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 Crystallog-raphy* (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 (°).

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The Crystal Structure of Sodium Tetrasulphide, Na₂S₄

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Sodium tetrasulphide, Na₂S₄, is tetragonal and crystallizes in space group $I\overline{4}2d$ 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 α 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 $I_o > \Delta I$. The crystal structure is built up of unbranched S₄²⁻ ions surrounded by Na⁺ ions. The distance between different S₄²⁻ ions is about 3.60 Å. The S₄²⁻ 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)⁵ 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

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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References

- International Tables for X-ray Crystallography (1962). Vol. III, pp. 202, 270, 276. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- KARLE, J. & HAUPTMAN, H. (1956). Acta Cryst. 9, 635-651.
- KARLE, J. & KARLE, I. (1966). Acta Cryst. 21, 849-859.
- OLSEN, C. E. (1969). Studies on 5-Hydroxy and 5-Amino- Δ^2 -1,2,3-Triazolines. Thesis, The Technical Univ. of Denmark.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The X-RAY System, Univ. of Maryland, College Park, Maryland.
- SABESAN, M. N. & VENKATESAN, K. (1971). Acta Cryst. B27, 986–993.

their structures in the solid and liquid states (Rosén & Tegman, 1972; Tegman, 1972). The structure of Na_2S_4 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 Na₂S₄ with accurate dimensions for the S-S and Na-S distances and includes some comments on the sulphursulphur bond characters.

Experimental

Crystal preparation

Polycrystalline Na₂S₄, prepared by the reaction between Na₂S and S at 300°C, was used as starting material in the single-crystal preparations (Rosén & Tegman, 1971). The polycrystalline Na₂S₄ 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 Na₂S₄ for some hours at 25°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. Na₂S₄ is extremely hygroscopic and sensitive to humid air oxidation. All handling operations of the open Na₂S₄ system were therefore performed in a glove-box filled with purified and dried nitrogen.

Crystal data

Chemical formula	Na.S.
FW	174.24
Melting point	295°C
Habit	Dipyramidal
Crystal system	Tetragonal
Unit coll dimonsions	Tettagonal
at 23°C	0 - 0 - C - C - C - S
a	9·5965 (3) A
С	11·7885 (5) Å
V	1085·6 (1) ų
Z	8
$D_{\rm calc}$	2.13 g cm^{-3}
$D_{\rm meas}$	$2 \cdot 12 \text{ g cm}^{-3}$
$\mu(Mo K\alpha)$	17.65 cm^{-1}
F(000)	688
λ (Mo K α)	0·710688 Å
Space group	14 2d (No. 122)

Table 1. Computer programs used for crystallographic calculations

PIRUM	Indexing and refinement of cell parameters from powder data	PE. Werner, Stockholm, Sweden
SOSYT	Primary reduction of diffractometer data	G. Ivarsson & B. Lundberg; modified by R. Tegman, Umeå, Sweden
DATA P2	Lp and absorption corrections. Preparative calculations for extinction corrections accord- ing to Zachariasen	P. Coppens, L. Leiserowitz & D. Rabinovich, Rehovoth, Israel; modified by O. Olofsson & M. Elfström, Uppsala, Sweden. Inclusion of calculations for extinc- tion corrections by B. C. Brandt & S. Åsbrink, Stockholm, Sweden
EXDATA	Applies extinction corrections according to Zachariasen	B. G. Brandt, Stockholm, Sweden
DRF	Fourier summations and structure factor calculations	A. Zalkin, Berkeley, U.S.A.; modified by R. Liminga & JO. Lundgren, Uppsala, Sweden
LALS	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., & JO. Lundgren, R. Liminga and C-I Brändén, Uppsala, Sweden
ORTEP	Thermal ellipsoid plot program for crystal structure illustrations	C. K. Johnson, Oak Ridge, U.S.A.
DISTAN	Calculates distances and angles with standard deviations	A. Zalkin, Berkeley, U.S.A.; modified by JO. Lundgren & R. Liminga, Uppsala, Sweden
LAYOUT	Editing of structure factor tables	O. Mårtensson, Umeå, Sweden

