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THE INVERSION OF CORRELATION BETWEEN γ -EFFECT VALUES AND DIHEDRAL ANGLE: NONTRADITIONAL CHAIR-BOAT CONFORMATIONAL EQUILIBRIUM IN SEVEN- AND EIGHT-MEMBERED DITHIOACETALS

E.N. KLIMOVITSKII, I.A. LITVINOV, O.N. KATAEVA, D.Yu. STREL'NIK and G.N. SERGEEVA

A.M. Butlerov Scientific Research Chemical Institute, V.I. Ul'yanov-Lenin Kazan State University, Kazan 420008 (U.S.S.R.)

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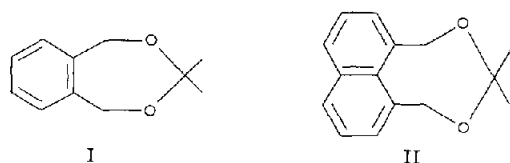
ABSTRACT

^{13}C NMR γ -*anti* effect data versus dihedral angle R-C-X-C (X=O, S; R=Me, Ph, t-Bu) in a series of six eight-membered cyclic acetals and dithioacetals are summarized. The inversion of Lambert's correlation, determined for carbocycles, has been derived. X-Ray data for chair and boat forms of eight-membered cyclic dithioacetals is presented and the equilibrium of these structures is discussed.

INTRODUCTION

Seven- and eight-membered ring systems of series **I** and **II** with partly fixed geometry (planar fragment) are of great conformational interest. In solutions of these systems the chair-like conformation coexists either with the twist-boat form, as in 1,5-dihydro-3H-2,4-benzodioxepin [1-5], or with the boat form, as in 2,4-dioxa-3,5-dihydro-1H-cycloocta [d,e]naphthalenes [6,7]. In order to facilitate further comparison in the series of six eight-membered cycles with acetal or thioacetal structures the positions of heteroatoms will be indicated as 1 and 3 in this work.

The preliminary publications [8, 9] contain the results of the ^1H NMR study of compounds **III** (a-e) and **IV** (a-e),



which are the thioanalogues of series **I** and **II**. Analysis of slow exchange spec-