LETTERS TO THE EDITOR

2,2-DIMETHYL-1,3-DITHIA-5,6-BENZOCYCLOPENTENE: THE FIRST EXAMPLE OF THE COEXISTENCE OF CHAIR, BOAT, AND TWIST FORMS

R. R. Shagidullin, I. Kh. Shakirov, P. N. Sobolev,
D. Yu. Strel'nik, and E. N. Klimovitskii

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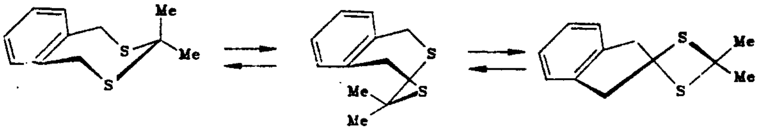
The replacement of two methylene groups in the chair-form benzocycloheptene [1] by oxygen or sulfur has a considerable effect on the conformation state. In 1,3-dioxa-5,6-benzocycloheptene the partner of the chair-form structure is the twist form [2, 3], whereas in the dithia-analog it is the boat form [4]. There have been no reports of the observation in such systems of the joint presence of chair, boat, and twist conformations.

We have found that 2,2-dimethyl-1,3-dithia-5,6-benzocycloheptene is a unique model of these three forms, which are of similar energies. The existence of a three-component mixture (I) has been demonstrated by comparison of the Raman spectra of the liquid, crystal, and solutions in CS$_2$, CCl$_4$, CH$_3$CN, and DMF, and also from a consideration of the extents of depolarization.



The most informative regions were 470-520 (deformational vibrations of the ring) and 750-780 cm^{-1} (asymmetrical stretching vibrations of the heterocyclic moiety). On changing from the crystal to the melt (solutions), the single peaks at 478 and 772 cm^{-1} were converted into triplets 474 (p), 490 (p), 500 (p) and 761 (p), 769 (dp), and 777 cm^{-1} (dp). In solution, the more polar chair form predominated [4], and this persisted in the crystal. As the polarity of the medium was increased, the relative intensities of the "frozen" peaks decreased. The peaks at 769 (chair) and 777 cm^{-1} were depolarized, i.e., the latter corresponded to a conformation with the same symmetry C$_s$ (boat). The third form (twist) is less symmetrical giving rise to a peak at 761 cm^{-1}.

LITERATURE CITED

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A. M. Butlerov Institute of Chemistry, V. I. Ulyanov-Lenin State University, Kazan' 420008. A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR, Kazan' 420083. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, p. 993, July, 1987. Original article submitted July 14, 1986.

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