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N-ACETYL-OCTACYCLOHEPTATHIOIMIDE, $C_2H_3NOS_7$

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Preliminary Information. As a part of a program aiming the determination of the crystal and molecular structure of a serie of eight member S-N rings derivatives, the crystal structure of the title compound has been undertaken. The crystals were provided by Dr. García-Fernandez from CNRS, Bellevue (France).

Crystal Data. This compound crystallizes in the orthorhombic system, with $a=14.661(3)$, $b=8.8474(10)$ and $c=7.6749(9)$ Å, space group $P2_12_12_1$ (No.19), $Z=4$, $\mu_{Cu}=21.5 \text{ cm}^{-1}$, $D_x=1.78 \text{ gcm}^{-3}$.

Intensity Data, Structure Determination and Refinement. A crystal of dimensions $0.32, 0.45, 0.10$ mm was selected to collect the data. The intensities of 2002 reflexions (1001 Bijvoet pairs) were measured on an automatic four-circle diffractometer with CuK_α radiation ($\lambda=1.5418$ Å), graphite monochromated, up to $\sin\theta/\lambda=0.5875 \text{ \AA}^{-1}$. The structure was solved by direct methods from the moduli of the hkl set of reflexions. 20 of them were considered as unobserved after the criterion $I < 2\sigma(I)$. The structure was refined by full matrix least-squares procedures. The weighting scheme applied by

means of the PESOS program (Martínez-Ripoll et al. 1975) was

$$w=0.6086/|0.6972+0.0481 F_{\text{obs}}+0.0007 F_{\text{obs}}^2|^2.$$

As the H atoms could not be located in the ΔF synthesis, they were fixed at six geometrically calculated positions with an occupancy factor of 0.5. Their atomic coordinates and the isotropic temperature factors were left invariant during the refinement.

The absolute configuration, shown in Fig.1, was determined from a least-squares refinement of both enantiomers using the moduli of the 1001 Bijvoet pairs, giving rise to R values of 0.096 and 0.097 (weighted residuals being 0.116 and 0.118). Moreover, this was confirmed by comparing the 40 more relevant Bijvoet pairs giving the following indices (Martínez-Ripoll et al. 1977): $R_1=1.133$ (2.453 for the enantiomorph) and $R_2=0.061$ (0.199), where $R_1=$ Bijvoet difference and $R_2=$ Bijvoet ratio. Despite the absorption correction applied to the intensity data a rather poor convergence was obtained. The final atomic and thermal parameters are listed in Table 1 and the interatomic distances and angles are given in Table 2. In both tables the atoms have been labelled as in figure 1 in which only three of the six H-atoms included in the structure factor calculation have been represented.

Table 1. Final atomic coordinates and thermal parameters ($U_{ij} \times 10^4 \text{ \AA}^2$).

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	-.4444 (1)	-.7888 (2)	-.5533 (2)	269 (9)	453 (10)	335 (10)	99 (8)	2 (8)	-104 (9)
S(2)	-.5078 (1)	-.6107 (2)	-.6674 (3)	276 (9)	496 (10)	311 (11)	10 (8)	66 (8)	71 (9)
S(3)	-.6454 (1)	-.6602 (3)	-.6794 (3)	274 (9)	635 (13)	246 (10)	43 (10)	-30 (7)	-38 (9)
S(4)	-.7079 (1)	-.5632 (2)	-.4700 (3)	243 (9)	417 (10)	377 (11)	62 (8)	24 (8)	44 (9)
S(5)	-.7114 (1)	-.7228 (2)	-.2772 (3)	180 (8)	430 (10)	333 (10)	-62 (7)	37 (7)	38 (9)
S(6)	-.6000 (1)	-.6812 (2)	-.1215 (2)	242 (9)	435 (10)	243 (10)	-3 (8)	20 (7)	-38 (8)
S(7)	-.5001 (1)	-.8317 (2)	-.1865 (3)	227 (8)	347 (9)	383 (11)	-15 (7)	2 (7)	83 (8)
N	-.4306 (4)	-.7469 (7)	-.3372 (8)	205 (29)	412 (35)	233 (29)	18 (26)	35 (25)	31 (31)
O	-.3224 (4)	-.5745 (8)	-.4019 (9)	317 (30)	549 (35)	614 (42)	-111 (29)	145 (32)	-55 (37)
C(1)	-.3623 (5)	-.6454 (9)	-.2921 (11)	162 (32)	447 (42)	375 (44)	101 (30)	24 (31)	71 (39)
C(2)	-.3423 (6)	-.6244 (10)	-.0998 (12)	372 (44)	491 (46)	393 (48)	-27 (40)	-150 (37)	-70 (40)
H(1)	-.3024	-.6897	-.0238	507					
H(2)	-.3140	-.5321	-.0451	507					
H(3)	-.3897	-.6240	-.0025	507					
H(4)	-.2811	-.6065	-.0451	507					
H(5)	-.3683	-.5409	-.0238	507					
H(6)	-.3567	-.6985	-.0025	507					

