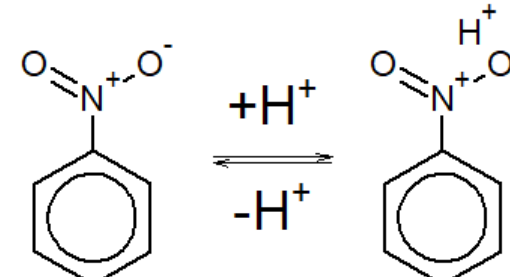


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Acid-catalyzed alkylation reactions are widely used in industrial processes and in laboratory practice. The course of these reactions largely depends on the acidity of the solution used. A practical interest lies in the discovery and improvement of methods for comparing Bronsted acids of various strengths in non-aqueous solutions.



Here we studied nitrobenzene as Hammett's indicator compound for Hammett acidity function determination by ^{13}C NMR in mixtures with different ratios of acetic, phosphoric and sulfuric acids.

UV-Vis spectroscopy was used as a reference method. Electronic absorption spectra were measured at room temperature on a Thermo Scientific Evolution 300 spectrometer (School of Nonferrous Metals and Materials Science SibFU).

The most intense band in the absorption spectra corresponds to an electronic transition with charge transfer from the benzene ring to the nitro group. In pure acetic acid and small amounts of sulfuric acid, the maximum of the spectral line hardly shifts. A bathochromic shift is observed with an increase in the mole fraction of concentrated sulfuric acid.

^{13}C -NMR with proton decoupling were measured at 25°C on a Bruker Avance III 600 MHz spectrometer (Krasnoyarsk center of research equipment of the KSC SB RAS) at an operating frequency of 126 MHz in standard NMR ampoules 5 mm in diameter. A sealed capillary with acetonitrile was used as an external standard to correct for changes in the magnetic susceptibility of the solution with an increase in the molar ratio of mineral acid.

According to the calculations (B3LYP, 6-31G(d;p)), the HOMO and HOMO-1 orbitals are close in energy (almost degenerate) and have the character of a π -bond with a significant contribution from the benzene ring. The *meta*-positions have a higher electron density localization in the HOMO than the *ortho*- and *para*-positions. This confirms the experimental data that the nitro group is a *meta*-orienting agent. The main contribution to the formation of LUMO is made by the π^* orbital of the nitro group.

In the aci form, the removal of degeneracy from the HOMO-1 and HOMO orbitals is noticeable (the energy difference is 0.52 eV). It can be seen that the protonated nitro group contributes more to the formation of HOMO-1 and does not participate in the formation of HOMO. There is also a shift in the electron density of LUMO from *meta*- and *ipso*-carbon atoms towards the protonated nitro group.

Table 1. ^{13}C -NMR chemical shifts of nitrobenzene in AcOH- H_2SO_4 mixtures at 25°C

$\alpha(\text{H}_2\text{SO}_4)$	$\alpha(\text{AcOH})$	$\Delta\delta(^{13}\text{C}), \text{ppm}$	
		<i>ortho</i> -C	<i>meta</i> -C
0	1	5,58	11,62
0,106	0,894	5,45	11,8
0,314	0,686	5,42	11,77
0,365	0,635	5,53	11,55
0,466	0,534	5,64	11,82
0,516	0,484	5,61	11,72
0,566	0,434	5,67	11,64
0,665	0,335	5,76	11,76
0,713	0,287	5,77	11,63
0,906	0,094	5,99	11,8
1,000	0	6,07	11,74

Table 2. ^{13}C -NMR chemical shifts of nitrobenzene in AcOH- H_3PO_4 mixtures

$\alpha(\text{H}_3\text{PO}_4)$	$\alpha(\text{AcOH})$	T = 25°C		T = 60°C	
		$\Delta\delta(^{13}\text{C}), \text{ppm}$		$\Delta\delta(^{13}\text{C}), \text{ppm}$	
		<i>ortho</i> -C	<i>meta</i> -C	<i>ortho</i> -C	<i>meta</i> -C
0	1	5,69	11,74	5,9	11,96
0,108	0,892	5,46	11,75	5,74	11,99
0,319	0,681	5,41	11,73	5,58	11,92
0,522	0,478	5,41	11,70	5,57	11,84
0,718	0,282	5,39	11,720	5,56	11,81
0,907	0,093	5,90	11,76	5,69	11,69
1	0	-	-	5,69	11,58

It can be assumed that in the studied systems of acetic-sulfuric acid mixtures there is a shift in the equilibrium of the nitro and aci-nitro forms of the indicator in solution. In this case, the reason for the change in chemical shifts is the apparent change in electron density on carbon atoms. The increase in the chemical shift of ^{13}C at the *ortho*- and *para*-positions and its decrease for *ipso*-carbon do not contradict general considerations about the mesomeric effect.

