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The Structure of Sodium 3,5-Diacetylimino-1,2-dithiole Trihydrate

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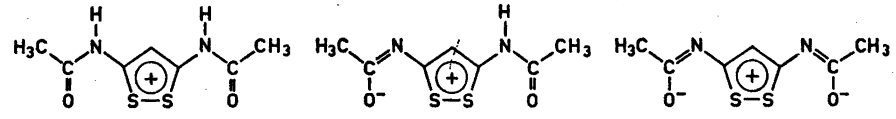
An X-ray structure investigation of crystals of sodium 3,5-diacetylimino-1,2-dithiole trihydrate has been carried out. The crystals belong to the space group *Cmcm*, with unit cell dimensions: $a = 16.18$ Å, $b = 12.00$ Å, and $c = 6.94$ Å. There are four formula units per unit cell.

The structure was solved from Patterson and Fourier projections, and the atomic parameters were refined by least squares methods.

The 3,5-diacetylimino-1,2-dithiole ion, of symmetry *mm*, lies in the crystallographic mirror plane normal to the *c* axis and across the mirror plane normal to the *a* axis, with the latter plane passing through the midpoint of the sulphur-sulphur bond. The bond lengths are: S–S = 2.05 ± 0.015 Å, C–S = 1.76 ± 0.02 Å, C–C (cyclic) = 1.43 ± 0.025 Å, C–N = 1.34 and 1.40 ± 0.025 Å, C–C = 1.51, and C–O = 1.23 ± 0.025 Å. There are two intramolecular S···O close contacts of 2.63 ± 0.02 Å, with O···S–S···O approximately linear; ∠ O···S–S = 168.1 ± 0.8°.

Two of the water molecules are associated with the sodium ion, Na···O = 2.35 ± 0.025 Å, and the third approaches the sulphur atoms of the disulphide group, S···O = 2.74 ± 0.02 Å, in a triangular three-center arrangement. The former water molecules probably form hydrogen bonds to the carbonyl oxygens of the anion.

3-Acetylimino-5-acetamido-1,2-dithiole (II) accepts a proton in acid solution to give the cation (I) and donates a proton in alkaline solution to form the anion (III).[1] The structure of (I) has been determined through an X-ray crystallographic investigation of the bromide.[2] From the results, the cation (I) is nearly planar; the oxygen atoms form close contacts of 2.51 and 2.57 Å, respectively, with the sulphur atoms of the disulphide group. The sulphur-



(I) (II) (III)

sulphur bond in (I) was found to be 2.080 ± 0.005 Å, and it was concluded that the partial bonding between oxygen and sulphur affects the length of the sulphur-sulphur bond only to a small degree.

There may be more negative charge available for the oxygen atoms in the anion (III) than in the cation (I) and it was thought possible that this might cause a stronger partial bonding between oxygen and sulphur, which in turn should affect the length of the sulphur-sulphur bond more extensively than in (I). The present investigation was undertaken with this view.

EXPERIMENTAL

On dissolving 3-acetylimino-5-acetamido-1,2-dithiole (II) in dilute sodium hydroxide,[1] sodium 3,5-diacetylimino-1,2-dithiole trihydrate crystallizes over night. One monoclinic and one orthorhombic crystal modification have been obtained, and the unit cell dimensions and space groups for these have been published earlier.[3]

The orthorhombic crystals, which the present structure investigation is based on, are colourless needles elongated along the c axis, with cell dimensions, $a = 16.18$ Å, $b = 12.00$ Å, $c = 6.94$ Å. There are four formula units per unit cell; density, calc. 1.44, found 1.41 g/cm³. From systematic absences, the space group is $Cmcm$, $Cmc2_1$ or $C2cm$. The subsequent refinement of $hk0$ data indicates that the correct space group is $Cmcm$.

The crystals are very unstable; they become opaque and give powder patterns after a few hours. It was therefore rather difficult to obtain X-ray photographs good enough for intensity measurements. The intensities of the $hk0$ reflections were estimated visually from a single Weissenberg photograph, taken with unfiltered copper radiation. Both α and β reflections were measured, and the average value of the ratios between α and β intensities for equivalent reflections was used to put the intensities on a relative scale. 52 reflections were observed and measured. The intensities were corrected for Lorentz and polarization factors.

STRUCTURE REFINEMENT

The position of the atoms in the anion (III) were found from Patterson c projection, and the positions of the sodium ion and the water molecules revealed themselves during a subsequent Fourier synthesis.

