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# THERMODYNAMIC PARAMETERS OF 5-(NITROPHENYL)-FURAN-2-CARBOXYLIC ACIDS SOLUTIONS IN PROPAN-2-OL

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Based on the temperature dependence of the solubility of 5-(2-nitrophenyl)-furan-2-carboxylic acid, 5-(3-nitrophenyl)-furan-2-carboxylic acid and 5-(4-nitrophenyl)-furan-2-carboxylic acid in propan-2-ol, the enthalpy and entropy of their dissolution were calculated. Taking into account the enthalpy and entropy of melting recalculated to 298 K, the enthalpies and entropies of mixing were calculated. The dependence of the solubility of carboxyl-containing substances at 298 K on their melting point was determined.

Key words: solubility; enthalpy of dissolution; enthalpy of mixing; enthalpy of melting; 5-(2nitrophenyl)-furan-2-carboxylic acid; 5-(3-nitrophenyl)-furan-2-carboxylic acid; 5-(4-nitrophenyl)furan-2-carboxylic acid.

#### Introduction

For a long time, leading laboratories have been synthesizing new compounds containing a fragment of phenylfuran [1-4]. Compounds of this kind are widely used as various catalysts [5, 6] in the processing of cellulose [7], and are used as modifying agents in the synthesis of polymeric materials [8, 9]. In addition, such compounds are components in the synthesis of biologically active compounds [10]. Comparing to the furan fragment, substances containing the phenylfuran fragment are less toxic [11, 12]. The wide range of applications indicates the need to synthesize substances with high purity, which requires a suitable purification method. Usually, the method of recrystallization with organic solvents is used to purify solids, which allows to obtain pure products. Therefore, the study of the thermodynamic parameters of solubility will allow us to determine the energy properties of molecules, which in turn will make it possible to estimate the energy consumption at the stages of synthesis and purification of substances.

The present study is a continuation of a series of works on determining the thermodynamic properties of the solubility of acids with furan and phenylfuran fragments in a number of organic solvents [13–16]. **The purpose of the study** to determine the thermodynamic parameters of the solubility of positional isomers of 5-(nitrophenyl)-furan-2-carboxylic acid in propan-2-ol.

## Materials and research methods

5-(2-nitrophenyl)-furan-2-carboxylic acid (I), 5-(3-nitrophenyl)-furan-2-carboxylic acid (II), and 5-(4-nitrophenyl)-furan-2-carboxylic acid (III) were chosen to study the thermodynamic parameters of solubility in propan-2-ol.

The synthesis of acids was carried out in a reactor equipped with a thermometer, stirrer and reflux condenser according to the scheme shown in Fig. 1.

To a solution of 0.2 mol of furan-2-carboxylic acid and 2 g of CuCl<sub>2</sub>·2H2O in 80 ml of propan-2-ol, stirring, was added a solution of arendiazonium chloride cooled to 273–278 K, obtained by diazotation (HCl, NaNO<sub>2</sub>) of 0.21 mol of the corresponding aromatic amine. The temperature was maintained in the range of 293–303 K so that nitrogen was released at a rate of 2–3 bubbles per second. The reaction was carried out until the nitrogen release stopped, after which 200 mL of water was added. The reaction product was filtered off and recrystallized from an ethanol-dimethylformamide mixture [17].

The structure of the synthesized acids was confirmed by nuclear magnetic resonance spectroscopy (NMR). The <sup>1</sup>H NMR spectra were recorded on a Varian 600 spectrometer (600 MHz).

Deuterated dimethyl sulfoxide (DMSO-d6) was used as a solvent. Chemical shifts ( $\delta$ . ppm) are indicated relative to the DMSO signal (2.50 ppm) Table 1.



Fig. 1. 5-(Nitrophenyl)-furan-2-carboxylic acids scheme synthesis

Table 1

# <sup>1</sup>H NMR values of chemical shifts of the studied compounds protons

Sub.	Chemical shifts, δ, ppm
Ι	<sup>1</sup> H NMR (600 MHz, DMSO) $\delta$ 7.06 (d, $J$ = 3.7 Hz, 1H, fur), 7.35 (d, $J$ = 3.7 Hz, 1H, fur), 7.69 (t, $J$ = 7.8, 1H,
	$C_6H_4$ ), 7.81 (t, $J = 7.8$ Hz, 1H, $C_6H_4$ ), 7.90 (d, $J = 7.8$ , 1H, $C_6H_4$ ), 7.99 (d, $J = 7.8$ Hz, 1H, $C_6H_4$ ), 13.32 (br.s,
	1H, COOH).
Π	<sup>1</sup> H NMR (600 MHz, DMSO) $\delta$ 7.38 (d, $J = 3.7$ Hz, 1H, fur), 7.45 (d, $J = 3.7$ Hz, 1H, fur), 7.79 (t, $J = 8.0$ Hz,
	1H, $C_6H_4$ ), 8.24 (d, $J = 8.3Hz$ , 1H, $C_6H_4$ ), 8.26 (d, $J = 8.4$ Hz, 1H, $C_6H_4$ ), 8.55 (d, $J = 1.8$ Hz, 1H, $C_6H_4$ ), 13.38
	(br.s, 1H, COOH)
III	<sup>1</sup> H NMR (600 MHz, DMSO) $\delta$ 7.40 (d, $J = 3.7$ Hz, 1H, fur), 7.47 (d, $J = 3.7$ Hz, 1H, fur), 8.07 (d, $J = 8.8$ Hz,
	2H, $C_6H_4$ ), 8.34 (d, $J = 8.8$ Hz, 2H, $C_6H_4$ ), 13.43 (br.s, 1H, COOH)

Propan-2-ol manufactured by Merck was used for solubility studies; CAS-Number 67-63-0; EC-Number 200-661-7; mass fraction of the main substance  $\geq$ 99 % by mass. Propan-2-ol is an organic solvent with a wide range of applications, available, non-toxic and with a low boiling point. Before use, propan-2-ol was fractionally distilled and dried with silica gel. The purity of the distilled and dried solvent was checked by the method of gas-liquid chromatography on the LHM-8D device with a thermal conductivity detector. A column with a length of 2 m and a diameter of 0.4 cm was filled with a Chromator N-AW solid phase with a particle size of 0.20-0.25 mm. The carrier gas is helium. The temperature of the heater is 333 K, the evaporator - 363 K. The current of the catharometer bridge is 120 mA. The content of the main component was 99.9 % by mol.

