INVESTIGATION OF THE ASSOCIATION OF 2,3-DICARBOXYQUINOXALINE AND ITS N,N-DIOXIDE IN DIMETHYLFORMAMIDE AND CARBON TETRACHLORIDE

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The association of 2,3-dicarboxyquinoxaline and its N,N-dioxide in dimethylformamide and carbon tetrachloride was studied. The concentration and temperature dependences of the chemical shifts of the protons of the carboxyl groups in the NMR spectra were measured. Assumptions regarding the state of these compounds in solutions are expressed.

In the present research we have studied the concentration and temperature dependences of the chemical shift of the NMR signals of the protons of the carboxyl groups of 2,3-dicarboxyquinoxaline and its N,N-dioxide in order to ascertain the structures of these compounds in solution. The investigated compounds are practically insoluble in inert solvents, and we therefore used mixtures of dimethylformamide (DMF) with carbon tetrachloride. The measurements were made with a Varian A-60A spectrometer equipped with a thermostatting device. The temperature was controlled with an accuracy of $\pm 1°C$.

The NMR spectrum of 2,3-dicarboxyquinoxaline consists of a multiplet of the AA'BB' type centered at $\tau = 1.83$ ppm, which is due to the α and β protons of the benzene ring, the chemical shifts of which are, respectively, 1.92 and 1.74 ppm, and a singlet from the protons of the carboxyl groups, the position of which depends substantially on the temperature. As seen from Table 1, the signal of the protons of the carboxyl group is shifted to weak field, i.e., in the direction opposite to that which is expected on cleavage of hydrogen bonds [1], when the 2,3-dicarboxyquinoxaline concentration is constant and the fraction of CCl_4 in the solvent composition increases. This fact is probably explained by the change in the type of association as the solvent composition changes. It can be assumed that as the CCl_4 fraction increases, the associates of 2,3-dicarboxyquinoxaline with DMF decompose and yield to acid dimers in which the hydrogen bond is stronger. A similar phenomenon was previously observed when acetic acid was diluted with an inert solvent [1, 2]. The dependence of τ^{COOH} on the solvent composition for a fixed 2,3-dicarboxyquinoxaline concentration is linear. When the concentration of the investigated compound is decreased further, this dependence is described by a family of straight lines, the slope of which decreases correspondingly. Extrapolation of these lines to zero DMF concentration made it possible to establish the dependence of τ^{COOH} on the 2,3-dicarboxyquinoxaline concentration in CCl_4 (Fig. 1). Because of the poor solubility of the investigated compound in inert solvents, the minimum percentage of DMF for the entire studied series of concentrations was 33%. Extrapolation of the lines to zero DMF concentration seems of little reliability for the DMF concentration in the dissolved mixture. However, we supposed that this sort of extrapolation is permissible on the basis that the character of the shift of the band of the carboxyl group is retained for a 2,3-dicarboxyquinoxaline concentration of 0.02 mole/liter, where the DMF content in the mixture could be lowered to 6%. As seen from Fig. 1, the dependence of τ^{COOH} on the concentration is linear for low concentrations of the investigated substance (0.05-0.01 mole/liter); this makes it possible to assume a monomer–dimer equilibrium of 2,3-dicarboxyquinoxaline under these conditions. When the concentration is raised from 0.075 to 0.200 mole/liter, deviation of the dependence from linear character is observed; this is apparently due to the formation of other types of associates.

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TABLE 1. Dependence of τ^{COOH} of 2,3-Dicarboxyquinoxaline on the Concentration and Composition of the Solvent

Solvent composition, DMF: CCl_4 (vol.)	Conc., M						
	0,200	0,150	0,100	0,075	0,040	0,025	0,010
5 : 1	4,43	4,63	5,03	5,32	6,27	6,42	6,50
4 : 2	4,10	4,25	4,68	4,95	5,98	6,25	6,49
3 : 3	3,73	4,05	4,42	4,74	5,87	6,15	6,52
2 : 4	3,41	3,72	3,97	4,28	5,63	5,93	6,50
0 : 6*	2,72	3,07	3,28	3,57	5,10	5,67	6,50

*The data were obtained by extrapolation

TABLE 2. Dependence of τ^{COOH} of 2,3-Dicarboxyquinoxaline on the Temperature and Composition of the Solvent (c 0.200 M)

Solvent composition, DMF: CCl_4 (vol.)	Temperature, °C					
	25	30	38	45	50	60
5 : 1	4,30	4,36	4,43	4,53	4,59	4,68
4 : 2	3,93	3,98	4,08	4,19	4,24	4,35
3 : 3	3,53	3,63	3,73	3,83	3,88	4,00
2 : 4	3,20	3,30	3,40	3,47	3,53	3,68
0 : 6*	2,45	2,58	2,71	2,27	2,82	3,00

*The data were obtained by extrapolation.

