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References

ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* A27, 157–165.

BANTING, L., SMITH, H. J., JAMES, M., JONES, G., NAZARETH, W., NICHOLLS, P. J., HEWLINS, M. J. E. & ROWLANDS, M. G. (1988). *J. Enzyme Inhib.* **2**, 215–229.

BLESSING, R. H. (1987). *Crystallogr. Rev.* **1**, 3–57.

BULLION, K. A., OSAWA, Y. & BRAUN, D. G. (1990). *Endocrinol. Res.* **16**, 255–267.

Enraf–Nonius (1979). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.

JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

SANTEN, R. J., SANTNER, S., DAVIS, B., VELDHUIS, J., SAMOJLIK, E. & RUBY, E. (1978). *J. Clin. Endocrinol. Metab.* **47**, 1257–1265.

SCHIAVO, D. M., GREEN, J. D., TRIANA, V. M., SPAET, R. & ZAIDI, I. (1988). *Fundam. Appl. Toxicol.* **10**, 329–334.

SHAW, M. A., NICHOLLS, P. J. & SMITH, H. J. (1988). *J. Steriod Biochem.* **31**, 137–146.

STEELE, R. E., MELLER, L. B., SAWYER, W. K. & BROWN, L. J. (1987). *Steroids*, **50**, 147–161.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, pp. 457. New York: Macmillan.

Tripos Associates, Inc. (1988). *SYBYL*. A molecular modeling program. Tripos Associates, Inc., St Louis, Missouri, USA.

VAN ROEY, P., BULLION, K. A., OSAWA, Y., BOWMAN, R. M. & BRAUN, D. G. (1991). *Acta Cryst.* C47, 829–832.

VAN ROEY, P, BULLION, K. A., OSAWA, Y., BROWNE, L. J., BOWMAN, R. M. & BRAUN, D. G. (1990). *J. Enzyme Inhibit.* In the press.

Acta Cryst. (1991). C47, 1018–1021

Structure of Sodium 1,2,3,4-Thiatriazole-5-thiolate Dihydrate and 5-Benzoylthio-1,2,3,4-thiatriazole

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Abstract. Sodium 1,2,3,4-thiatriazole-5-thiolate (*A*) dihydrate, $Na^+.CS_2N_3^-.2H_2O$, $M_r = 177{\cdot}18$, monoclinic, $P2_1/n$, $a = 5{\cdot}821\ (2)$, $b = 18{\cdot}494\ (7)$, $c = 6{\cdot}786\ (3)$ Å, $\beta = 114{\cdot}84\ (3)°$, $V = 663{\cdot}0$ Å^3, $Z = 4$, $D_x = 1{\cdot}77$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 7{\cdot}6$ cm^{-1}, $F(000) = 360$, $T = 173\ (1)$ K, $R = 0{\cdot}024$ for 1160 observed reflections. 5-Benzoylthio-1,2,3,4-thiatriazole (*B*), $C_8H_5N_3OS_2$, $M_r = 223{\cdot}28$, triclinic, $P\bar{1}$, $a = 7{\cdot}420\ (3)$, $b = 11{\cdot}115\ (2)$, $c = 5{\cdot}642\ (1)$ Å, $\alpha = 91{\cdot}50\ (2)$, $\beta = 98{\cdot}42\ (2)$, $\gamma = 79{\cdot}68\ (2)°$, $V = 452{\cdot}8$ Å^3, $Z = 2$, $D_x = 1{\cdot}64$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 5{\cdot}3$ cm^{-1}, $F(000) = 228$, $R = 0{\cdot}026$ for 1435 observed reflections. The structure of the reaction product of sodium azide and carbon disulfide is unequivocally established as (*A*). The exocyclic C—S bond length is 1·704 (1) Å in contrast with the bond length of 1·580 Å predicted by MNDO methods [Conti, Franco & Trsic (1986). *Inorg. Chim. Acta*, **113**, 71–74]. Benzoylation of (*A*) is established to occur at the exocyclic S atom rather than at an N atom of the thiatriazole ring, yielding (*B*).

