On the Planarity of the Lactone Group

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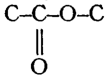
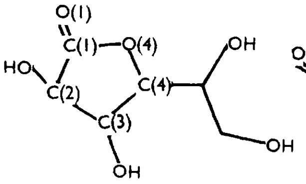
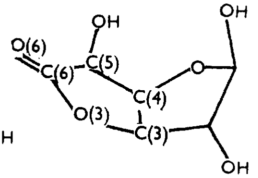
IN a recent Communication,[1] reference is made to the deduction from crystal structure analyses that the lactone group $\mathrm{C{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}C}$ is planar.[2,3] Two recent crystal-structure determinations of simple γ-lactones show an interesting contrast of circumstances under which this group is and is not strictly planar. These analyses were done in the absence of heavy atoms, whose presence may be helpful in solving crystal structures but which may have an adverse effect on the accuracy. These compounds are galactonolactone (I)[4] and glucuronolactone (II).



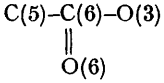
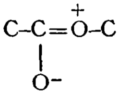
In (I) the lactone group is planar, with a maximum displacement from the best least-squares plane of 0·03Å, which is about six times the estimated standard deviations, σ, of the atomic positions. The ring atom, C(3), which is not part of the lactone group, is 0·62Å out of this plane.



(I)



(II)

In glucuronolactone, on the other hand, the deviations from the best plane through the lactone group vary within +0·08 and −0·10Å. However, the  $\mathrm{C(5)\!-\!\underset{\underset{O(6)}{\|}}{C(6)}\!-\!O(3)}$ group is exactly planar within an observed ±0·003Å, and C(3) is 0·26Å out of that plane, which is about sixty times σ. Another planar group consists of the ring atoms C(4) C(3) O(3) C(6), which is within an observed ±0·0003Å, with atoms C(5) and O(6) −0·25 and +0·20Å out of the plane, respectively. These results suggest that the strain induced in the five-membered rings by their fusion overrides the planarity associated with the valence-bond representation  $\mathrm{C\!-\!\underset{\underset{O^-}{|}}{C}\!=\!\overset{+}{O}\!-\!C}$ of the lactone group, and that only the bonds of the carbonyl carbon atom are sufficiently rigid to remain planar.

This result does not necessarily invalidate the deductions concerning the conformation of δ-lactones[1] which prompted this Communication, but serves to remind us that in detail of the order of tenths of an Ångstrom unit, the stereochemistry of carbohydrate ring systems may be especially sensitive to the steric requirements for minimum configuration energy of its substituents.

Both crystal-structure analyses were based on three-dimensional data and were refined by full-matrix least-squares using anisotropic temperature factors. The data for (I) were photographic and the refinement terminated at an R-value of 7·8%; the data for (II) were collected on a Picker 4-angle automatic diffractometer and the refinement terminated at an R-value of 4·0%.

(*Received, March 3rd,* 1966; *Com.* 137.)

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[1] K. K. Cheung, K. H. Overton, and G. A. Sim, *Chem. Comm.*, 1965, 634.
[2] J. Fredricksons and A. McL. Mathieson, *Acta Cryst.*, 1962, **15**, 119.
[3] A. McL. Mathieson, *Tetrahedron Letters*, 1963, 81.
[4] M. Vlasse, Ph.D. thesis, University of Pittsburgh, 1965.