The Crystal and Molecular Structure of 1,6:8,13-Butane-diylidene[14]annulene

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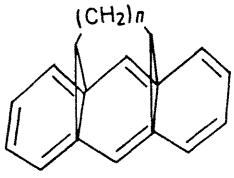
Summary The crystal structure of 1,6:8,13-butanediylidene[14]annulene has been determined; the *mm*2 molecular symmetry predicted by the empirical extended Westheimer method has been verified experimentally in the crystal.

IT has been pointed out[1] that the series of bridged [14]-annulenes opens the possibility of studying the influence of



geometry on the properties of the [14]annulene ring. Two members of the series have recently been synthesized, *i.e.* the compounds with $n=1$ and $n=2$.[1,2] The crystal structure of one of them ($n=1$) has already been determined.[3] We present here the results of an *X*-ray diffraction structure determination of the other ($n=2$), 1,6:8,13-butanediylidene[14]annulene.

The compound crystallizes in the orthorhombic system (space group *Fmm*2) with $a = 18{\cdot}034$, $b = 11{\cdot}399$, $c = 6{\cdot}059$ Å, $Z = 4$, $D_m = 1{\cdot}216$, $D_c = 1{\cdot}239$ g.cm^{-3}. The intensities of all the independent reflexions occurring in the Cu-K_α sphere have been measured by a Pailred Philips diffractometer, using Mo-K_α radiation.

The geometry of an isolated molecule of 1,6:8,13-butanediylidene[14]annulene has been calculated by means of an empirical extended Westheimer method.[4,5] It was assumed that the molecule had point-group symmetry 2 (C_2) and that all bond lengths in the annulene ring were 1·397 Å. The energy was calculated as the sum of π-electron, stretching, bending, torsional, and nonbonded-interaction contribution, and was minimized with respect to the eleven internal degrees of freedom of the carbon-atom skeleton. Standard values were assumed for the C–H bond lengths, whereas the directions of these bonds were determined by orthogonality conditions for the hybrid carbon orbitals.

The minimum-energy geometry was found to correspond to *mm*2 symmetry, leading to an eclipsed conformation for the contiguous CH_2 groups.

In a cell of space group *Fmm*2 and $Z = 4$, the molecules must occupy special positions and conform to point-group symmetry *mm*2. In this case, the two molecular symmetry

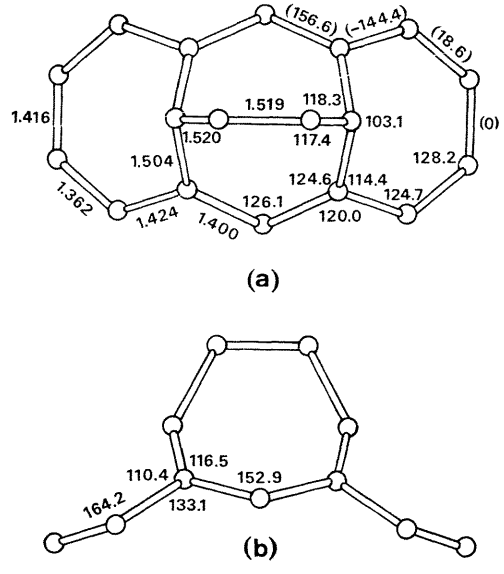


FIGURE. *Experimental geometry of the carbon skeleton of* 1,6:8,13-*butanediylidene*[14]*annulene.* (a) *Bond lengths, angles, and (in parentheses) torsion angles.* (b) *Dihedral angles.*

planes can only be arranged in two possible orientations with reference to the *a* and *b* axes. However, because of the *mmm* symmetry of the weighted reciprocal lattice, the polar axis cannot be distinguished *a priori* from the other crystallographic axes and the possibility of dealing with *Fm*2*m* and *F*2*mm* had to be considered. Therefore, we had to consider *six* possible orientations, and five of these were readily dismissed on the basis of packing considerations and intermolecular energy calculations. Structure-factor calculations for an initial model in the permitted orientation gave $R = 0{\cdot}24$, which was reduced by least-squares refinement to $R = 0{\cdot}049$. The corresponding geometry is summarized in the Figure.

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[1] E. Vogel, W. Sturm, and H. D. Cremer, *Angew. Chem. Internat. Edn.*, 1970, **9**, 516.
[2] E. Vogel, A. Vogel, H. K. Kübbeler, and W. Sturm, *Angew. Chem. Internat. Edn.*, 1970, **9**, 514.
[3] G. Casalone, A. Gavezzotti, A. Mugnoli, and M. Simonetta, *Angew. Chem. Internat. Edn.*, 1970, **9**, 519.
[4] F. H. Westheimer, "Steric Effects in Organic Chemistry," ed. M. S. Newman, Wiley, New York, 1956, ch. 12.
[5] G. Casalone, C. Mariani, A. Mugnoli, and M. Simonetta, *Mol. Phys.*, 1968, **15**, 339.