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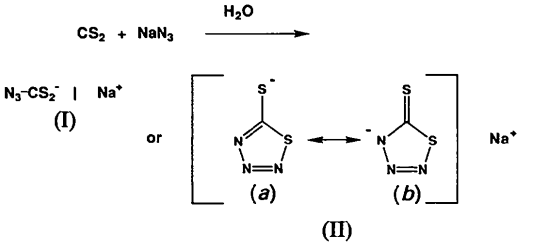
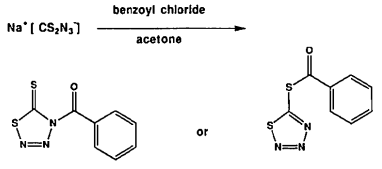
Introduction. Brown & Hoel (1922) reported the reaction of carbon disulfide and sodium azide to give what was thought to be an azidodithiocarbamate (I). From infrared spectroscopic measurements Lieber, Pilli, Ramachandran & Hites (1957) concluded that the reaction product was actually the 1,2,3,4-thiatriazole-5-thiolate anion (II). Discussion has continued concerning the structure of (II) and its protonated form as to whether the thiol (II*a*) or the thione (II*b*) structure is the major resonance contributor (Lieber, Oftedahl & Rao, 1961; Christopherson & Holm, 1971); L'abbe, Toppet, Willocx & Mathys, 1977). Recently the MNDO method has been applied to the problem and Conti, Franco &



(II)

Trsic (1986) calculated structure (II) to be more stable than structure (I). In view of this situation, the crystal structure of the reaction product of carbon disulfide with sodium azide was determined. The structure of the benzoyl derivative of sodium 1,2,3,4-thiatriazole-5-thione is also the subject of some uncertainty. For example, Lieber, Oftedahl & Rao (1961) reported that reaction with benzoyl chloride occurs at the 4-position (III). Christopherson & Holm (1971) made a strong case for reaction instead at the 5-position yielding 5-benzoylthio-1,2,3,4-thiatriazole (IV).



(III) (IV)

The crystal structure was determined in order to define the reaction site unequivocally.

Experimental. Sodium thiatriazole was prepared by the reaction of equimolar amounts of carbon disulfide and sodium azide in water. The mixture was stirred overnight, filtered, and the water evaporated. Crystals suitable for X-ray analysis were obtained from acetone. A faintly yellow crystal having approximate dimensions 0·30 × 0·30 × 0·30 mm was cut from a larger sample under STP oil treatment. This fluid served as a protectant of the hygroscopic material and (at low temperature) as an adhesive for the sample which was transferred to a glass fiber and positioned in a cold gas stream for the X-ray experiment. Intensities were measured with an Enraf–Nonius CAD-4 diffractometer using variable-speed ω scans. Unit-cell constants were determined from a least-squares fit to angular data for 25 reflections in the angular range $10 < \theta < 15°$. Data were collected to $(\sin\theta)/\lambda$ of 0·594 Å^{-1}, $-6 \le h \le 6$, $0 \le k \le 22$, $-8 \le l \le 8$. As a check on crystal and electronic stability three reflections were measured every 60 min. The intensities of these standards remained constant within experimental error throughout data collection. No decay correction was applied. 2306 reflections were measured and averaged (R_{int} = 2·6%) to 1160 unique data, 1124 reflections with $I > 3\sigma(I)$ were considered observed. The structure was solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and Fourier methods. In the first E map the Na atom, all atoms of the ring, and the exocyclic S atom could be located. It later became apparent that something else was present in the sample, namely water, and the remaining atoms were located in successive difference Fourier syntheses. H atoms were located and their positions and isotropic thermal parameters were refined. All other atoms were refined anisotropically for a total of 98 variables. An empirical absorption correction based on a series of ψ scans (North, Phillips & Mathews, 1968) was applied to the data. Relative transmission coefficients ranged from 0·939 to 0·996 with an average value of 0·971. Full-matrix least squares minimized $\sum w(\Delta F)^2$, $w = 1/\sigma^2(F_o)$. Final $R = 0{\cdot}024$, $wR = 0{\cdot}056$, $S = 2{\cdot}67$. Final $(\Delta/\sigma)_{max} = 0{\cdot}03$, $\Delta\rho_{max} = 0{\cdot}25$ (5), $\Delta\rho_{min} = -0{\cdot}34$ (6) e Å^{-3}, on final difference map. Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computer programs used were those of Enraf–Nonius (1982) *Structure Determination Package*.

