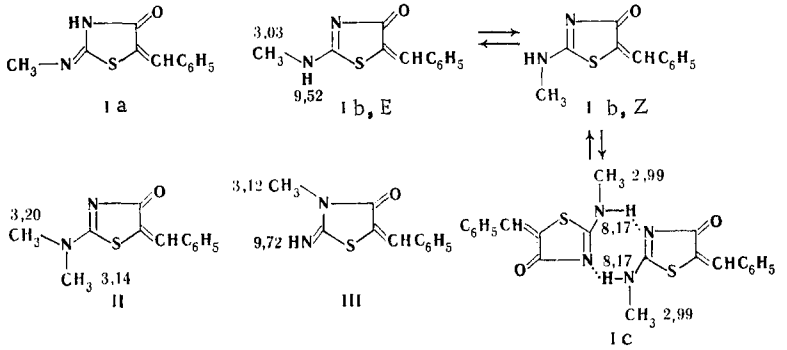
STRUCTURE OF METHYLATED DERIVATIVES OF 2-IMINO-5-BENZYLIDENE-4-THIAZOLIDINONE

S. M. Ramsh, S. Yu. Solov'eva, and A. I. Ginak

UDC 547.789.1.3:541.623:543.422

By means of PMR spectroscopy, on the basis of the multiplet character of the signal of the methyl protons and its change upon deuteration and upon raising the temperature it is shown that 2-methylamino-5-benzylidene-4-thiazolinone in solution in d_6-DMSO exists in the form of the E conformer of the amino form. The degree of self-association, as a result of which dimers of the Z conformer are formed, is insignificant in d_6-DMSO and much greater in $CDCl_3$.

In [1], on the basis of the results of IR and PMR spectroscopy, it was established that 2-methylimino-5-benzylidene-4-thiazolidinone (I) exists in imino form Ia both in the solid state and in solutions. The data that we obtained make it possible to assert that I in deuterodimethyl sulfoxide exists primarily in amino form Ib.



Although a comparison of the IR spectra of crystalline samples of I and the model compounds 2-dimethylamino-5-benzylidene-4-thiazolinone (II) and 2-imino-3-methyl-5-benzylidene-4-thiazolidinone (III) confirms the conclusions in [1] that I has an imino structure in the solid state, the assignment of the frequencies of the stretching vibrations of the C=N bonds, which we base on a calculation of νC=N for similar compounds that are not substituted in the C_5 position [2], differs from that presented in [1]. These frequencies, as we have previously demonstrated [3], are sufficiently characteristic to enable the elucidation of the position of the C=N– bond in or outside of the ring. For I-III they lie, respectively, in complex bands at 1590-1630, 1545-1580, and 1595-1625 cm^{-1}, being "mixed" with the νC=C frequencies of the bezene ring, $\nu C_5{=}C$, and, possibly, δN–H. The frequencies of 1650, 1625, and 1620 cm^{-1} were assigned to the νC=N vibrations of I-III in [1]; we did not observe the first frequency at all in the IR spectrum of I.

No difficulties were encountered in the interpretation of the PMR spectra of model compounds II and III. Two resonances of N-methyl protons at 3.14 and 3.20 ppm with identical intensities are observed in the PMR spectrum of II in d_6-DMSO at room temperature; as in the case of the analogous 2-dimethylamino-4-oxazolines [4, 5] and 2-dimethylamino-4-thiazolinone [2], this is explained by hindered rotation of the dimethylamino group about the partially double $C_2{=}N_{2'}$ bond. The coalescence temperature of the signals, which was determined by dynamic NMR spectroscopy, amounts to 73-74°C. This constitutes evidence that the $C_2{-}N_{2'}$ bond is almost a double bond. The activation parameters for rotation were not determined in view of the small difference in the chemical shifts of the individual signals and the insufficient accuracy in the monitoring of the temperature of the samples. In the PMR spectrum of III the signal of the imino proton at 9.72 ppm is a narrow singlet, which indicates its rapid exchange [6].

Lensovet Leningrad Technological Institute, Leningrad 198013. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 761-763, June, 1983. Original article submitted November 15, 1982.