Rotation photographs around the b and c axes and corresponding Weissenberg photographs taken with Cu Ka 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 $(I\overline{4}md)$ No. 109 and $(I\overline{4}2d)$ No. 122. Accurate unit-cell parameters were obtained from an X-ray powder photograph taken with a Guinier-Hägg focusing camera using Cu $K\alpha_1$ radiation ($\lambda = 1.54051$ Å) with $Pb(NO_3)_2$ as an internal standard (a = 7.8570 Å). 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 Na_2S_4 . since the powder pattern from single crystals and that from the congruently melting Na₂S₄ phase found in the Na₂S-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 Mo K radiation ($\lambda =$ 0.71069 Å). These measurements gave a=9.598, c=11.786 Å at 25°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 $0.35 \times 0.35 \times 0.40$ mm along the crystallographic *a*, *b* and *c* axes and a crystal volume of $1.33 \cdot 10^{-2}$ mm³. To protect the crystal from moisture it was mounted in a sealed Lindemann glass capillary with a diameter of 0.5 mm.

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

monochromated by a LiF crystal. The collimator diameter was 0.95 mm and the detector aperture was 2.0° .

Diffracted intensities were measured about the *b* axis for the layers k=0-12 and with 2θ up to 90° , 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 $hk\overline{l}$ reflexions were measured by the diffractometer.

All reflexions were measured with a half ω -scan interval of 1.2° for $\theta > 20^\circ$ and 1.6° for $\theta < 20^\circ$ and with a scan speed of 0.5°/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 ΔI 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 cm⁻¹. The calculated transmission factors varied between 0.70 and 0.75 for different reflexions. After correction the mean intensities for hkl and *hkl* 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.

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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 $I\overline{4}2d$ and $I\overline{4}md$ 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 $I\overline{4}2d$ 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 θ/λ . 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 Zachariasen. The correction was calculated and applied by the program EXTDATA using a procedure described by Asbrink & Werner (1966). The value obtained for c in Zachariasen's formula $F_{corr} \approx F_o[1 + c \cdot I_o\beta(2\theta)]$ 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

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

	x	у	Z
Na(1)	0	0	0.16953 (10)
Na(2)	0.27647 (12)	$\frac{1}{4}$	1
S(1) S(2)	0·03373 (3) 0·14693 (4)	0·24952 (4) 0·11600 (4)	0·29644 (3) 0·39956 (3)

between the scale factor and the thermal parameters β_{ij} for the sulphur atoms.

All calculations were made with a full matrix leastsquares 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 S⁰ 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 eÅ⁻³ and a lowest electron density of $-0.64 eÅ^{-3}$.

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 aniso-tropic 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 3. Anisotropic thermal parameters β_{ij} (× 10⁵) with estimated standard deviations and r.m.s. radial thermal displacements r (Å)

The	form o	of I	the	anisotropi	c temperature	factor	is e	xp	$[\Sigma \beta_{ij}]$	hih	l_i	
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	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{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

end atom S(1) and the middle atom S(2) in a S_4^{2-} ion and two sodium ions represented by Na(1) and Na(2). The structure is built up of unbranched and separated S_4^{2-} ions surrounded by Na⁺ ions. The two shortest distances between sulphur atoms in different S_4^{2-} ions are 3.59 and 3.60 Å for S(2); S(2) and S(1); S(1) respectively.

The S_4^{2-} ions in the Na₂S₄ structure are built up of S(1)–S(2)–S(2)–S(1) units thus giving only two crystallographically independent sulphur–sulphur bond distances and one independent sulphur–sulphur bond angle in the structure. The terminal sulphur–sulphur bond distance is 2.074 (1) Å and the central sulphur–sulphur bond distance is 2.061 (1) Å. The S(1)–S(2)–S(2) bond angle is 109.76 (2)°, which is very close to the tetrahedral angle (109.49°) in an sp^3 orbital. The dihedral angle

Table 4. Observed and calculated structure factor $magnitudes \times 10$

An asterisk after the reflexions indicates that zero weight was used in the refinement.