The benzoyl derivative was synthesized by the dropwise addition of benzoyl chloride to a solution of sodium thiatriazole in acetone. Water was added to dissolve the sodium chloride formed in the reaction. Crystals suitable for X-ray analysis were obtained from acetone. A pale-yellow block-shaped crystal of approximate dimensions 0·30 × 0·30 × 0·30 mm was cleaved from a larger crystal and coated with STP oil treatment and data were collected as previously described to $(\sin\theta)/\lambda$ of 0·594 Å^{-1}, $-6 \le h \le 6$, $-12 \le k \le 13$, $0 \le l \le 8$. As a check on crystal and electronic stability three reflections were measured every 166 min; the intensities remained constant within experimental error. 1674 reflections were measured and averaged (R = 0·9%) to 1585 unique data, 1435 reflections with $I > 3\sigma(I)$ were considered observed. The structure was solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and Fourier methods. Empirical absorption corrections were made using the method of Walker & Stuart (1983); min. and max. absorption corrections of 0·841 and 1·22 were applied. Full-matrix least squares minimized $\sum w(\Delta F)^2$, $w = 1/\sigma^2(F_o)$. H atoms were located and their positions were refined in least squares. Attempts to refine the isotropic thermal parameters of the H atoms were unsuccessful, resulting in unrealistic C—H distances, therefore the hydrogen temperature factors were held fixed at 1·5 times the average B_{eq} for the hydrogen-bearing ring C atoms (3·0 Å^2). All other atoms were refined anisotropically for 142 variables. Final R = 0·026, $wR = 0{\cdot}044$, $S = 1{\cdot}96$. Final $(\Delta/\sigma)_{max} = 0{\cdot}01$, $\Delta\rho_{max} = 0{\cdot}30$ (9), $\Delta\rho_{min} = -0{\cdot}28$ (9) e Å^{-3} on final difference map. Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Computer programs used were those of Enraf–Nonius (1982) *Structure Determination Package*.

Table 1. *Positional parameters with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B(Å^2)
Sodium 1,2,3,4-thiatriazole-5-thiolate dihydrate				
S1	0·99033 (7)	0·70089 (2)	−0·06926 (6)	1·972 (8)
S2	0·73019 (7)	0·56942 (2)	0·00501 (5)	1·512 (8)
Na	0·3225 (1)	0·99777 (3)	0·15280 (8)	1·58 (1)
N1	0·8991 (3)	0·78240 (7)	−0·0266 (2)	2·02 (3)
N2	0·7207 (3)	0·77710 (7)	0·0369 (2)	1·85 (3)
N3	0·6470 (2)	0·70994 (7)	0·0580 (2)	1·84 (3)
C1	0·7754 (3)	0·66042 (9)	0·0044 (2)	1·31 (3)
O1	1·0143 (2)	0·92562 (6)	−0·1249 (2)	1·70 (2)
O2	0·6470 (2)	0·92652 (6)	0·1306 (2)	1·69 (2)
H1	1·060 (4)	0·9230 (9)	−0·227 (3)	1·5 (4)*
H2	1·006 (3)	0·881 (1)	−0·100 (3)	2·5 (4)*
H3	0·644 (4)	0·884 (1)	0·090 (3)	3·1 (5)*
H4	0·804 (5)	0·930 (1)	0·226 (4)	3·7 (5)*
5-Benzoylthio-1,2,3,4-thiatriazole				
S1	0·14957 (5)	0·30391 (3)	0·01322 (6)	2·062 (7)
S2	0·32247 (5)	0·04757 (3)	0·24003 (6)	1·923 (7)
O1	0·1391 (1)	0·08817 (9)	−0·1941 (2)	2·36 (2)
N1	0·1775 (2)	0·4219 (1)	0·1971 (3)	2·79 (3)
N2	0·2676 (2)	0·3866 (1)	0·4004 (3)	3·01 (3)
N3	0·3215 (2)	0·2641 (1)	0·4299 (2)	2·60 (3)
C1	0·2670 (2)	0·2062 (1)	0·2339 (2)	1·82 (3)
C2	0·2214 (2)	0·0085 (1)	−0·0556 (2)	1·56 (2)
C3	0·2482 (2)	−0·1235 (1)	−0·1054 (2)	1·54 (2)
C4	0·3436 (2)	−0·2108 (1)	0·0628 (2)	1·83 (3)
C5	0·3617 (2)	−0·3331 (1)	0·0076 (3)	2·26 (3)
C6	0·2878 (2)	−0·3707 (1)	−0·2146 (3)	2·31 (3)
C7	0·1942 (2)	−0·2846 (1)	−0·3851 (3)	2·16 (3)
C8	0·1732 (2)	−0·1613 (1)	−0·3312 (2)	1·79 (3)
H1	0·389 (2)	−0·183 (2)	0·203 (3)	3·0†
H2	0·419 (2)	−0·393 (2)	0·124 (3)	3·0†
H3	0·292 (2)	−0·454 (1)	−0·257 (3)	3·0†
H4	0·141 (2)	−0·310 (1)	−0·536 (3)	3·0†
H5	0·112 (2)	−0·103 (2)	−0·432 (3)	3·0†

* Atoms refined isotropically.
† Atoms refined with fixed temperature factors.

