The Crystal and Molecular Structure of (−)-3β-Acetoxy-4α-t-butylcarbamoyl-3α-methyl-7β-(*p*-bromophenyl)acetamidocepham 1α-Oxide, $C_{22}H_{28}N_3O_6BrS$

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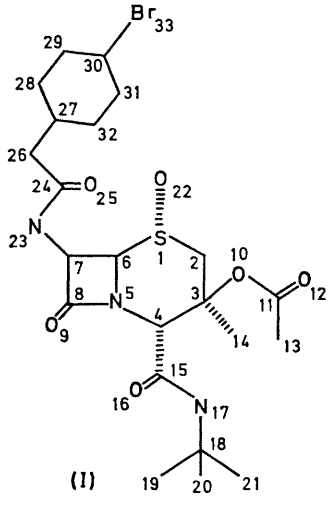
Summary The crystal structure of an oxidised rearrangement product from a penicillin sulphoxide has been determined.

THE title compound is obtained as the major product from the oxidation of the corresponding acetoxy-cepham with sodium periodate.[1] The crystal structure of this compound has been determined from three-dimensional *X*-ray diffraction data. Crystals were obtained from dichloromethane as colourless triangular plates, with the unit-cell data:— $C_{22}H_{28}O_6N_3BrS$, $M = 542{\cdot}4$, space group $P1$ (No. 1), $a = 9{\cdot}123$, $b = 12{\cdot}135$, $c = 12{\cdot}525$ Å, $\alpha = 93°\,49'$, $\beta = 93°\,52'$, $\gamma = 91°\,45'$, $U = 1380$ Å^3, $Z = 2$, $D_m = 1{\cdot}30 \pm 0{\cdot}01$ (flotation), $D_c = 1{\cdot}30$ g cm^{-3}.

The space group must be $P1$ in view of the observed optical activity of this compound.[1]

Using Ni-filtered Cu-K_α radiation, 2207 independent data were measured to $\theta = 45°$, on a Siemens four-circle automatic diffractometer; 72 reflections were judged insignificant. The structure was solved by conventional heavy-atom techniques, and block-diagonal refinement has reached $R = 0{\cdot}092$ with refinement still continuing. The amount of data was limited by severe thermal attenuation, and since there are 2 molecules (66 atoms) in the asymmetric unit, the precision of the parameters is rather poor.

The structure of one molecule is given schematically in (I) and as a stereodiagram[2] in the Figure. The molecules have an extended configuration, and pack side by side

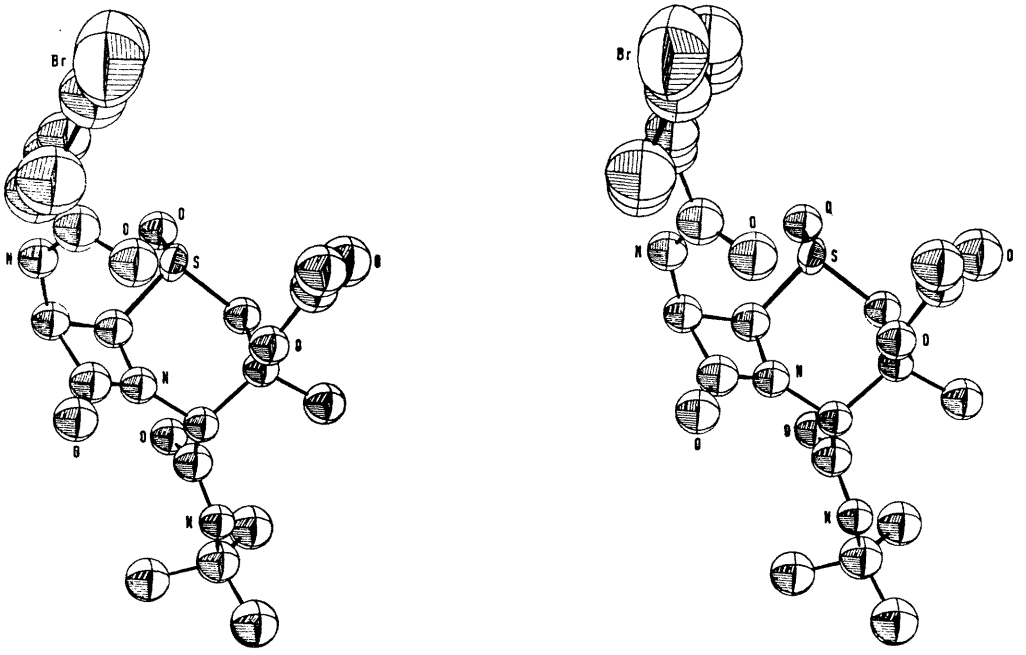


(I)

approximately parallel to *b*, to give a roughly "cube-shaped" unit-cell. The two molecules are very similar structurally, and at this stage of refinement the only significant difference between them is a relative rotation of

the acetoxy-group by *ca.* 120° about the C(3)–O(10) single bond. The absolute configuration of the synthetic molecule has not yet been checked by *X*-ray fluorescence.

and makes angles of 32° and 27° with the mean planes through C(2), C(3), N(5), C(6), in the two molecules. The independent molecules are linked together in pairs by an



FIGURE

The structure confirms that predicted from nuclear Overhauser and mechanistic evidence.[1] The six-membered, sulphur-containing ring forms a well-defined chair, in contrast to cephalosporin *C*,[3] where the presence of the 3-double bond confers a twist-boat conformation on this ring. The sulphoxide oxygen is α (equatorial), the 3-acetoxy-group β (axial), the 3-methyl group α (equatorial), and the 4-t-butylamide group α (axial). The S–O bond lengths of 1·46 and 1·49 Å are within experimental error of literature values.[4]

The β-lactam ring is planar within experimental error, N–H · · · · O hydrogen bond (2·76 Å) between the amide nitrogen, N(23), and the oxygen, O(9), of the β-lactam ring. Weaker intermolecular N–H · · · O interactions (2·92 and 2·93 Å) between the t-butylamide nitrogen, N(17), and the sulphoxide oxygen, O(22), tend to link the molecules in infinite chains. These are, no doubt, influencing factors in the adoption of a crystal structure with two molecules in the unit-cell. In addition an intramolecular bond of the type C–H · · · O (2·91 Å) is suggested between C(2) and O(12) in one of the molecules.

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