H L FO FC	" L FO FC	Η Ι ΓΟ Γ Ο	H L FO FC	H L TO FC	H L FO FC	H L FO FC
	15 0 00 84	13 2 76 63	10 6 214 217	8 17 163 163	7 3 516 514	• 10 151 159
0 2 27 01	16 7 220 216	13 4 162 160	10 12 147 140	8 19 50 29 9 0 247 245	7 7 161 174	* 17 · 11 · 40
0 1 1 71 1710	10 6 156 146	13 10 50 25+	10 16 61 41	9 2 373 378 9 4 521 523	7 11 257 254	7 0 +11 +19
0 12 501 510	17 1 86 85	11 14 70 68	1 3 176 174	* * 503 500	7 14 226 225	7 2 544 530
0 20 316 329			11 7 89 93	9 10 140 164	1 10 10 11 2 15 5	7 6 445 477
3 962 944	1 232 253	1. 7 104 167	11 11 129 132	9 14 107 115	8 6 267 246	7 10 280 287
7 307 304			11 12 12 12	0 16 42 25 10 1 291 285	a a 241 237 a 10 a3 194	7 10 103 104
1 11 442 443	0 1060 1060	5 25 257	12 2 154 159	10 2 11 431	4 12 109 191	7 18 60 64
1 5 67 61	0 13 70 72	15 4 163 177	12 6 259 244	10 7 224 216	4 16 143 135	8 3 200 204
	217 227 22	15 8 30 70	12 10 240 540	10 11 224 226	0 1 401 403	8 7 136 136
2 2 676 686	1 2 639 667	1. 101 110		10 15 93 91	0 7 200 200	8 11 127 122
4 1461 1531	1 10 374 374	14 4 105 104	13 3 251 256	11 0 400 104	0 11 132 132	17 192 193
2 10 103 153	1 14 240 250		11 7 07 01	1 6 242 249	0 15 02 05	9 0 93 90 9 2 73 71
14 454 458	2 1 798 826		13 11 40 40	11 4 120 120	10 2 353 354	9 a 156 153 9 a 627 626
2 14 140 144	2 5 565 503	a 2 601 684	14 0 167 146	11 12 04 48	10 4 273 275	9 10 109 110
3 1 1 1 4 3 1 4 4 0	2 9 544 535	0 0 1003 000	1 6 251 245	1 16 62 51	10 8 144 142	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2
3 9 954 969	2 13 270 287	0 8 510 538	14 8 45 27	12 3 61 56	14 12 244 242	10 1 272 27
3 4 34 27	2 17 184 185	0 12 313 311	14 12 43 144	12 2 256 261	11 1 163 184	10 5 254 256
1 11 144 195	2 21 45 101	0 14 67 51		12 13 240 237	11 3 351 270	10 9 107 100
3 17 115 132	3 2 1537 1651	1 1 193 826	15 7 48 17	13 0 204 210	11 7 219 234	10 13 74 90
3 21 29 63	3 6 1055 1007	5 561 563	15 11 46 144	13 6 56 51	11 15 128 125	10 17 105 107
106 703	3 10 501 505	4 544 514	16 2 50 52	3 8 214 210	12 0 190 188	11 2 137 125
1 121 711	3 14 162 156	1 13 204 247	16 6 109 123	13 14 54 54	17 6 247 247	11 6 59 83
14 72 71	1 10 100 11	17 183 145	17 1 44 20	14 3 254 256	17 8 103 100	11 8 162 162
10 55 50	1 1242 1253	1 21 93 101		14 7 77 74	11 1 201 202	11 12 172 169
5 3 323 325	* 5 946 954 * 7 179 173	2 2 89 6+	0 1 1377 1440	15 0 203 203	13 7 225 222	12 1 75 87
5 7 220 214	- 9 10- 300	2 6 18 0*	0 3 64 10	15 6 72 67	11 9 160 182	12 3 151 149
2 11 82 61	• 13 147 166	2 10 49 04	0 7 33 2+	15 8 40 220	13 13 75 70	12 4 224 222
5 15 257 240	4 17 166 168	2 14 227 227	0 11 143 144	10 3 102 73	14 2 360 279	12 15 54 53
5 10 02 04	1 121 113	3 1 404 300	0 15 431 419	17 . 78 7	14 6 113 107	13 2 170 180
6 2 886 802	2 757 754	3 5 721 711	0 10 70 A4 0 21 74 A3	** *	1 12 110 121	13 6 220 217
6 6 352 348 6 8 92 95	5 6 1233 1263 5 8 361 361	1 9 180 175	1 0 000 000	0 . 00. 783		13 13 64 66
