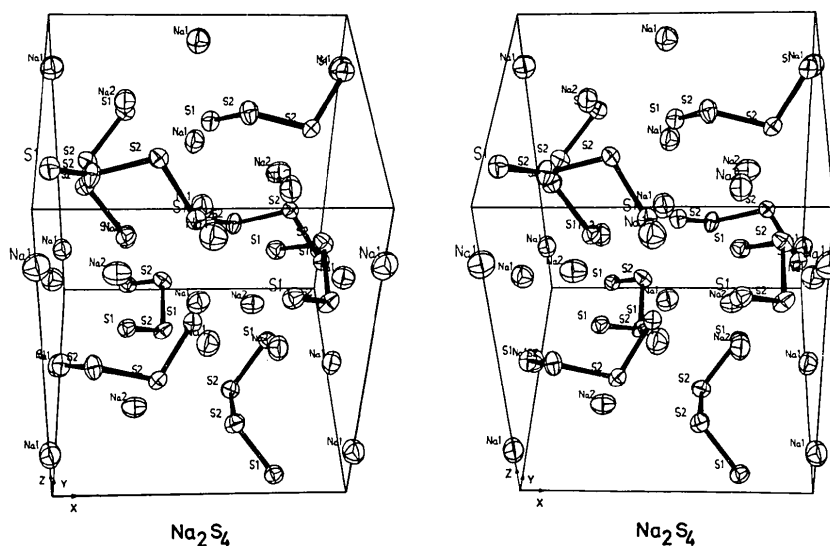


Fig. 1. A stereoscopic view of the contents of the unit cell. The origin of the unit cell is in the lower left corner. The thermal ellipsoids are drawn at the 75% probability level.

### Structure determination and refinement

All the atomic positions in the structure were deduced from a sharpened three-dimensional Patterson function using a conventional solution procedure. Of the two possible space groups  $I\bar{4}2d$  and  $I\bar{4}md$  the latter was excluded since the Harker lines at  $\pm 2u, 0, 0$  and  $0, \pm 2v, 0$  in the Patterson space had no high peaks. With the space group  $I\bar{4}2d$  all the sulphur atoms could be placed in two 16-fold positions and all the sodium atoms in two 8-fold positions. The Patterson synthesis was well resolved and showed no foreign peaks.

A least-squares refinement of the observed position parameters with isotropic temperature factors gave an  $R$  value of 0.076. Anisotropic temperature factors were then introduced, decreasing  $R$  to 0.047. At this stage of the refinement it became clear that the strongest reflexions were affected by secondary extinction since the observed structure factors were numerically less than the calculated ones, especially so for those with small values of  $\sin \theta/\lambda$ . Therefore the strongest reflexions were initially excluded in a stepwise manner in the refinement. Intensity data with  $|F_o| < 80$  and  $\sin \theta/\lambda > 0.26$  gave a minimum  $R$  value of 0.036. At this stage of the refinement it was found worth while to apply secondary extinction corrections instead of excluding the affected reflexions. The expression for the corrected structure factor was that given by Zachariassen. The correction was calculated and applied by the program *EXTDATA* using a procedure described by Åsbrink & Werner (1966). The value obtained for  $c$  in Zachariassen's formula  $F_{\text{corr}} \approx F_o[1 + c \cdot I_o \beta(2\theta)]$  was  $2.531 \cdot 10^{-5}$  giving a maximum correction in  $F$  of 35% for the strongest reflexion, 440.

In the final refinement, the scale factor, positional parameters and anisotropic temperature factors for all the atoms were calculated. The parameter shifts in the final least-squares cycle were less than 20% of the standard deviations of the corresponding parameters. The correlation between refined parameters was low. The highest correlation coefficient of +0.35 occurred

between the scale factor and the thermal parameters  $\beta_{13}$  for the sulphur atoms.

All calculations were made with a full matrix least-squares technique (program *LALS*). The quantity being minimized in the refinement was  $\sum w(|F_o| - |F_c|)^2$ . The atomic scattering factors for the sulphur atoms were the averages of values given for  $S^0$  and  $S^-$  and for sodium, the values given for  $Na^+$ . All values were taken from *International Tables for X-ray Crystallography* (1962). No corrections for dispersion were applied since a simple correction is not applicable to averaged data.