Atomic parameters were refined by least squares methods on an IBM 1620 II computer, using a program designed by Mair.[4] Weighting scheme No. 3, recommended by Mair, was used with $a = 54$ and $b = 34$. Anisotropic temperature factor was applied to sulphur, and isotropic temperature factors were applied to sodium, oxygen, nitrogen and carbon. The hydrogen atoms were neglected.

During the least squares refinement it became clear that only about 50 % of the positions of the water molecule on m at $x = 0$ were occupied. This probably explains the observed difference between the calculated density, 1.44 g/cm³ and found density 1.41 g/cm³. With 2 ½ molecules of water of hydration, the calculated density becomes 1.40 g/cm³. Scattering factor values for the oxygen atom in question were accordingly halved in the final stage of the refinement.

The conventional agreement factor R did not improve beyond 0.074. A Fourier c projection of the structure is shown in Fig. 1. Final atomic coordinates and temperature factors are listed in Table 1, and the corresponding

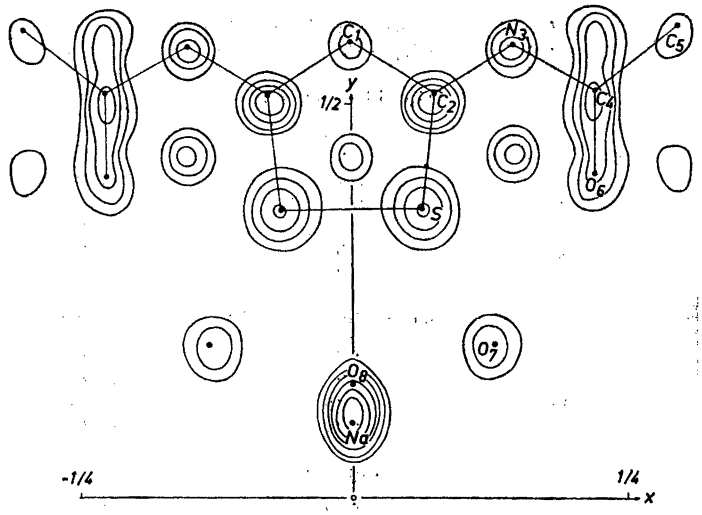


Fig. 1. Electron density projection of sodium 3,5-diacetylimino-1,2-dithiole trihydrate along the *c* axis. Contours at arbitrary but equal intervals.

Table 1. Atomic coordinates in fractions of corresponding cell edges, and temperature parameters, B in $\exp[-B(\sin^2\theta/\lambda^2)]$. For sulphur, the temperature factor used was $\exp-(0.0037h^2 + 0.0032k^2 + 0.0029hk)$.

Atom	x	y	B (Å^2)
S	0.0633	0.3680	
C_1	0.0000	0.5762	0.5
C_2	0.0750	0.5135	1.8
N_3	0.1463	0.5699	1.8
C_4	0.2221	0.5149	2.0
C_5	0.2946	0.5945	0.9
O_6	0.2217	0.4126	2.7
O_7	0.1279	0.2033	2.4
O_8	0.0000	0.1576	2.0
Na	0.0000	0.1111	2.9

set of observed and calculated structure factors are given in Table 3. The F_c values are based on the scattering curves for sulphur, sodium ion, oxygen, nitrogen and carbon given in *International Tables*,[5] the first set of the listed scattering factors for carbon being used.

DISCUSSION

The bond length and bond angles, listed in Table 2 and shown in Fig. 2, are based on the coordinates in Table 1. From the values in Table 2 it seems obvious that the anion (III) lies in the mirror plane normal to the *c* axis and across the mirror plane normal to the *a* axis. The correct space group is therefore most probably *Cmcm*, which means that the complete crystal structure is known from the results of the *c* axis projection.

Table 2. Bond lengths (Å), atomic distances (Å) and bond angles in sodium 3,5-diacetylimino-1,2-dithiole trihydrate, with standard deviations.

	Bond length (Å)	σ (Å)
S—S	2.05	0.015
S—C_2	1.76	0.020
C_1—C_2	1.43	0.025
C_2—N_3	1.34	0.025
N_3—C_4	1.40	0.025
C_4—C_5	1.51	0.030
C_4—O_6	1.23	0.025
	Atomic distances (Å)	**σ (Å)**
S···O_6	2.63	0.020
O_6···O_7	2.79	0.025
O_7···Na	2.35	0.025
O_8···S	2.74	0.020
	Angle (°)	**σ (°)**
S′—S—C_2	96.2	0.8
S—C_2—C_1	115.7	1.3
S—C_2—N_3	126.6	1.3
C_1—C_2—N_3	117.6	1.5
C_2—N_3—C_4	121.3	1.5
N_3—C_4—O_6	117.9	1.4
N_3—C_4—C_5	112.5	1.7
C_5—C_4—O_6	129.6	1.5
C_2—C_1—C_2′	115.2	1.6