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6 18 230 238 7 1 132 27+	5 20 65 30	3 21 60 74	1 16 157 156	0 18 46 29	17 5 186 186	
7 3 381 371 7 5 399 397	6 3 1257 1264	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	2 1 403 304	1 1 1200 1253		1 1 1
7 7 455 464	6 7 358 358 6 9 378 385	a a 100 400	2 5 729 711	9 977 954	1 1 242 731	12 2 2 2
7 11 354 355 7 13 101 103	6 11 312 317 6 13 183 184	• 15 555 516	2 0 162 175	• 310 300	5 309 293	15 6 129 126
7 15 145 158	6 17 200 237	4 10 9A 97	2 13 219 219	1 13 171 100	0 0 315 313	15 10 60 32
8 0 1417 1454 8 2 324 321	7 0 1363 1178			1 17 104 100	13 96 97	
8 4 506 568 8 6 473 427	7 4 242 242	1179 1176	5 5 5 5 5 5 7		5 19 52 94	17 0 119 129
12 66 62		3 7 407 408		2 2 442 935	2 760 754	** 6
	7 12 295 297	11 144 140	1 16 46 04	2 6 768 749	6 1271 1263	0 2 840 MB2
9 4 403 402	7 1 1 1	5 15 101 108	4 1 317 314	2 10 330 320	1 10 268 269	0 4 202 192
9 5 314 317	1 153 144	4 10 0A 05 A 0 153 124	• 5 3#2 370 • 7 673 659	2 16 320 321	1 14 200 288	0 10 113 104
2 11 237 225	4 5 141 138	6 2 275 276	a 9 874 876 a 11 a17 a77	2 18 214 214	1 20 43 36	0 12 434 435
9 17 72 73	8 9 713 725	6 A 222 216 6 F 709 704	13 13 13	1 1 341 335	2 3 1187 1175	0 10 233 236
10 2 534 541	8 13 70 71	6 10 104 108 6 12 487 507	17 148 187 18 61 67	3 7 673 659	9 127 117	3 1313 1204
10 8 497 492	8 17 151 153 8 19 44 39	6 16 131 127 6 16 135 139	5 2 350 346	3 11 035 027	2 13 140 144	9 301 105
10 10 60 69	9 0 334 300 9 2 451 445	6 20 103 100		1 19 56 57	5 17 173 169	1 13 141 184
10 14 106 107	9 4 187 183 9 6 347 348	7 3 22# 227	5 10 250 243	3 19 57 67	5 21 46 63	117 206 207
11 3 255 251	9 12 169 189	7 7 208 201	3 12 31 370	27-0 2073	3 3 354 344	21 105 105
11 7 180 184	· 16 · 60	7 11 304 304	3 18 149 175		1 6 61 46	2 2 273 279
11 9 258 255	10 1 324 327	7 15 69 75	6 1 251 244	4 10 18 0+	10 267 203	2 6 226 216
	10 3 699 712	1 19 50 34	3 397 341	16 147 167	1 14 239 237	2 10 112 108
12 6 515 517	10 7 186 185	2 250 240	6 4 564 546	1 10 10	1 16 174 173	2 14 130 127
12 12 51 33	10 13 135 135		6 12 214 244	5 305 395	1 110 111	2 20 44 100
17 1 61 63	10 17 136 136	10 350 359		5 9 546 567	5 381 395 7 228 21A	1 1 100 470
	11 6 25 23	6 14 240 239	7 9 67 49	5 15 11 76	a 9 572 567	1 7 296 295
13 9 43 25	11 8 149 186	1 1 1 1	7 4 175 140	4 19 46 53	• 13 •2 10• • 15 06 78	3 11 344 144
13 13 137 139	11 12 221 225	4 5 263 260 9 7 276 260	7 8 135 178	6 2 277 270	110 52 53	3 15 142 140
1. 2 201 203	11 16 95 100	9 9 176 172	7 12 154 154	6 6 721 714 6 9 203 201	* 2 771 746 * 0 713 702	3 19 42 34
1. 1. 136	12 1 230 247	0 13 86 90	7 18 124 111	6 10 148 182	101 101 103 18 277 278	* 2 275 270
10 10 20 20		10 17 60 40	8 3 430 47A 8 5 708 7A	6 16 234 232	A 1 452 534 A 3 769 769	* # 723 714 * # 205 201
15 1 21- 205	12 13 41 40	10 2 3-8 342	8 1 37 18 8 11 90 92	6 18 67 36 6 20 60 53	* 7 350 351	12 100 184
15 7 5 200	13 6 114 103	10 6 340 341	0 13 216 219	7 1 521 516	• • •20 •30	• 14 236 232