In a case of a mixture of phosphoric and acetic acids, NMR measurements were carried out at 60°C due to the fact that nitrobenzene is immiscible with phosphoric acid.

An increase in the temperature of the system does not affect the character of the dependences, but it becomes possible to measure the solution $\alpha(\text{H}_3\text{PO}_4) = 1$ due to the greater homogeneity of the system.

Linear dependences of changes in the chemical shifts of the *para*- and *ipso*-positions allow one to use them to determine the Hammett acidity function.

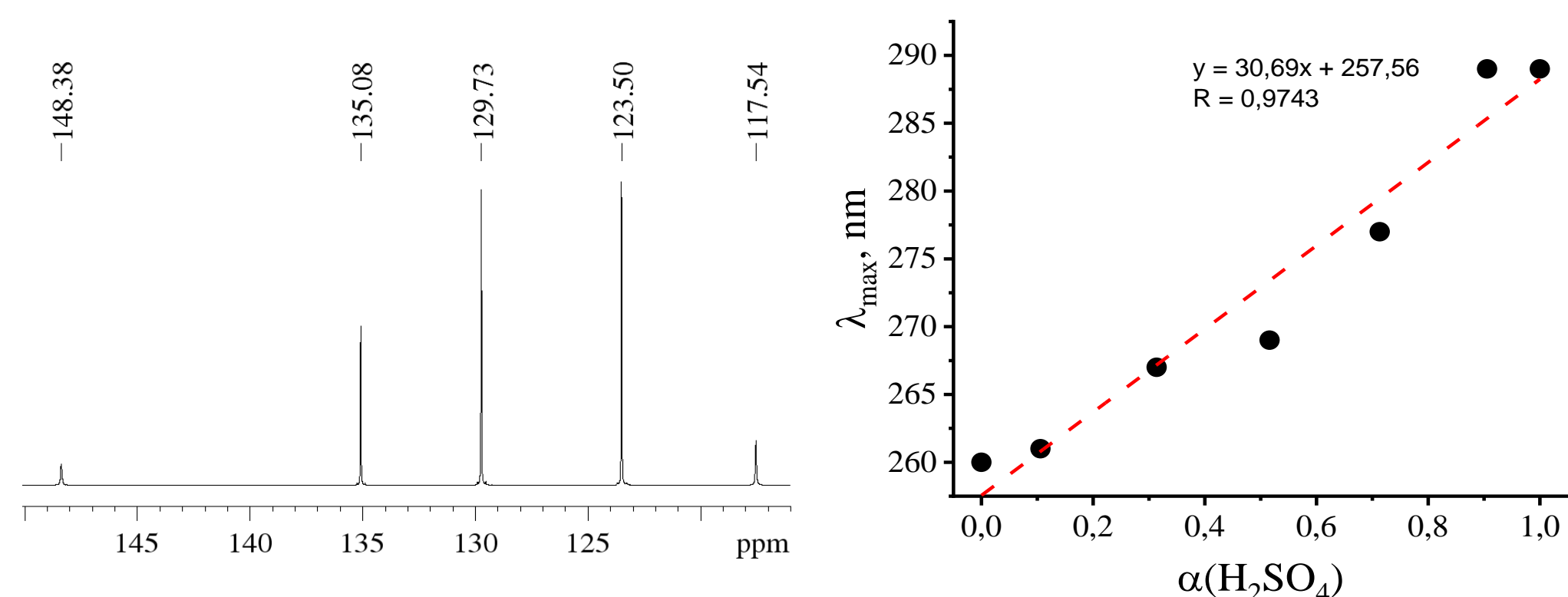


Fig. 2. ^{13}C -NMR spectra of nitrobenzene in acetonitrile

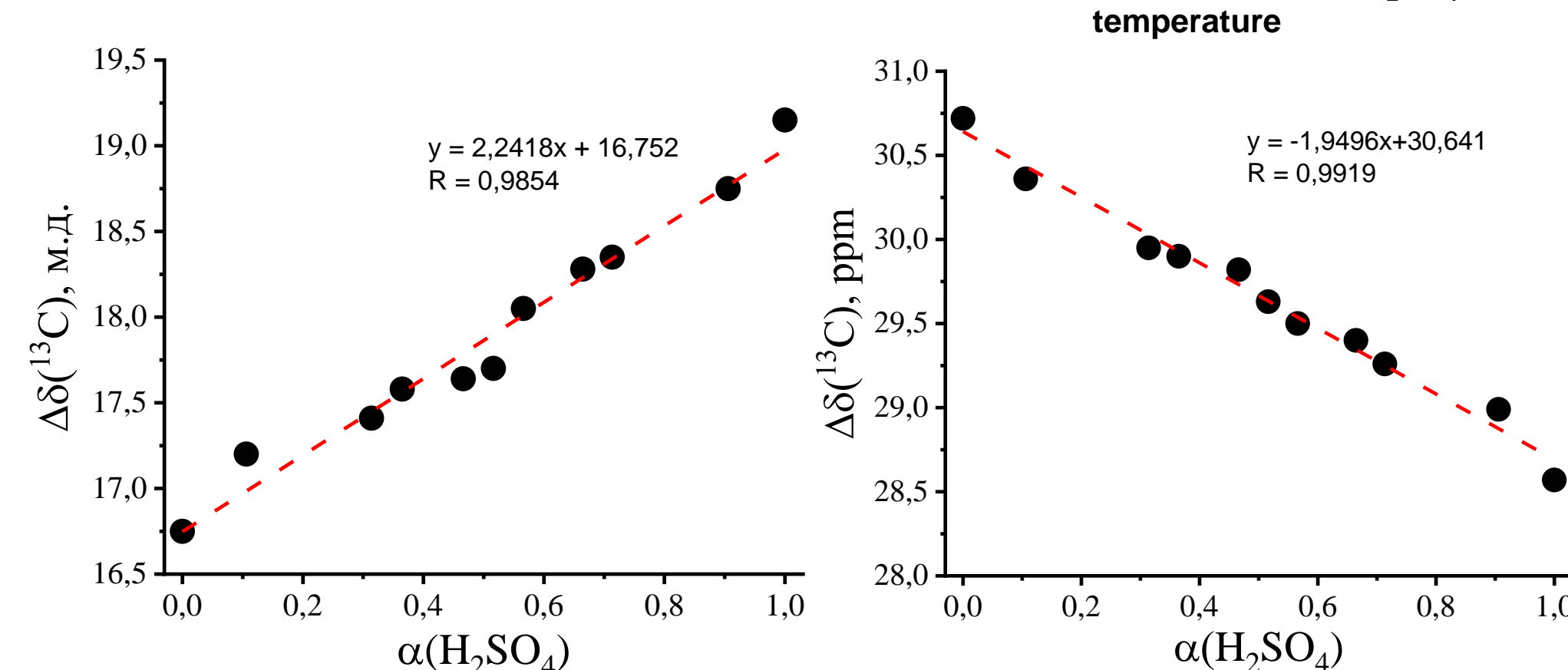


Fig. 3. Dependence of the chemical shift of nitrobenzene relative to acetonitrile on the mole fraction of phosphoric acid at 60°C *ortho*-C (left), *ipso*-C (right)