The final reliability index  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  obtained was 0.030 with all observed data (1749 reflexions) and 0.026 with 50 zero weight data excluded. The weighted reliability index was 0.031. The weights used in the refinement were those given by Cruickshank with  $w = (25 + F_o - 0.012 F_o^2 + 0.00021 F_o^3)^{-1}$ . Data outside the limits  $0.5 < F_o/F_c < 2.0$  were given zero weight. The number of observations per refined parameter was 59. A difference Fourier synthesis using refined parameters has a highest electron density of  $0.70 \text{ e}\text{\AA}^{-3}$  and a lowest electron density of  $-0.64 \text{ e}\text{\AA}^{-3}$ .

The final atomic parameters and their standard deviations as calculated in the last cycle of the least-squares refinement are given in Table 2. The anisotropic thermal parameters and their standard deviations are given in Table 3. The observed and calculated structure factor magnitudes are listed in Table 4. An asterisk after the reflexions in Table 4 indicates that a zero weight was used in the refinement. Calculated interatomic distances and angles with standard deviations are given in Table 5. The standard deviations in distances and angles were calculated from standard deviations in the atomic positional parameters and the standard deviation in the unit-cell parameters. The superscripts in Table 5 distinguish crystallographically equivalent atoms in different asymmetric units.

### Description and discussion of the structure

The crystal structure of  $Na_2S_4$  is illustrated in Fig. 1 by a stereoscopic drawing of the atoms in one unit cell. All atoms are drawn as 75% probability thermal ellipsoids (Johnson, 1965). The covalent bonds between sulphur atoms in the  $S_4^{2-}$  ions have also been marked in the drawing.

The crystal-chemical unit of the  $Na_2S_4$  structure comprises two sulphur atoms represented by the

Table 2. Fractional atomic coordinates with estimated standard deviations ( $\times 10^5$ )

	$x$	$y$	$z$
Na(1)	0	0	0.16953 (10)
Na(2)	0.27647 (12)	$\frac{1}{4}$	$\frac{1}{8}$
S(1)	0.03373 (3)	0.24952 (4)	0.29644 (3)
S(2)	0.14693 (4)	0.11600 (4)	0.39956 (3)

Table 3. Anisotropic thermal parameters  $\beta_{1j}$  ( $\times 10^5$ ) with estimated standard deviations and *r.m.s.* radial thermal displacements  $r$  (Å)

The form of the anisotropic temperature factor is  $\exp [\sum \beta_{ij} h_i h_j]$ .

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	$r$
Na(1)	560 (10)	719 (11)	527 (7)	-135 (17)	0	0	0.1795
Na(2)	926 (13)	488 (8)	431 (6)	0	0	-20 (12)	0.1792
S(1)	441 (3)	513 (3)	306 (2)	10 (5)	4 (4)	76 (4)	0.1483
S(2)	393 (3)	539 (3)	338 (2)	-142 (5)	1 (4)	219 (4)	0.1497



Table 5 (cont.)

Na(1 <sup>1</sup> ) tetrahedron angles		Na(2 <sup>1</sup> ) 'octahedron' angles	
S(1 <sup>1</sup> )—Na(1)—S(1 <sup>11</sup> )	116.47 (4)	S(1 <sup>1</sup> )—Na(2)—S(1 <sup>111</sup> )	81.89 (3)
S(1 <sup>1</sup> )—Na(1)—S(1 <sup>1*</sup> )	105.70 (0)	S(1 <sup>1</sup> )—Na(2)—S(1 <sup>1*</sup> )	74.09 (2)
S(1 <sup>1</sup> )—Na(1)—S(1 <sup>1*</sup> )	105.66 (0)	S(1 <sup>1</sup> )—Na(2)—S(1 <sup>1*</sup> )	98.25 (2)
S(1 <sup>11</sup> )—Na(1)—S(1 <sup>1*</sup> )	106.66 (0)	S(1 <sup>1</sup> )—Na(2)—S(2 <sup>1</sup> )	139.01 (3)
S(1 <sup>11</sup> )—Na(1)—S(1 <sup>1*</sup> )	105.70 (0)	S(1 <sup>1</sup> )—Na(2)—S(2 <sup>111</sup> )	67.01 (1)
S(1 <sup>1*</sup> )—Na(1)—S(1 <sup>1*</sup> )	118.22 (4)	S(1 <sup>111</sup> )—Na(2)—S(1 <sup>1*</sup> )	98.25 (2)
		S(1 <sup>111</sup> )—Na(2)—S(1 <sup>1*</sup> )	74.09 (2)
		S(1 <sup>111</sup> )—Na(2)—S(2 <sup>1</sup> )	67.01 (1)
		S(1 <sup>111</sup> )—Na(2)—S(2 <sup>111</sup> )	139.07 (3)
		S(1 <sup>1*</sup> )—Na(2)—S(1 <sup>1*</sup> )	170.08 (5)
		S(1 <sup>1*</sup> )—Na(2)—S(2 <sup>1</sup> )	84.40 (1)
		S(1 <sup>1*</sup> )—Na(2)—S(2 <sup>111</sup> )	98.01 (1)
		S(1 <sup>1*</sup> )—Na(2)—S(2 <sup>1</sup> )	98.01 (1)
		S(1 <sup>1*</sup> )—Na(2)—S(2 <sup>111</sup> )	84.40 (1)
		S(2 <sup>1</sup> )—Na(2)—S(2 <sup>111</sup> )	152.04 (5)