 0009-3122/83/1906-0608$07.50

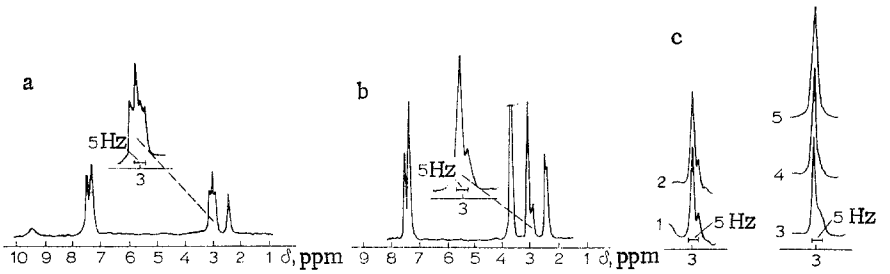


Fig. 1. PMR spectrum of 2-methylamino-5-benzylidene-4-thiazolidinone (I) in d_6-DMSO: a) 80 MHz; b) 80 MHz after isotope exchange with D_2O; c) 60 MHz. Temperature dependence of the signal of the protons of the methyl group: 1) 29°C; 2) 47°C; 3) 56°C; 4) 60°C; 5) 62°C.

The interpretation of the PMR spectrum of I in d_6-DMSO (Fig. 1a) is as follows. The broad signal at 9.52 ppm, the intensity of which is not reproduced from spectrum to spectrum and amounts to 0.3-0.7H, and the very weak signal at 8.17 ppm, which is observed only under great intensification, were assigned as follows: the first to the resonance of the NH proton of amino form Ib, and the second to the resonance of its dimer Ic. Despite prior purification of the solvent, the change in the intensity of the signal at 9.52 ppm has random character and is probably due to exchange processes that arise as a result of impurities present in the solvent. First and foremost, the multiplet character of the signal of the N_2'—CH_3 protons at 2.99-3.07 ppm (Fig. 1a) constitutes evidence in favor of the amino structure rather than the imino structure of I in solution in d_6-DMSO. The signal of methyl protons in the PMR spectrum of 2-methylamino-5-phenyl-4-oxazolinone has the same form [4]. The resolution of the lines in this multiplet is not reproduced from spectrum to spectrum, and after isotope exchange with heavy water, the form of the multiplet changes substantially (Fig. 1b); the two signals at 2.99 and 3.03 ppm, of which the weak-field signal is ∿20 times more intense, remain at the same integral intensity (3H), whereas the components of the multiplet at 3.01 and 3.07 vanish. We assume that these components appear as a result of spin—spin coupling of the methyl and amino protons in the CH_3—N_2'—H fragment; the signal of the CH_3 protons of only that part of the molecules of I the NH protons of which are detected in the spectrum is split, i.e., they do not participate in the solvent-induced (or, more precisely, the effects produced by the impurities present in the solvent) exchange processes. The splitting of the methyl protons by the amino proton even at room temperature constitutes evidence for its slow exchange, which, in turn, indicates the significant positive charge on the nitrogen atom [6].

Just as Rapi and co-workers [5] did for the analogous oxazolinone, we assigned the signals at 3.03 and 9.52 ppm to the monomeric form of Ib, which, because of steric requirements, should have the E conformation (Ib-E), whereas the signals at 2.99 and 8.17 ppm were assigned to the dimer of (Ic) of this compound, which is possible only for the Z conformation of the amino form. Because of the low solubility of I, we were unable to study the concentration dependence of its PMR spectra. The form and position of the signals of the CH_3 protons at 2.99 and 3.03 ppm do not change when the temperature is raised (Fig. 1c), but the intensity of the signal at 2.99 ppm decreases, and the signal vanishes at ∿60-65°C, which is in agreement with the assumption of exothermal dimerization of I in d_6-DMSO. We were unable to estimate the ΔH value for dimerization from the PMR spectral data because of the marked shift of the equilibrium to favor the monomer. Despite its extremely low solubility, we were able to detect in the PMR spectrum of I in deuterochloroform doubled resonance of the methyl protons at 3.02 and 3.13 ppm with a relative intensity of ∿3.5:1; this is in agreement with the greater capacity to form dimeric structures (self-associates) in $CDCl_3$ than in d_6-DMSO.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in d_6-DMSO and $CDCl_3$ were recorded with Tesla BS-467 (60 MHz) and Tesla BS-487C (80 MHz) spectrometers with hexamethyldisiloxane as the internal standard. The IR spectra were recorded with an IKS-20 spectrometer. The UV spectra of solutions in ethanol (10^{-4} mole/liter, l = 1 cm) were recorded with an SF-16 spectrophotometer. The deuterodimethyl sulfoxide was maintained for 1 day over 4A molecular sieves and distilled *in vacuo* (∿2-3 mm) in a stream of dry nitrogen. Thin-layer chro-

matography (TLC) was carried out on Silufol UV-254 plates with acetone–hexane (1:2) as the eluent.

