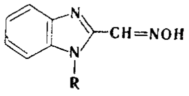
CONFIGURATION OF 1-SUBSTITUTED BENZIMIDAZOLE-2-ALDOXIMES

I. N. Somin and V. A. Gindin

UDC 547.785.5:541.634

The anti configuration was assigned [2,3] to 1-(5'-chloropentyl)benzimidazole-2-aldoxime [I, R = $Cl-(CH_2)_5$] [1-3] on the basis of chemical data. This assignment might have been extended also to other oximes [I, R = CH_3, Hal$(CH_2)_n$, $R_2N(CH_2)_n$] obtained from chloral oxime and o-phenylenediamines [1-5] because of the common source of the oximinomethyl group, the identical conditions of the synthesis, and the proximity of the chemical shifts of the methylidyne proton [2,3]. However, chemical methods for establishing the configuration of oximes are not reliable enough [6], and absolute determination only on the basis of the chemical shifts is possible only when both stereoisomers are present. The recently observed [7, 8] stereospecificity of the geminal spin–spin coupling of $N^{15}=C-H$ in aldoximes eliminates these difficulties. The magnitude of this coupling for cis orientation of the unshared pair of electrons of nitrogen and the methylidyne proton (anti-aldoxime) is 14-16 Hz compared with 2-4 Hz [7, 8] for a trans orientation (syn-aldoxime).



I

We obtained 1-methylbenzimidazole-2-aldoxime-N^{15} (I, R = CH_3, mp 212-213°)* and its methiodide (II, mp 205°)* by the usual method starting from the corresponding aldehyde and N^{15}-hydroxylamine hydrochloride (95% enrichment); they were identical to the oximes obtained by the method mentioned above [4,5]. PMR spectra (δ, ppm) in dimethyl sulfoxide (Varian HA-100D-15 spectrometer); I, R = CH_3; 8.25 (=CH, doublet, 2.2 Hz); 12.00 (OH, doublet, about 0.9 Hz); II, 8.78 (=CH, doublet, 2.1 Hz); 13.45 (OH, broad singlet), and 1-N^{14}, R = $Cl(CH_2)_5$, 8.24 (=CH, singlet); 12.00 (OH, singlet). These values, despite [2,3], constitute evidence for a syn configuration of the examined oximes.

LITERATURE CITED

1. A. S. Petrov, I. N. Somin, and S. G. Kuznetsov, Khim. Geterotsikl. Soedin., No. 1, 152 (1967).
2. R. Garner and H. Suschitzky, Chem. Comm., 129 (1967).
3. R. Garner and H. Suschitzky, J. Chem. Soc. (C), 2536 (1967).
4. I. N. Somin and A. S. Petrov, Zh. Obshch. Khim., 34, 3131 (1964).
5. S. G. Kuznetsov, A. S. Petrov, and I. N. Somin, Khim. Geterotsikl. Soedin., No. 1, 146 (1967).
6. G. Wettermark, Svensk. Kemisk. Tidskrift, 79, 249 (1967).
7. J. P. Kintzinger and J. M. Lehn, Chem. Comm., 660 (1967).
8. D. Crepaux and J. M. Lehn, Mol. Phys., 14, 547 (1968).

---

*The melting points given are for the unrecrystallized samples.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 572-573, April, 1972. Original article submitted September 21, 1971.