The Crystal and Molecular Structure of *retro*-β-Ionylideneacetyl *p*-Bromoanilide

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Summary The configuration of *retro*-β-ionylideneacetic acid is *cis* with respect to the C(8)–C(9) double bond.

IN order to determine the configuration of *retro*-β-ionylideneacetic acid, a structure analysis of *retro*-β-ionylideneacetyl *p*-bromoanilide was carried out. *retro*-β-Ionylideneacetic acid is an intermediate in the vitamin A synthesis of Huisman *et al.*[1] According to these authors the acid is likely to have the all-*trans*-configuration.

We synthesized the *p*-bromoanilide by a method using dicyclohexylcarbodi-imide at room temperature.[2] The monoclinic crystals have cell constants of $a = 9{\cdot}70$, $b = 21{\cdot}56$, $c = 19{\cdot}36$ Å, $\beta = 90{\cdot}0°$. The space group is $P2_1/a$, with $Z = 8$, or two independent molecules in the asymmetric unit. The positions of the 48 non-hydrogen atoms have been found following the heavy-atom technique. The structure has been refined by block-diagonal least-squares methods down to a discrepancy factor $R = 15\%$ for 2300 observed reflections.

A bond lengths and bond angles calculation gives standard deviations of approximately 0·03 Å in the lengths and 2° in the angles. Apart from two deviations as a result of disorder in one of the cyclohexene rings there are no significant differences between the independent molecules.

The most unexpected feature of the structure is that the chain of the β-ionylidene part of the molecule is *cis* with respect to the C(8)–C(9) double bond (see Figure). This explains the failure of the structure determination of the acid itself by conventional Patterson methods.

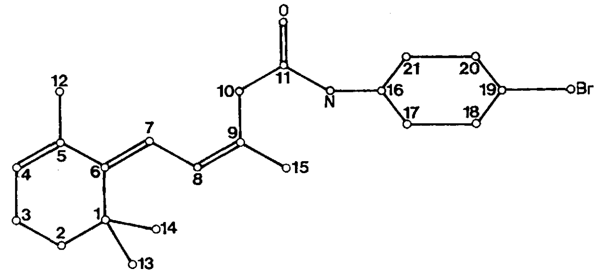

FIGURE. *Conformation of the molecule and numbering of the atoms.*

In most of the carotenoids and vitamin A-related compounds for which the crystal structures have been determined (see ref. 4), the conformation about the C(6)–C(7) single bond is such that the plane of the double bond in the ring is rotated by approximately 140° about the C(6)–C(7) bond from the *trans*-configuration. An exception was found in the structure of β-ionylidenecrotonic acid[5] where the conformation is practically *s-trans* about this bond. In *retro*-β-ionylideneacetic acid the configuration was expected to be either *cis* or *trans* with respect to the C(6)–C(7) double bond. It is found to be *trans*.

The influence of steric hindrance by the methyl groups of the ring becomes evident in the abnormally large chain angle of 130° at C(7), and in the angles at C(5) where the angle C(4)–C(5)–C(12) is smaller than the angle C(12)–C(5)–C(6) (116 and 121°, respectively). Even so, several distances between carbon atoms which are not next-nearest neighbours are still smaller than 3 Å. In *trans*-β-ionylidene crotonic acid, where the conformation is *trans* with respect to the C(6)–C(7) single bond, the chain angle at C(7) is also abnormally large, *i.e.* 129°.[6]

The plane of the carboxyl group makes an angle of 84° with the plane of the conjugated polyene system; with the benzene ring the angle is 30°.

We thank Dr. P. H. van Leeuwen for providing the *retro*-β-ionylideneacetic acid and Mr. A. Kreuger for his help in the experimental stage of the investigation.

(*Received, October* 15*th*, 1969; *Com.* 1566.)

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