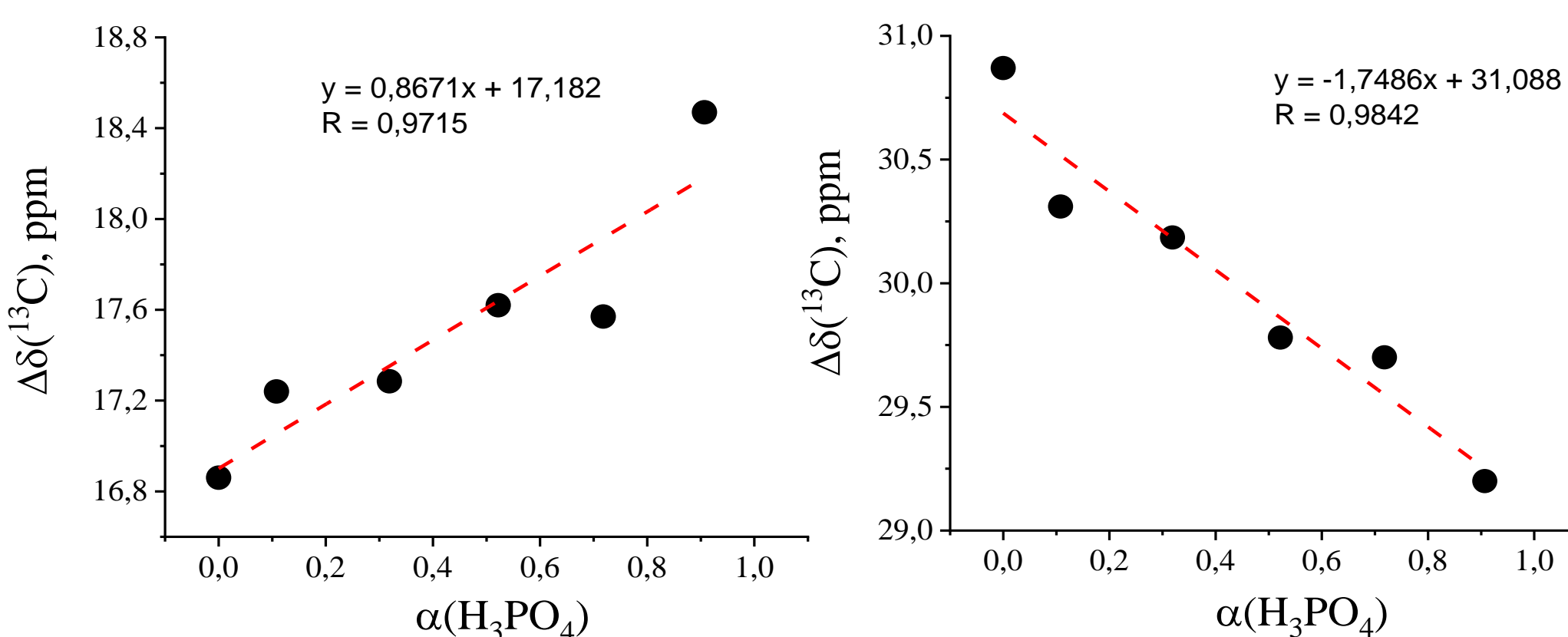


Fig. 4. Dependence of the chemical shift of nitrobenzene relative to acetonitrile on the mole fraction of phosphoric acid at 25°C *ortho*-C (left), *ipso*-C (right)

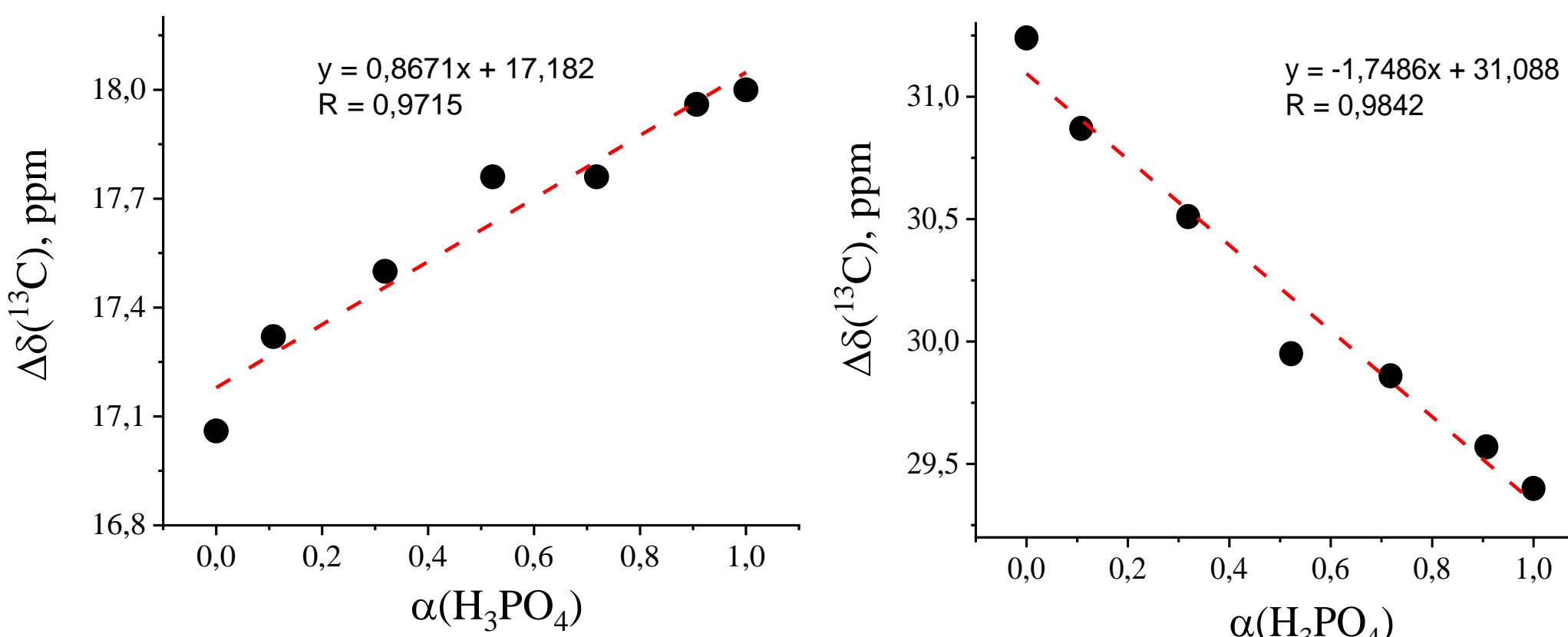


Fig. 5. Dependence of the chemical shift of nitrobenzene relative to acetonitrile on the mole fraction of phosphoric acid at 60°C *ortho*-C (left), *ipso*-C (right)