INVERSION OF THE 1,4,5-BENZOTRIAZOCINE RING

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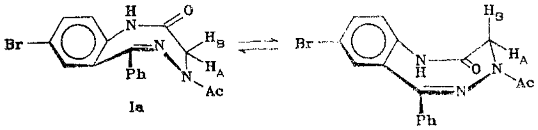
It was established by dynamic PMR spectroscopy that interconversion of the ring between two equivalent conformations with $\Delta G_{298}^{\neq}$ = 85 kJ/mole exists in a solution of 4-acetyl-8-bromo-6-phenyl-1,2,3,4-tetrahydro-1,4,5-benzotriazocin-2-one.

Little study has been devoted to 1,4,5-benzotriazocine derivatives, which have a depressive effect on the central nervous system [1]. In the case of 8-methyl-4-tosyl-6-phenyl-1,2,3,4-tetrahydro-1,4,5-benzotriazocin-2-one we have previously shown [2] that the tetrahydro-1,4,5-benzotriazocine ring has a distorted pseudoboat form. In the present research we have established by dynamic PMR spectroscopy that inversion of the ring between two equivalent conformations (Ia and Ib) occurs in a solution of 4-acetyl-8-bromo-6-phenyl-1,2,3,4-tetrahydro-1,4,5-benzotriazocin-2-one (I):



Ia

Ib

As in the study of the analogous process in the 1,4-benzodiazepine series [3-6], to observe the inversion we used the signals of the diastereotopic protons of the methylene group. In the PMR spectrum of a solution of I in d_6-DMSO at 25°C the methylene group gives an AB quartet. When the temperature is raised, its lines broaden and merge to give a singlet peak at ∿150°C, which constitutes evidence for interconversion of the tetrahydro-1,4,5-benzotriazocine ring.

The kinetic parameters of ring inversion in I were obtained by analysis of the complete form of the lines (ACFL) by means of the Alexander equation [7]. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values and the free energies of activation of the inversion $\Delta G^{\neq}$ were calculated from the rate constants found from the Eyring equation [8]. The rate constant (k_{298}) and the barrier to inversion ($\Delta G_{298}^{\neq}$) of the ring of I are $7.1 \cdot 10^{-3}$ sec^{-1} and 85 kJ/mole. It should be noted that the barrier to inversion of the ring of this compound is somewhat higher than for most of the investigated 1,4-benzodiazepines (40-80 kJ/mole) [5].

EXPERIMENTAL

The PMR spectra were obtained with a Tesla BS 487-C spectrometer (80 MHz) with hexamethyldisiloxane (δ +0.05 ppm) as the internal standard. The temperature of the samples was maintained with an accuracy of ±1°C in conformity with the scale calibrated with respect to methanol and ethylene glycol. The IR spectrum was recorded with a Perkin—Elmer 576 spectrometer.

4-Acetyl-8-bromo-6-phenyl-1,2,3,4-tetrahydro-1,4,5-benzotriazocin-2-one (I). A 2.4-g (30 mmole) sample of acetyl chloride was added to a solution of 5 g (15 mmole) of 8-bromo-6-phenyl-1,2,3,4-tetrahydro-1,4,5-benzotriazocin-2-one in 200 ml of chloroform, and the mixture was refluxed for 3 h. It was then cooled and evaporated *in vacuo*, and the residue was recrystallized from ethanol to give 5 g (89%) of a product with mp 204°C. IR spectrum (in chloroform): 3320 (N—H), 1680 (C=O), and 1620 cm^{-1} (C=N). PMR spectrum (d_6-DMSO, 25°C): 6.7-8.0 (9H, m, aromatic protons and NH); 5.1, 3.9 (2H, two d, CH_AH_B, J = 13.5 Hz); 2.8 ppm (3H, s, CH_3). Found: C 54.8; H 3.7; N 11.2%. $C_{17}H_{14}BrN_3O_2$. Calculated: C 54.8; H 3.7; N 11.2%.

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FLUORESCENCE OF N-TRIAZOLYL DERIVATIVES OF AZOMETHINES

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It was demonstrated by structural modeling that the long-wave band in the UV spectra of azomethine derivatives of o-methoxybenzaldehyde is associated with transfer of electron density in the aldehyde fragment. The development of luminescence in the azomethines is due to the planarity of the molecule, a consequence of which is exclusion of the quenching fluorescence of the n—π interaction and a sufficient magnitude of the energy gap between the n,π* and π,π* states. In the investigated series 4-(2-methoxybenzylideneamino)-1,2,4-triazole molecules have such properties.

The absence of fluorescence of the benzenoid form of N-arylazomethine molecules is due to rapid intercombination conversion (ICC) [1]. It has been previously shown [2] that the following three conditions must be met for the realization of this emissiveless process: 1) localization of the lowest (or closest to it, $\Delta E \sim 3000$ cm^{-1}) electron transition in the amide fragment; 2) the possibility of the realization of bending and rotational deformations in this fragment; 3) the presence in this fragment of specific (for this type of molecule) interaction of the n electrons of nitrogen and the electrons of the aromatic π system (an $n-\pi_{Ar}$ interaction).

A sharp decrease in the rate of ICC and the development of fluorescence are observed when at least one of these necessary conditions is absent. It may be assumed that to obtain luminescing systems it is sufficient to replace the N-aryl group by an N-alkyl group in order to exclude the first and third condition. However, in this case the presence of a close n,π_N^* state [3] is also responsible for rapid emissiveless deactivation and the absence of fluorescence [4]. It should therefore be expected that fluorescing molecules can be obtained by attaching to the nitrogen atom of the C=N group a group (other than an aryl group) that, on the one hand, excludes the third condition and, on the other, creates a more favorable orientation of the n,π_N^* and π,π^* [or intramolecular charge transfer (ICT)] states. It seems to us that this situation can be realized by various methods.

One such method was previously examined in [5] in the case of methylphenyl- and diphenylhydrazone molecules, in which $n-\pi_{Ar}$ interaction is excluded, and the energy gap between the lowest singlet ICT state and the higher n,π_N^* state reaches 6000 cm^{-1}. As a consequence

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