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FROM THE STEREOCHEMISTRY OF A MOLECULE TO THE STEREOCHEMISTRY OF A CRYSTAL: CHIRAL CRYSTALLIZATION OF *ENDO*-ISOMERS COMPARED WITH CENTROSYMMETRIC CRYSTALLIZATION OF *EXO*-ISOMERS OF THIIRANE AND OXIRANE DERIVATIVES OF PHENYL-SUBSTITUTED SEVEN-MEMBERED ACETAL

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The chiral type of crystallization of *endo*-isomers of 4-phenyl-3,5,8-trioxabicyclo[5.1.0]octane and 4-phenyl-3,5-dioxa-8-thiabicyclo[5.1.0]octane and the formation of racemic crystals by molecules corresponding *exo*-isomers are established. The relationship between the structural organization of molecules and the stereochemical type of intermolecular interactions and the formation of different types of crystals is analyzed.

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INTRODUCTION

Some achiral compounds can spontaneously crystallize into chiral crystals (i.e. those having neither center nor plane symmetry elements). Some examples of achiral organic compounds exhibiting chiral crystallization are binaphthyl, hippuric acid, a series of methoxy substituted amides of naphthoic acid, etc. [1]. In solutions of these compounds, the substituent rotates freely with respect to the aromatic fragment, and such compounds crystallize as an asymmetric conformation to form crystals of two mirror enantiomers. Such chiral crystals are used in asymmetric synthesis as a precursor, chiral catalyst, or chiral inductor [2-8]. By comprehensively surveying crystal structures deposited with the Cambridge Crystallographic Data Centre [9], Matsuura revealed in 1998 that the statistical probability for the chiral crystallization of achiral compounds was 8%, showing that chiral crystallization is not an exceptionally rare phenomenon [10].

Benzophenone is one simplest achiral organic compound crystallizing in a chiral form. While freely rotating in solution, benzene rings have a fixed clockwise or counterclockwise torsion angle along the C–C bond between the carbonyl group and the phenyl ring and form enantiomorphic crystals belonging to the orthorhombic space group $P2_12_12_1$ [11]. There are numerous examples of chiral crystals for compounds with the $C2$ axis, similarly to benzophenone. The probability of

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