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112	100	202	\$ 19	245	207	- : :	267	264	; ;;	142	1.0		200	284 341	;;	323	120	11		
	453		3	112	100	::	255	256	3 10	239			236	167		200			1.24	122
11	101	150	32	47			100	191	- 1 1	522	-	11	103	179	- 22			2 10	230	
	211	219		150	111	÷ 14	127	135	í.	504	100	- 317	77	74	3 19	37		2 14	138	133
	105	101		146	103	;;	687 204	201	3 12	329	217	;;	277	;;;	;;	373	310	2 18	110	11
0 14	;;	72	• 13	12	121		513	110	- 2 1	304	,	3.4	217	216	- 11	220			3	36
• •	607	6.56	: 17	110	100	- 20	1.1	122		294	244	- 12	-			121	118		314	326
	136	112	12	550	553	- 5 15	122	185		124	127	3 17			1 14	120	130	111		3
::;	120	124	11	276	101		;	•;;	: 13	78	1.5	- : :	270	158	- 11	103	18.		.33	100
	171		11	229	228		162	160	: !	108	127			1.2		262	10		14	12
10 2	1	125		222	221		212	210		74			288	292		165	167		100	100
10 0	140	171	8 9	360	389	· 12	102	101	- ; ;	629	1 34	. 16	44	**	: 13	129	125	: :	::	
18 19	110		18	107	199	2 12	3		3 12	104	149	33		503	- ''	720	20		100	100
11 11		137		196	189	- ; ;	209	214		#1			107	103	- 11	1.3	14		1.7	12
ii ș	**	**		134	132	11	34)	349		6C7	110	- 13	116	115	1.0	140	142		227	222
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iš ž	20	108	10 3	284	281		186	187	17	127	120		247	253		114	114		160	145
12 1	201	201	10 7	75 230	231	* ie	110	141	;;	184	7 15	6 10	143	139	::	330	336		187	183
15 15	12,	120	10 13	110	11-		1-0	130			132		105		- 3 8	101	62			12
K T	255	255	10 17	17	75		212	209	7 10	112	172	; ;	210	58		126	126	; ;	112	114
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13 11	01	131	11 10	***	-02	10 0	174	170		1	1	1	236	23)		2	-02	1		
1. 2	146	140		151	1	10 .	98	104	1	139	110	15	22		7 17		24		1	79
	122	137	12 1	169	114	10 10	114	100	1,1	210	219	::	300	304	14		31		153	158
14 12	50	30	12 1	187	100	10 10		20	117	1			116	117		371	172		120	134
12 1		84	15 11			11 1		-		371	344	12	100	işe		150	157			1.10.
15 7	34	**	13 0	108	110	- ii ;	171	172	0 14	339		8 14	- 25	20	11	40	- 45	8 14		53
16 2	1.1	192	33	143	100	11.1	151	144	10 3	55	274	: ;	101	158		118	119		60	14
17 5	95 95	103	13 16	143 64	68	11 12		63	10 1	137	13		127	15		204			27	14
,			1		-	12 4	1.0	134	10 15	134	178	9 11	51	43		183	101	10	100	197
12	382	371	:;;	;	22	12 10		14.	11 2	217	212		51	130	• 10	100		10	108	113
	365	370	1.1		59	88	1	53	11 6	1.47		10 8	202	201	10 1	11	120	10 10		1
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	243	242	:: ;	71	71	- 6 6			12 .	-	×.	- H d				- 13	11		80	
	214	207				1. 2	124				52	12 2	198	107	12 14	4) 93	19		100	10
11	307	297		54.	321	1: :	167	40		122	141	12 6	112	175		123		12 1	107	104
114		37		51	57	12	117	114	10 1	*2	•;	12 19	**	20		84	10		44	56
- 23	10-	ij.	0 14	10	10		105	10,	1: ;	10		33		195	12 13	124	127	ii i		64 52
1;	205	340	6 1# 0 20	107	141	1. ;			15 0	1+7	14	- 13 5	132	120	11	25	2			
1	304	30-		450	146		•1	••	15 2	\$7		1. 0	2	241		**	43 39	14 4	74	76