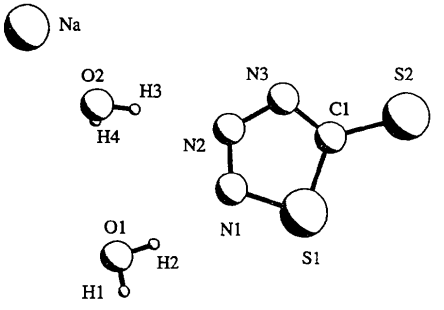


Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing of sodium 1,2,3,4-thiatriazole-5-thiolate dihydrate.

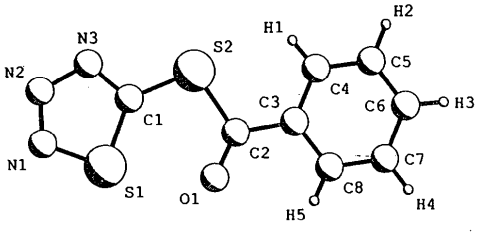


Fig. 2. *PLUTO* (Motherwell & Clegg, 1978) drawing of 5-benzoylthio-1,2,3,4-thiatriazole.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Sodium 1,2,3,4-thiatriazole-5-thiolate dihydrate			
N3—C1	1·326 (1)	O1—H1	0·84 (2)
N2—N1	1·284 (1)	O1—H2	0·86 (2)
S2—C1	1·704 (1)	O2—H3	0·84 (2)
S1—N1	1·664 (1)	O2—H4	0·87 (2)
S1—C1	1·703 (2)		
N3—N2	1·341 (1)		
5-Benzoylthio-1,2,3,4-thiatriazole			
S1—N1	1·674 (2)	C3—C2	1·470 (2)
S2—C1	1·737 (1)	C4—C5	1·373 (2)
S2—C2	1·802 (1)	C5—C6	1·378 (2)
S1—C1	1·704 (1)	C6—C7	1·393 (2)
O1—C2	1·212 (1)	C7—C8	1·382 (2)
N3—N2	1·356 (2)	C4—H1	0·88 (1)
N3—C1	1·313 (2)	C5—H2	0·96 (2)
N2—N1	1·273 (2)	C6—H3	0·95 (1)
C3—C4	1·396 (2)	C7—H4	0·94 (1)
C3—C8	1·399 (2)	C8—H5	0·89 (2)

Sodium 1,2,3,4-thiatriazole-5-thiolate dihydrate			
N1—S1—C1	91·11 (5)	S2—C1—N3	125·20 (8)
N2—N3—C1	111·60 (9)	S1—C1—N3	110·19 (8)
N3—N2—N1	116·52 (9)	H3—O2—H4	101 (1)
S1—N1—N2	110·58 (7)	H1—O1—H2	100 (1)
S2—C1—S1	124·60 (6)		
5-Benzoylthio-1,2,3,4-thiatriazole			
C2—S2—C1	101·64 (5)	C5—C6—C7	120·0 (1)
N1—S1—C1	89·41 (5)	C6—C7—C8	120·1 (1)
N2—N3—C1	110·4 (2)	C3—C8—C7	119·7 (2)
N3—N2—N1	116·1 (1)	S2—C2—O1	120·25 (9)
S1—N1—N2	111·80 (9)	S2—C2—C3	114·25 (8)
C4—C3—C8	119·5 (2)	O1—C2—C3	125·5 (2)
C4—C3—C2	122·7 (1)	S2—C1—S1	130·96 (7)
C8—C3—C2	117·7 (1)	S2—C1—N3	116·77 (9)
C3—C4—C5	120·1 (2)	S1—C1—N3	112·27 (9)
C4—C5—C6	120·5 (1)		

Discussion. Atomic parameters are given in Table 1,* bond lengths and bond angles in Table 2. Atomic numbering schemes are shown in Figs. 1 and 2.

The MNDO geometry optimization reported by Conti, Franco & Trsic (1986) for the 1,2,3,4-thiatriazole-5-thiolate anion is in generally good agreement with the crystal structure reported here. They predicted that the cyclic structure (II) would be more stable than all reasonable models considered for structure (I).