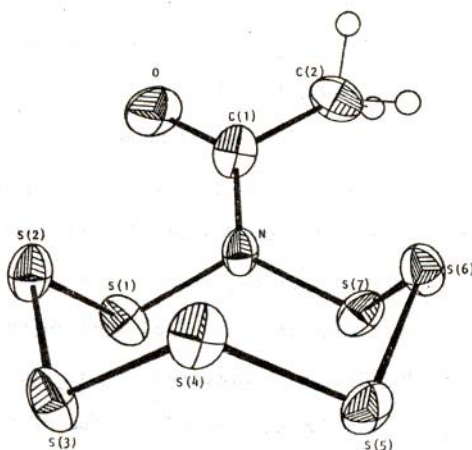


Figure 1. ORTEP drawing of the molecule showing its absolute configuration.

Table 2. Interatomic distances (Å) and angles (°).
The C-H bondlengths have been omitted.

S(1)-S(2)	2.029 (3)	S(1)-N-S(7)	119.3 (4)
S(2)-S(3)	2.066 (3)	C(1)-N-S(1)	117.8 (1)
S(3)-S(4)	2.039 (3)	C(1)-N-S(7)	122.9 (5)
S(4)-S(5)	2.047 (3)	C(2)-C(1)-O	121.6 (7)
S(5)-S(6)	2.057 (2)	C(2)-C(1)-N	117.5 (7)
S(6)-S(7)	2.041 (3)	O-C(1)-N	120.9 (8)
N-S(1)	1.712 (6)	N-S(1)-S(2)	107.7 (2)
N-S(7)	1.714 (6)	S(1)-S(2)-S(3)	107.6 (1)
N-C(1)	1.390 (10)	S(2)-S(3)-S(4)	108.4 (1)
C(1)-O	1.202 (11)	S(3)-S(4)-S(5)	106.9 (1)
C(1)-C(2)	1.516 (13)	S(4)-S(5)-S(6)	106.0 (1)
		S(5)-S(6)-S(7)	108.1 (1)
		S(6)-S(7)-N	107.8 (2)

Comments. The interatomic distances in the acetyl group are as expected. The two S-N distances are shorter than those found in Sulfamic acid (Bats et al. 1977). This indicates a π bond contribution between S and N. The best least-squares plane has been calculated (Schomaker et al. 1959) for the C(1), N, S(1), S(7) group. The deviations of the atoms from this plane are not significant within the e.s.d's., and the consequent sp^2 hybridization of nitrogen is confirmed (Table 2) by the angle distribution

around the N atom. Considering the half ring formed by N, S(1), S(2), S(3) and S(4) atoms, the S(1)-S(2) bondlength is significantly shorter than S(2)-S(3) and S(3)-S(4) distances. This could be explained by a charge transfer from N to S(1) which would increase the bond order between S(1) and S(2) with a consequent weakness of the adjacent S(2)-S(3) bond. These conclusions are not so evident for the other half ring. Although the S(6)-S(7) distance is significantly shorter than the S(5)-S(6) bondlength, the former is equivalent to the S(4)-S(5) distance. Moreover, if an increase in the bond order between S(1) and S(2) is assumed, a smaller value of the S(1)-S(2) distance should be expected when compared with the S-S distances calculated in the orthorhombic sulfur (Abrahams, 1955) where similar values (2.031 Å) have been found for the S-S bond (mean value, 2.037(8) Å) and where no donator atom, as N, is present.

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