Table 4 (cont.)

S(1)S(2)S(2)/S(2)S(2)S(1) is 97.81°. It is interesting that Pauling (1949) postulated the values of the dihedral angle in the tetrasulphide ion to be about 100°.

Table 5. Interatomic distances (Å) and angles (°)

The standard deviations of the last digits are given in parentheses.

S-S bond distances $S(2^{i})$ S(2 ^{*iii})2·061 (1) $S(1^{i})$ S(2 ⁱ) 2·074 (1) $S(2^{*iii})$ -S(1 ^{*iii})2·074 (1) $S(2^{i})/Na \text{ distances}$ S(2)Na(2 ^{*i})3·043 (0) S(2)Na(1 ⁱ) 3·253 (1)	$\begin{array}{l} S(1^{i})/Na \ distances \\ S(1) \cdots Na(1^{iv}) \ 2 \cdot 826 \ (1) \\ S(1) \cdots Na(1^{v}) \ 2 \cdot 842 \ (1) \\ S(1) \cdots Na(2^{vii}) \ 2 \cdot 887 \ (0) \\ S(1) \cdots Na(2^{i}) \ 3 \cdot 084 \ (1) \end{array}$
$\begin{array}{l} Na(2^{i})/S^{*}octahedron^{*}\\ distances\\ Na(2)\cdots S(1^{v_{1}}) \ 2.887\ (0)\\ Na(2)\cdots S(1^{v_{1}}) \ 2.887\ (0)\\ Na(2)\cdots S(2^{v_{11}}) \ 3.043\ (0)\\ Na(2)\cdots S(2^{v_{11}}) \ 3.084\ (1)\\ Na(2)\cdots S(1^{i_{1}}) \ 3.084\ (1)\\ \end{array}$	$\begin{array}{l} Na(1^{i})/S \ tetrahedron \\ distances \\ Na(1)\cdots S(1^{i_3})2\cdot826 \ (1) \\ Na(1)\cdots S(1^{i_3}) 2\cdot826 \ (1) \\ Na(1)\cdots S(1^{i_3}) 2\cdot842 \ (1) \\ Na(1)\cdots S(1^{i_3})2\cdot842 \ (1) \end{array}$