However, there is a large discrepancy for the C—S exocyclic bond which the MNDO calculations predict to be 1·580 Å compared with an experimental value of 1·704 (1) Å. The calculated value is in fact shorter than the bond length given by Pauling (1960) for a C—S double-bond (1·61 Å) and a recently reported C—S double-bond length of 1·645 Å (Bocelli & Rizzoli, 1989). Clark (1985) has pointed out that systematic errors occur in MNDO calculations for specific elements, including calculations for C–S bonds, which are consistently predicted to be too short in thiocyanates. Another difference is that

* Lists of structure factors, anisotropic thermal parameters, least-squares planes and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53519 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

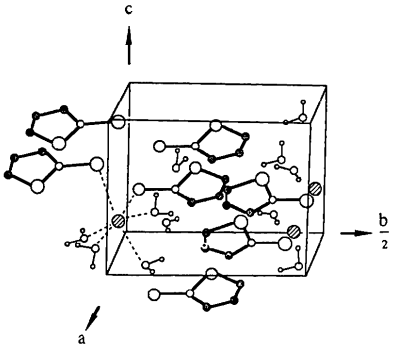


Fig. 3. *PLUTO* (Motherwell & Clegg, 1978) illustration of octahedral sodium 1,2,3,4-thiatriazole-5-thiolate dihydrate.

MNDO calculations indicated strict planarity for the anion, in contrast to slight but definite distortions from planarity found from the best least-squares plane: S2 0·0092, S1 −0·0040, C1 −0·0084, N3 −0·0090, N2 0·0080, N1 0·0042 Å, all displacements being three or more times greater than the estimated standard deviation. The pattern of the deviations is consistent with a slight bowing of the molecule.

The coordination of the sodium ion in this complex is very similar to that observed in $NaCN.2H_2O$ (Van Rij & Britton, 1978) and $NaCl.2H_2O$ (Klewe & Pedersen, 1974). In this case the coordination octahedron consists of four water molecules and two S atoms as illustrated in Fig. 3.

The 5-benzoylthio-1,2,3,4-thiatriazole molecule is close to planar with the dihedral angle between the best least-squares plane of the phenyl and thiatriazole rings being 0·9 (1·6)° and no torsion angle in the molecule being further than 1° from planarity. For the thiatriazole ring no atom deviates by more than 0·0024 Å from the best least-squares plane, most displacements being of the order of experimental error.

References

BOCELLI, G. & RIZZOLI, C. (1989). *Acta Cryst.* C**45**, 119–121.

BROWN, A. W. & HOEL, A. B. (1922). *J. Am. Chem. Soc.* **44**, 2315–2320.

CHRISTOPHERSON, C. & HOLM, A. (1971). *Acta Chem. Scand.* **25**, 2015–2022.

CLARK, T. (1985). *A Handbook of Computational Chemistry*, p. 151. New York: John Wiley.

CONTI, M., FRANCO, D. W. & TRSIC, M. (1986). *Inorg. Chim. Acta*, **113**, 71–74.

Enraf–Nonius (1982). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

KLEWE, B. & PEDERSEN, B. (1974). *Acta Cryst.* B**30**, 2363–2371.

L'ABBE, G., TOPPET, S., WILLOCX, A. & MATHYS, G. (1977). *J. Heterocycl. Chem.* **14**, 1417–1418.

LIEBER, E., OFTEDAHL, E. & RAO, C. N. R. (1961). *J. Org. Chem.* **28**, 194–199.

LIEBER, E., PILLI, C. N., RAMACHANDRAN, J. & HITES, R. D. (1957). *J. Org. Chem.* **22**, 1750–1751.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN*11/82. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*78. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1986). *Acta Cryst.* A**24**, 351–359.

PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.

VAN RIJ, C. & BRITTON, D. (1978). *Acta Cryst.* B**34**, 2080–2084.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* A**39**, 158–166.

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Structure of 7-Methoxy-8-(morpholinocarbonylmethyl)coumarin

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Abstract. $C_{16}H_{17}NO_5$, $M_r = 303·3$, monoclinic, $P2_1/c$, $a = 10·191$ (3), $b = 13·792$ (3), $c = 11·469$ (4) Å, $\beta = 112·14$ (2)°, $V = 1493·2$ (8) Å^3, $Z = 4$, $D_x = 1·349$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·062$ mm^{-1}, $F(000) = 640$, room temperature, $R = 0·061$ for 1383 observed reflections. The structure of

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