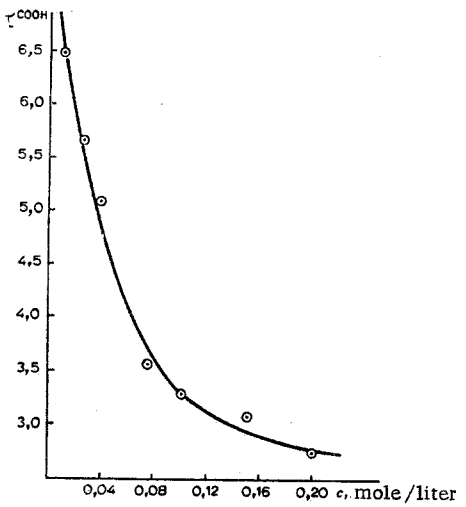

Fig. 1

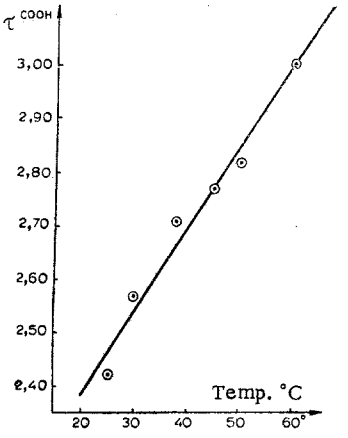

Fig. 2

Fig. 1. Dependence of the chemical shift of the carboxyl groups of 2,3-dicarboxyquinoxaline on the concentration in CCl_4.

Fig. 2. Temperature dependence of the chemical shift of the proton of the carboxyl group of 2,3-dicarboxyquinoxaline in CCl_4.

The results of an investigation of the dependence of τ^{COOH} of 2,3-dicarboxyquinoxaline at a concentration of 0.200 mole/liter on the temperature and composition of the solvent are presented in Table 2. The τ^{COOH} value is shifted to strong field as the temperature rises, and this attests to decomposition of the associates formed due to the hydrogen bonds. At different temperatures, this dependence is described by a series of lines with identical slopes. Extrapolation of the lines to zero DMF content made it possible to establish the dependence of τ^{COOH} on temperature in CCl_4. This dependence is linear (Fig. 2) and is described by the following equation, obtained by the method of least squares: $\tau^{COOH} = 2.10 + 1.52 \cdot 10^{-2} t$, r 0.991.

In an investigation of the effect of substituents and solvents on the structure of the NMR spectra of quinoxaline derivatives [3, 4], it was found that 2,3-dicarboxyquinoxaline behaves in a different manner than the other quinoxaline derivatives with substituents that are not capable of forming hydrogen bonds. Thus, in contrast to the narrowing of the benzene multiplet and shift of it to weak field that are observed for most compounds on passing from solutions in dimethyl sulfoxide (DMSO) or DMF to solutions in trifluoroacetic acid (TFA), the corresponding signal of 2,3-dicarboxyquinoxaline is broadened and is shifted to strong field. This fact should apparently be explained by the change in the state of this compound under the influence of the solvent. It can be assumed that the dissolving of 2,3-dicarboxyquinoxaline in concentrated TFA leads to decomposition of the associates, while the other derivatives, which are incapable of forming hydrogen bonds when they dissolve in TFA, are only protonated.

The oxidation of 2,3-dicarboxyquinoxaline to the corresponding N,N-dioxide leads to a substantial change in the NMR spectrum. At 39°, it consists of two singlets with $\tau = 2.9$ ppm and $\tau = -1.68$ ppm, respectively, for the protons of the benzene ring and the carboxyl groups. The shift to the strong-field region as the temperature rises, which is described by the equation $\tau^{COOH} = 2.09 + 6.61 \cdot 10^{-3} t$, and the absence of a shift in this band as the N,N-dioxide concentration in DMSO changes make it possible to assume the formation of intramolecular hydrogen bonds, i.e., they attest predominantly to the monomeric form of this compound in solution.

On the basis of the above investigation, it can be assumed that 2,3-dicarboxyquinoxaline forms several types of associates in DMF–CCl_4, while its N,N-dioxide exists primarily in the monomeric form under these conditions.

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