Na(1 ⁱ) tetrahedron angles	Na(2 ⁱ) 'octahedron' angles	
$S(1^{1}) - Na(1) - S(1^{11}) 116.47 (4)$	$S(1^{i})$ —Na(2)– $S(1^{iii})$ 81.89 (3)
$S(1^{1}) - Na(1) - S(1^{1x}) 105.70(0)$	$S(1^{1}) - Na(2) - S(1^{v1}) = 74.09$	2)
$S(1^{1}) - Na(1) - S(1^{x}) = 105.66(0)$	$S(1^{1}) - Na(2) - S(1^{x}) = 98.25$ (1)	2)
$S(1^{11})-Na(1)-S(1^{1x}) 106.66(0)$	$S(1^{i}) - Na(2) - S(2^{v}) = 139.01$ (3)
$S(1^{11})-Na(1)-S(1^{x})$ 105.70 (0)	$S(1^{1})$ -Na(2)- $S(2^{v111})$ 67.01 (1)
$S(1^{*})-Na(1)-S(1^{*})$ 118.22 (4)	$S(1^{111})-Na(2)-S(1^{v1}) = 98.25$ (1)	2)
	$S(1^{111})-Na(2)-S(1^{x})$ 74.09 (2)
	$S(1^{111})-Na(2)-S(2^{v})$ 67.01 (1)
	$S(1^{111})-Na(2)-S(2^{v111})$ 139.07 (3)
	$S(1^{vi}) - Na(2) - S(1^{x}) = 170.08$ (5)
	$S(1^{vi})-Na(2)-S(2^{v}) = 84.40$ (1)
	$S(1^{vi})-Na(2)-S(2^{viii})$ 98.01 (1)
	$S(1^{x})$ -Na(2)-S(2 ^v) 98.01 (1)
	$S(1^{*}) - Na(2) - S(2^{*11}) = 84.40$ (1)
	$S(2^{v}) - Na(2) - S(2^{vH}) = 152.04$ (1)	5)
Symmetry code		
x. v. z	vii $-1+y+z+z$	
$-x_{2} - y_{2}z_{1}$	Viii $\frac{1}{2} - r v^{\frac{3}{2}} - 7$	
$x, \frac{1}{2} - y, \frac{1}{2} - z$	$ix -\frac{1}{2} + yx - \frac{1}{2} + x$	
$v_{1} + x_{2} + z_{3}$	$x = \frac{1}{2} - y - x - \frac{1}{2} + z$	

xi

Table 5 (cont.)

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 BaS₄. H₂O (Abrahams, 1954) and Ce₂S₆ (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_2S_4 since the terminal bond distance is 2.074 (1) Å. The errors in the sulphur-sulphur bond distances for Ce_2S_6 and BaS_4 . H_2O are about 0.03 Å, which suggest that comparisons of bond distances are unreliable. The terminal sulphur bond distance found in Na_2S_4 is significantly longer than the 2.02 Å bonds found in both Ce_2S_6 and BaS_4 . H_2O .

ii iii iv v

vi

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^{-1} were used and for the middle sulphur, S(2), scattering factor values of S° 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_4^2 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_4^{2-} ion is surrounded by 4 close Na⁺ ions and the middle atom S(2) is surrounded by 2 close Na⁺ 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_4^{2-} 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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References

ABRAHAMS, S. C. (1954). Acta Cryst. 7, 423-429.

- Abrahams, S. C. & Grison, E. (1953). Acta Cryst. 6, 206-213.
- FÖPPL, H., BUSMANN, E. & FRORATH, F.-K. (1962). Z. anorg. allgem. Chem. 314, 12–20.
- HORDVIK, A. (1966). Acta Chem. Scand. 20, 1885-1891.

- HORDVIK, A, & SLETTEN, E. (1968). Acta Chem. Scand. 22, 3029-3030.
- International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). ORTEP. Report ORNL-3794, 1–87, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- PAULING, N. (1949). Proc. Natl. Acad. Sci. Wash. 35, 495– 499.
- Rosén, E. & TEGMAN, R. (1971). Acta Chem. Scand. 25, 3329–3336.
- Rosén, E. & TEGMAN, R. (1972). Chem. Script. 2, 221-225.
- TEGMAN, R. (1972). Chem. Script. 2, 63–67.
- WERNER, P.-E. (1970). Ark. Kemi, 31, 513-516.
- ÅSBRINK, S. & WERNER, P.-E. (1966). Acta Cryst. 20, 407– 410.

Acta Cryst. (1973). B29, 1469

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; Lencrerot, 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° des molécules autour de (au moins) 2 des axes de symétrie du novau naphtalénique:* ce mouvement est rendu possible grâce à la faiblesse des interactions moléculaires malgré l'encombrement du substituant en 2.

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

^{*} 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.