## Symmetry code

i	$x, y, z$	vii	$-\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} - z$
ii	$-x, -y, z$	viii	$\frac{1}{2} - x, y, \frac{3}{4} - z$
iii	$x, \frac{1}{2} - y, \frac{1}{4} - z$	ix	$-\frac{1}{2} + y, x, -\frac{1}{4} + x$
iv	$y, \frac{1}{2} + x, \frac{1}{4} + z$	x	$\frac{1}{2} - y, -x, -\frac{1}{4} + z$
v	$\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$	xi	$\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$
vi	$\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} - z$		

From an analysis of sulphur-sulphur bond lengths and corresponding dihedral angles in different compounds Hordvik (1966) made a curve for predicting the central sulphur-sulphur bond length from the dihedral angle. This curve gave 2.04 Å for a dihedral angle of 98° which has to be compared with the actual distance of 2.061 Å. From the reported polysulphide sulphur-sulphur bond distances in BaS<sub>4</sub>.H<sub>2</sub>O (Abrahams, 1954) and Ce<sub>2</sub>S<sub>6</sub> (Abrahams & Grison, 1953), Hordvik also suggested that the two extra electrons in a polysulphide ion are localized on the terminal sulphur atoms and that the length of the terminal sulphur bond should be found to be 2.02 Å. This is obviously not true for Na<sub>2</sub>S<sub>4</sub> since the terminal bond distance is 2.074 (1) Å. The errors in the sulphur-sulphur bond distances for Ce<sub>2</sub>S<sub>6</sub> and BaS<sub>4</sub>.H<sub>2</sub>O are about 0.03 Å, which suggest that comparisons of bond distances are unreliable. The terminal sulphur bond distance found in Na<sub>2</sub>S<sub>4</sub> is significantly longer than the 2.02 Å bonds found in both Ce<sub>2</sub>S<sub>6</sub> and BaS<sub>4</sub>.H<sub>2</sub>O.

In order to clarify where the two extra electrons in the sodium tetrasulfide ion are localized, a separate least-squares refinement was performed with new atomic scattering factor values for the sulphur atoms. For the end sulphur, S(1), the atomic scattering factor values of S<sup>-1</sup> were used and for the middle sulphur, S(2), scattering factor values of S<sup>0</sup> were used instead of the previously used mean values (*International Tables for X-ray Crystallography*, 1962).

Compared with the earlier refinement the *R* value now increased from 0.030 to 0.032. This indicates that the two extra electrons are 'spread out' over the S<sub>4</sub><sup>2-</sup> ion and are not localized on the end sulphur atoms. The refinement also showed that the atomic position parameters are not very sensitive to small changes in scattering factor values. The parameter values agree within 0.5 standard deviations with those of the earlier

refinement. The end atom S(1) in the S<sub>4</sub><sup>2-</sup> ion is surrounded by 4 close Na<sup>+</sup> ions and the middle atom S(2) is surrounded by 2 close Na<sup>+</sup> ions. The thermal vibrations of S(1) and S(2), given in Table 3 as average root mean square displacements, are almost equal although S(1) is an end atom in the S<sub>4</sub><sup>2-</sup> chain and thus only has one covalent bonded neighbour. It is probable that 4 ionic sodium-sulphur bonds and 1 covalent bond give about the same bond force for S(1) as 2 ionic sodium-sulphur bonds and 2 covalent bonds give for S(2).