2-Methylamino-5-benzylidene-4-thiazolinone (I). This compound was obtained as described in [7]. The spectral characteristics were refined. IR spectrum (thin layer): 2800 (N–H), 1690 (C=O), 1590-1630 ($C_2=N_2'$, $C_5=C$, aromatic C=C, N–H), and 1490 cm^{-1} (aromatic C=C). PMR spectrum (in d_6-DMSO): 9.52 (0.3-0.7H, s, $N_2'H$), 8.17 (s, $N_2'H$), 7.55 (1H, s, $C_5=CH$), 7.46 (5H, m, C_6H_5), and 2.99-3.07 ppm (3H, m, CH_3). PMR spectrum (in $CDCl_3$): 7.50 (1H, s, C_5-CH), 7.18 (5H, m, C_6H_5); 3.02, 3.13 ppm (3H, CH_3).

2-Imino-3-methyl-5-benzylidene-4-thiazolidinone (III). This compound was obtained as described in [7]. The spectral characteristics were refined. IR spectrum (thin layer): 3275 (N–H), 1695 (C=O), and 1595-1625 cm^{-1} ($C_2=N_2'$, $C_5=C$, aromatic C=C and N–H). PMR spectrum (in d_6-DMSO): 9.72 (1H, s, $N_2'H$), 7.55 (1H, s, C_5-CH), 7.43 (5H, m, C_6H_5), and 3.12 ppm (3H, s, CH_3).

2-Dimethylamino-5-benzylidene-4-thiazolinone (II). A 15-ml sample of a 30% ethanol solution of dimethylamine was added to 3.0 g (0.012 mole) of 2-ethylthio-5-benzylidene-4-thiazolinone, and the reaction mixture was allowed to evaporate freely in air. The solid residue was crystallized from ethanol to give 1.8 g (65%) of a product with mp 178–180°C (183°C [1]). IR spectrum (thin layer): 1680 (C=O), 1615 ($C_5=C$), 1545-1580 (C_2-N_3, aromatic C=C), and 1490 cm^{-1} (aromatic C=C). UV spectrum, λ_{max} (log ε): 239 (3.86) and 330 nm (4.40). PMR spectrum (in d_6-DMSO): 7.28-7.50 (6H, m, $C_5=CHC_6H_5$), 3.14 (3H, s, CH_3), and 3.20 ppm (3H, s, CH_3). Found: N 12.1; S 13.8%. $C_{12}H_{12}N_2OS$. Calculated: N 12.1; S 13.8%.

The purities and individualities of I-III were confirmed by TLC.

LITERATURE CITED

1. S. Kambe, T. Hayashi, H. Yasuda, and A. Sakurai, Nippon Kagaku Zasshi, 92, 867 (1971).
2. Yu. G. Basova, Master's Dissertation, Leningrad (1980).
3. S. M. Ramsh, N. A. Smorygo, A. I. Ginak, and E. G. Cochilin, Zh. Org. Khim., 15, 1506 (1979).
4. C. F. Howell, W. Fulmor, N. Q. Quinones, and R. A. Hardy, J. Org. Chem., 29, 370 (1964).
5. G. Rapi, M. Ginanneschi, E. Belgodere, and M. Chelli, J. Heterocycl. Chem., 9, 285 (1972).
6. R. Silverstein, G. Bassler, and T. Morrill, Spectrophotometric Identification of Organic Compounds, Wiley (1974).
7. S. Yu. Solov'eva-Yavits, S. M. Ramsh, N. A. Smorygo, A. I. Ginak, and E. G. Sochilin, Khim. Geterotsikl. Soedin., No. 7, 929 (1980).