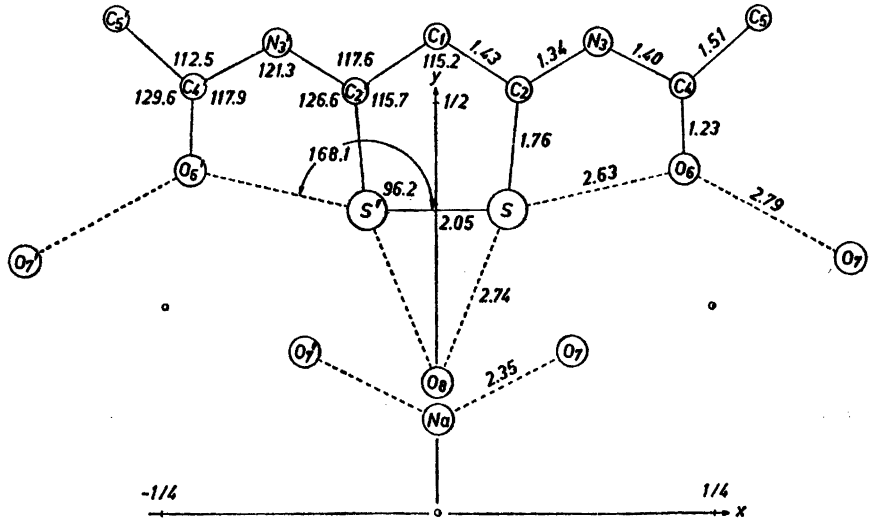


Fig. 2. Bond lengths (Å), interatomic distances (Å) and bond angles (°) in the crystals of sodium 3,5-diacetylimino-1,2-dithiole trihydrate.

The crystal structure emerges from the *c* projection of *Cmcm* in the following way, *cf.* Fig. 2. The sodium ion and O_8 which lie in *mm* positions, can not lie in the *same* but must lie in alternating *c* mirror planes, because in the *c* projection their distance is only 0.56 Å. Further, the projected $O_7 \cdots O_8$ distance of 2.14 Å, is too short for the atoms to be in the same *c* mirror plane. Therefore the sodium ion and O_7 have the same *z*-coordinate, giving a $Na^+ \cdots O^7$ distance of 2.35 Å in agreement with the length of such distances *e.g.* in sodium tetrathionate dihydrate,[6] 2.35—2.47 Å, and in sodium methanethiosulphonate monohydrate,[7] 2.39—2.49 Å. Finally the projected $S \cdots O_7$ distance of 2.24 Å shows that also S and O_7 lie in alternating *c* mirror planes.

Table 3. Observed and calculated structure factors for sodium 3,5-diacetylimino-1,2-dithiole trihydrate. The values are based on four asymmetric units. The reflection marked with an asterisk was given zero weight in the refinement because of assumed secondary extinction.

h	F_o	F_c	*h*	F_o	F_c
	*h*00		7	26.69	−28.03
2	19.28	16.87	9	40.32	−37.40
4	24.56	23.37			
6	12.33	−15.30		*h*40	
8	6.30	2.95	2	36.24	−34.51
10	50.24	48.82	4	32.16	−30.80
16	11.12	13.68	8	18.81	14.69
18	11.12	11.61	14	13.81	−16.31
			16	11.49	−12.46
k	0*k*0				
2	53.11	56.47		*h*50	
4	60.34	−58.32	1	18.63	18.79
6	13.53	−15.89	3	19.65	−18.95
8	20.02	21.08	5	24.28	−26.51
			9	8.99	− 9.27
	*h*10		11	16.50	−18.58
1	45.88*	−55.49			
3	15.57	16.56		*h*60	
5	21.32	15.98	2	20.58	22.50
7	49.13	49.46	4	11.40	−10.34
9	19.00	17.93	6	21.78	−21.25
11	23.36	24.20	8	15.29	−14.67
13	27.44	−26.10			
				*h*70	
			1	24.01	−25.02
	*h*20		5	22.71	24.31
2	23.08	−26.10	7	34.94	34.83
4	33.46	32.06	9	18.91	17.80
6	6.77	−10.44			
8	13.90	−10.47		*h*80	
14	17.24	16.68	2	26.05	25.22
16	8.99	10.09	4	13.63	15.82
			6	23.64	−25.20
	*h*30		8	27.81	−28.52
1	17.70	−15.09			
3	23.64	24.51		*h*90	
5	16.87	−17.23	7	26.69	25.79

The z-coordinates thus indicated are, for the atoms of the anion and O_8: $z = 1/4$, and for Na^+ and O_7: $z = 3/4$. From these values and the coordinates in Table 1 the $O_8 \cdots S$ distance is 2.74 Å, and there is thus close contacts between the water oxygen atom O_8 and the sulphur atoms of the disulphide group, the sum of van der Waals radii for sulphur and oxygen [8] being 3.25 Å. In 4-phenyl-1,2-dithiolium thiocyanate,[9] analogous three-center close contacts, of lengths 2.87 Å, have been found between the nitrogen atom of the thiocyanate ion and the sulphur atoms of the disulphide group.

