PMR SPECTRA OF DIFUROYL PEROXIDES

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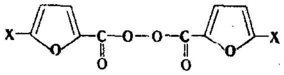
The PMR spectra of difuroyl peroxides were recorded. It is shown that the introduction of a peroxide grouping in place of an anhydride grouping does not lead to changes in the spectrum.

We have previously [1] described the synthesis and some properties of symmetrical furoyl peroxides. The present paper is devoted to a study of their PMR spectra. The spectrum of furoyl peroxide (X = H) is an AMX system with first-order coupling ($\nu_0\delta \gg J$). The ratio (1 : 1 : 1) of the integral intensities of the signals and the chemical shifts (7.49, 6.73, and 7.94 ppm) were determined proceeding from the assumption that the true position of the resonance absorption for each ring coincides with the center of symmetry of the multiplet; the coupling constants were J_{AX} = 1 Hz, J_{MX} = 1.6 Hz, and J_{AM} = 4 Hz. The relative signs of these constants are identical, as follows from experiments with double resonance for a similar system – furan-2-carboxylic acid [2].



The spectrum of 5,5'-dibromofuroyl peroxide (X = Br) contains two doublets; the distances between the components of each doublet are 4 Hz. The chemical shifts are 6.65 and 7.35 ppm. The spectrum of 5,5'-dinitrofuroyl peroxide (X = NO_2) is affiliated with the AB type ($J/\nu_0\delta \approx 1$). The ratio of the intensities of the inner and outer lines calculated on the basis of these values is 0.334, compared with the experimental value 0.360. The chemical shifts are 7.70 and 7.82 ppm.

No effect of the peroxide group on the electronic environment of the protons of the furan ring is observed. The PMR spectrum of the anhydride of furan-2-carboxylic acid, as in the case of furoyl peroxide, is an AMX system with the same chemical shift and spin–spin coupling constants ($\Delta\delta_{3,4}$ 0.76 ppm). Identical character of the PMR spectra is also observed for benzoyl peroxide and benzoic anhydride.

EXPERIMENTAL

The spectra of acetone and dioxane solutions were recorded with a JNM-3H-60 spectrometer with hexamethyldisiloxane (HMDS) as the internal standard. The mean-square error in the measurements was ±0.02 ppm.

LITERATURE CITED

1. V. G. Kul'nevich and N. N. Borisova, Khim. Geterotsikl. Soedin., No. 2, 48 (1970).
2. J. Emsley, J. Finet, and L. Sutcliff, High-Resolution Nuclear Magnetic Resonance Spectroscopy, Vol. 1, Pergamon.

Yaroslav Scientific-Research Institute of Monomers for Synthetic Rubber. Krasnodarsk Polytechnical Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, p. 163, February, 1974. Original article submitted June 5, 1972.

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