The two crystallographically different sodium ions Na(1) and Na(2), in the structure coordinate to 4 and 6 sulphur atoms respectively. Owing to the symmetry in the structure all distances around the sodium ions appear in crystallographically equal pairs. The coordination around Na(1) is tetrahedral with 2 different pairs of sodium-sulphur distances of 2.826 (1) and 2.842 (1) Å. The tetrahedral coordination is somewhat flattened in the *z* direction thus giving 2 coordination angles of 117° and 4 angles of 106°. The coordination around Na(2) forms a very distorted octahedron with 3 different pairs of sodium-sulphur distances with one short bond of 2.887 (1) Å and two longer bonds of 3.043 (1) and 3.081 (1) Å. The angles in the octahedron are also far from the values in a regular one. Detailed values of the distances and angles for the two coordination figures are given in Table 5.

The mean sodium-sulphur bond distances are 2.83 Å for Na(1) and 3.00 Å for Na(2). The ionic bonds around Na(1) and Na(2) are chemically equal, if the effect of the bond distances caused by different coordination numbers around Na(1) and Na(2) is considered in the comparison of the bonds. The thermal vibrations of Na(1) and Na(2) are also equal, which indicates that the ionic bond forces around Na(1) and Na(2) have similar strength.

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## Polymorphisme et Structure Cristalline de la Forme Métastable à 25°C du 2-Bromonaphtalène

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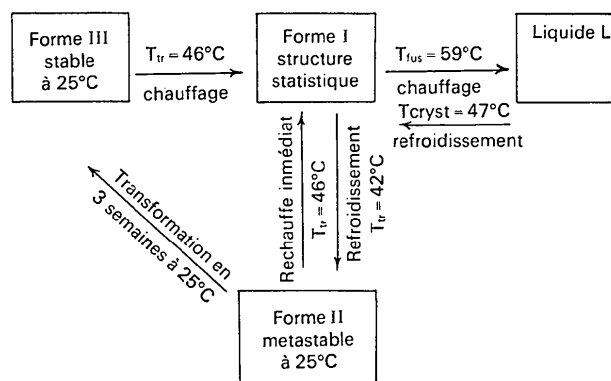
X-ray diffraction and thermal differential analysis of 2-bromonaphthalene have illustrated the transition of ordered structures (type III, low-temperature stable form and type II, low-temperature metastable form) into the disordered form (type I, high-temperature form). This polymorphism is typical of the 2R-substituted naphthalene series. The fusion and transition enthalpies have been determined. The crystalline structure of form II has been determined by the heavy-atom method ( $P2_1/c$ ,  $Z=4$ ,  $a=7,693$ ,  $b=5,926$ ,  $c=19,142$  Å,  $\beta=98^\circ 33'$ , 780 observed reflexions:  $R=0,105$ ). This structure is affected by high thermal agitation. The structure of form III has not been determined; form I has the naphthalene type structure ( $P2_1/a$ ,  $Z=2$ ).

Le 2-bromonaphtalène fait partie de la série des dérivés 2R substitués du naphtalène dont nous avons entrepris l'étude depuis quelques années. Ces dérivés sont caractérisés par un polymorphisme cristallin, de type II ordonné  $\rightarrow$  I désordonné. La forme cristalline stable à haute température (ou forme I) est une structure statistique, isotype de la structure du naphtalène (molécule centrosymétrique) (Coppens & Hearfields, 1965; Lencrèrot, 1969; Baumgarth, Chanh, Gay, Lascombe & Le Calve, 1966; Chezeau, 1971; Chanh & Haget, 1972). Les structures cristallines des formes stables à 'basse température' ne sont pas connues, à part celle du 2-naphtol (Hargreaves & Watson, 1957; Watson & Hargreaves, 1958). La nature statistique des molécules de la forme I résulte de la possibilité de retournement à  $180^\circ$  des molécules autour de (au moins) 2 des axes de symétrie du noyau naphtalénique: \* ce mouvement est rendu possible grâce à la faiblesse des interactions moléculaires malgré l'encombrement du substituant en 2.

\* Les résultats obtenus par étude r.m.n. (Cazaux, 1972) ont montré que les fréquences de ces mouvements moléculaires sont peu élevées, de l'ordre  $10^2$ – $10^4$  Hz. Bien que rares, ces retournements suffisent pour faire apparaître aux rayons X une 'molécule statistique' centrée.

### Polymorphisme du 2-bromonaphtalène

Le produit étudié vient de la firme 'Fluka', type 'puriss'. Nous avons entrepris l'étude du polymorphisme de ce composé à la fois par diffraction des rayons X à la chambre de Guinier-Lenné et par microanalyse thermique différentielle. L'ensemble des résultats obtenus nous permet de proposer le schéma des transitions suivantes.



Les transformations (III  $\rightarrow$  I  $\rightarrow$  L) sont observées sur les diagrammes de diffraction de rayons X et sur les