The Crystal Structure of 7-Methoxycarbonyl-*anti*-1,6:8,13-bismethano[14]annulene

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Summary Crystal structure determination confirms the polyenic behaviour of 7-methoxycarbonyl-*anti*-1,6:8,13-bismethano[14]annulene, in contrast with the aromaticity of the corresponding *syn*-derivatives.

STRICT correspondence has been found between the chemical properties[1] and molecular geometry[2] of bridged *syn*-[14]-annulene derivatives, which result in an aromatic structure of the annulene ring. However, spectral data and chemical behaviour predicted a non-aromatic structure for *anti*-1,6:8,13-bismethano-[14]annulene.[3] The paucity of n.m.r. lines observed at room temperature suggested the desirability of carrying out a structure determination by *X*-ray analysis. In this communication we report the crystal structure of the 7-methylacetate derivative.†

7-Methoxycarbonyl-*anti*-1,6:8,13-bismethano[14]annulene crystallizes in the monoclinic system (space group $P2_1/c$) with $a = 13{\cdot}889$, $b = 13{\cdot}186$, $c = 7{\cdot}576$ Å, $\beta = 103{\cdot}06°$, $Z = 4$, $D_m = 1{\cdot}302$, $D_c = 1{\cdot}295$ g cm^{-3}. The intensities of all the independent reflexions present in the Cu-K_α sphere have been measured on a Philips PAILRED diffractometer, using Mo-K_α radiation and graphite monochromator. The structure was solved by direct methods; the first *E*-map showed clearly all the carbon and oxygen atoms. Refinement of the parameters is in progress.

The Figure shows the molecular geometry after some least-squares cycles on *ca.* 1200 reflexions. Already at this stage ($R = 0{\cdot}13$) it is clear that in the annulene ring there is a striking alternation of long and short bonds, in contrast with the results obtained for [4*n* + 2] annulenes of the aromatic type.[2,5] In the title compound, the symmetry of the annulene perimeter is nearly *m*; the maximum deviation between absolute values of corresponding torsion angles is about 6°.

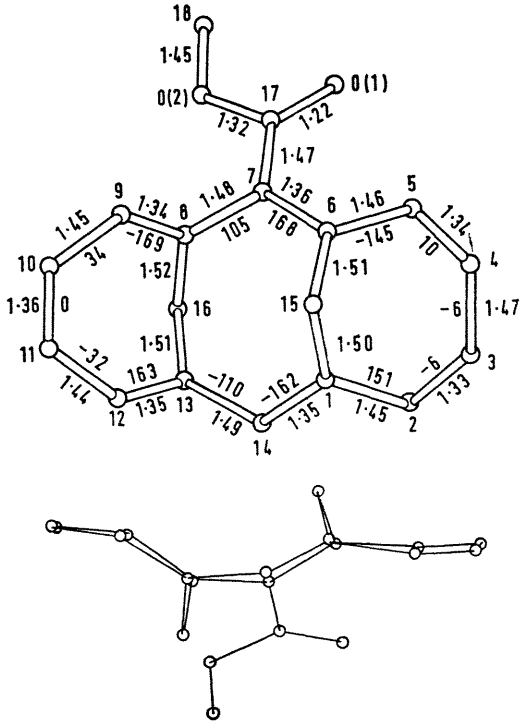

FIGURE. *Two views of the molecule of* 7-*methoxycarbonyl*-anti-1,6:8,13-*bismethano*[14]*annulene. Bond distances* (*in* Å) *and torsion angles* (*in degrees*) *around the annulene ring are indicated.*

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† During the preparation of this manuscript, a communication on the crystal and molecular structure of *anti*-1,6:8,13-bismethano-[14]annulenetricarbonylchromium appeared in *Chem. Comm.*[4] There is substantial agreement between the geometries of the annulene ring in the two compounds. This shows that the polyene structure is not imposed by the presence of the chromium atom but it is an intrinsic property of the annulene ring with two methano-groups in the *anti*-position.

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