There is no contact between O_8 and neighbouring sodium ions. Since only about 50 % of the O_8 water molecules are present, one may assume that O_8 is more loosely bonded than O_7, and this probably accounts for the instability of the crystals. The $O_7 \cdots O_6$ distance of 2.79 Å indicates that O_7, apart from being associated with the sodium ion, also participates in hydrogen bonding with O_6.

The dimensions of the anion (III), given in Table 2 and shown in Fig. 2, may now be compared with the dimensions of the cation (I), shown in Fig. 3.

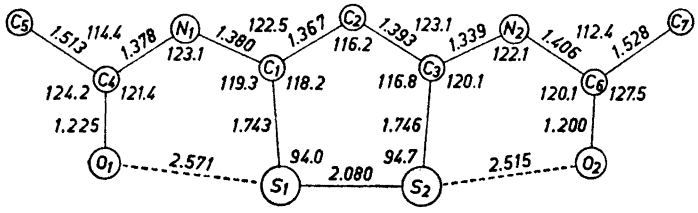


Fig. 3. Bond lengths (Å), close contacts (Å) and bond angles in the 3,5-diacetamido-1,2-dithiolium ion. The standard deviations in bond lengths are: S—S ± 0.005 Å; C—S ± 0.011 Å; C—C, C—N, C—O ± 0.02 Å.

The acetyl groups in (I), from the structure investigation of 3,5-diacetamido-1,2-dithiolium bromide,[2] are slightly bent out of the least squares plane through the ring atoms and the nitrogen atoms. From the present investigation the anion (III) is exactly planar, and symmetric about an axis through C_2 and the midpoint of the sulphur-sulphur bond. Fig. 3 shows that (I) is also nearly symmetric. There are no significant differences between the lengths of equivalent bonds in (I) and (III), *cf.* Figs. 2 and 3. The conjugation in (III) is therefore, as in (I), more pronounced in the carbon-nitrogen part of the ion than in the carbon-sulphur part.

There are two sulphur-oxygen close contacts, $S \cdots O_6 = 2.63 \pm 0.02$ Å, in (III). The corresponding contacts in (I) were found to be 2.515 and 2.571 ± 0.011 Å, and the partial bonding between sulphur and oxygen therefore seems to be slightly weaker in (III) than in (I). It is interesting to note that the oxygen atom which takes part in the longest intramolecular sulphur-oxygen contact in (I), is engaged in an additional, weaker contact with a symmetry-related sulphur atom. In (III), as mentioned above, O_6 probably participates in a hydrogen bond, and this may explain why the intramolecular sulphur-oxygen contacts there are weaker than in (I).

The sulphur-sulphur bond length in (I) is 2.080 ± 0.005 Å (corrected for rigid-body libration; uncorrected value 2.073 Å) and in (III), 2.05 ± 0.015 Å. Although the difference is not significant, it is in accordance with the closer S···O contacts in (I) and indicates a corresponding, slightly larger transfer of charge from the oxygen atoms in (I) into the antibonding σ-orbital of the sulphur-sulphur bond.

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REFERENCES

1. Schmidt, U. *Private communication* (1960).
2. Hordvik, A. and Kjøge, H. M. *Acta Chem. Scand.* **20** (1966) 1923.
3. Hordvik, A., Sletten, E. and Sletten, J. *Acta Chem. Scand.* **20** (1966) 1172.
4. Mair, G. A. *Structure Factor and Least Squares Programs for the IBM 1620*, Pure Chemistry Division, National Research Council, Ottawa, Canada 1963.
5. *International Tables for X-ray Crystallography*, Vol. III, Kynoch Press, Birmingham 1962, p. 204.
6. Foss, O. and Hordvik, A. *Acta Chem. Scand.* **18** (1964) 662.
7. Foss, O. and Hordvik, A. *Acta Chem. Scand.* **18** (1964) 619.
8. Pauling, L. *The Nature of the Chemical Bond.* 3rd. Ed., Cornell University Press, Ithaca, New York 1960.
9. Hordvik, A. and Kjøge, H. M. *To be published.*

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