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TRIAMANTANE: AN X-RAY CRYSTALLOGRAPHIC INVESTIGATION

H. L. Carrell and Jerry Donohue

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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Triamantane (I) is the third member of an adamantalogous series

Ia Ib

the three-dimensional ultimate of which is diamond (1). A hydrocarbon believed to be triamantane on the basis of its synthesis by rearrangement of a hydrocarbon known to have formula $C_{18}H_{24}$, and the mass, infrared, and n m r spectra of the product, has been reported by Williams, Schleyer, Gleicher, and Rodewald (2). Although all of the spectral properties of this substance are in complete agreement with those expected of triamantane, Williams, et al., considered that the information supplied is not really sufficient to establish the structure with absolute certainty. Nevertheless, they regarded the degree of uncertainty low enough to warrant their claim of synthesis of triamantane.

However, the desirability of establishing firmly by X-ray methods the structures of such large hydrocarbon molecules obtained by rearrangement is emphasized by recent results in the $C_{22}H_{28}$ series (3). Isomerization did not produce a tetramantane isomer, as expected, rather a "bastard" structure of only partial diamondoid character was revealed by X-ray analysis.

We report here the preliminary results of an X-ray crystallographic study which confirms that the assigned structure for triamantane is indeed correct.

Crystals of this hydrocarbon are orthorhombic, a = 18.09 Å, b = 22.01 Å, c = 12.87 Å.

Systematic absences observed on Weissenberg photographs lead uniquely to the space group Fddd (D_{2h}^{24}, No. 70). The number of molecules in the unit cell must thus be a multiple of 8: with 16 molecules per cell, the calculated density is 1.24 gm cm^{-3}; other multiples of 8 are highly unreasonable. The minimum molecular symmetry is thus 2-C_2, a result consistent with the expected symmetry mm-C_{2v} of I.

A satisfactory trial structure, assuming structure I, was obtained by packing considerations and other methods. Full matrix least squares refinement has been carried out on 693 $F_{hk\ell}$ observed with an automated Picker four circle diffractometer, allowance being made for anisotropic thermal motion of the 10 independent carbon atoms and isotropic thermal motion of the 12 independent hydrogen atoms. The present value of the discrepancy index, R, is 9.9%. An electron density difference map shows no spurious peaks. Although our refinement is not yet complete, and has been temporarily suspended, there is no doubt that the hydrocarbon reported by Williams, et al., has the triamantane structure.

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