The temperature dependence of the solubility of the studied acids was determined by the gravimetric method [18, 20].

The acids were dissolved in a sealed glass vessel equipped with a teflon stirrer, a thermometer and a sampling hole, which was immersed in a thermostat, the temperature of which was maintained to within  $\pm$  0.1 K. The stirrer speed was 30–40 rpm. The saturation of the solutions was carried out for 48 h

without stirring and 2 h with constant stirring. The experiments were performed in the mode of increasing and decreasing temperature. The absence of a hysteresis loop on the temperature dependence of solubility curve confirms the achievement of a state close to equilibrium.

Samples of the solutions were taken in series of two or three samples and transferred to pre-weighed sealed weighing bottle with subsequent solvent removal at a temperature of 333–343 K. The weighing bottle were weighed at all stages with an accuracy of  $\pm 0.0002$  g.

# **Results and discussion**

The results of the experimental study of acid dissolution are shown in Table 2, namely:  $m_2$  – mass of dissolved substance;  $x_2$  – mole fraction of the dissolved substance; T – temperature at which solubility is determined; linear equations determined as a result of processing the experimental values by the least squares method are given in the form of the Schroeder equation (1):

$$lnX_2 = -\Delta_{sol}H/RT + \Delta_{sol}S/R \tag{1}$$

where  $\Delta_{sol}H$  ra  $\Delta_{sol}S$  – enthalpy and entropy of solubility. Hereinafter, the errors of all values are given for a significance level of 0.95.

Table 2

Т, К	$m_1, g$	$m_2$ , g	$X_2 \cdot 10^3$	Т, К	$m_l$ , g	$m_2$ , g	$X_2 \cdot 10^3$	Т, К	$m_l, g$	$m_2$ , g	$X_2 \cdot 10^3$
5-(2-nitrophenyl)-furan-2-carboxylic acid (I)											
303.7	0.3717	0.0027	1.87	311.4	0.5859	0.0063	2.76	320.9	0.2615	0.0053	5.24
303.7	0.4449	0.0033	1.94	311.4	0.5647	0.0061	2.78	322.9	0.5982	0.0143	6.12
303.7	0.3340	0.0025	1.93	313.9	0.4668	0.0063	3.47	322.9	0.4608	0.0110	6.14
305.5	0.5107	0.0048	2.44	313.9	0.5699	0.0078	3.51	322.9	0.3811	0.0091	6.12
305.5	0.4463	0.0038	2.22	313.9	0.6003	0.0083	3.55	323.4	0.7519	0.0144	4.93
305.5	0.4955	0.0042	2.18	316.0	0.4950	0.0078	4.04	323.4	0.5969	0.0111	4.79
306.9	0.3961	0.0041	2.69	316.0	0.9208	0.0147	4.10	323.4	0.5460	0.0102	4.81
306.9	0.3772	0.0039	2.66	316.0	0.5109	0.0082	4.12	327.9	0.7824	0.0194	6.35
306.9	0.4611	0.0048	2.68	318.0	0.5245	0.0106	5.18	327.9	0.5706	0.0142	6.37
309.3	0.4368	0.0055	3.26	318.0	0.5385	0.0106	5.05	327.9	0.5056	0.0125	6.36
309.3	0.4968	0.0064	3.31	318.0	0.5256	0.0102	5.00	330.0	0.5033	0.0168	8.53
309.3	0.4720	0.0061	3.35	318.5	0.5743	0.0095	4.24	330.0	0.3761	0.0126	8.56
309.6	0.6145	0.0067	2.82	318.5	0.6209	0.0102	4.24	330.0	0.3908	0.0129	8.44
309.6	0.6622	0.0069	2.68	318.5	0.5670	0.0091	4.14	334.6	0.5307	0.0216	10.4
309.6	0.5037	0.0052	2.68	320.9	0.4503	0.0090	5.12	334.6	0.4892	0.0198	10.4
311.4	0.5106	0.0055	2.77	320.9	0.4352	0.0087	5.13	334.6	0.3609	0.0148	10.5
$\ln X_2 = (10.7 \pm 1.1) - (5129 \pm 346) \cdot 1/T$											
5-(3-nitrophenyl)-furan-2-carboxylic acid (II)											
292.4	0.6648	0.0009	0.37	301.6	0.5619	0.0012	0.59	316.6	0.6486	0.0033	1.33
292.4	0.8067	0.0011	0.38	303.5	0.8692	0.0021	0.67	322.1	0.5807	0.0043	1.90
292.4	0.4364	0.0006	0.38	303.5	0.8639	0.0022	0.70	322.1	0.6683	0.0041	1.60
293.2	0.5823	0.0008	0.38	303.5	0.6140	0.0015	0.68	324.5	0.7294	0.0061	2.17
293.2	0.5589	0.0008	0.40	308.0	0.6166	0.0021	0.88	324.5	0.6362	0.0054	2.18
294.0	0.8093	0.0012	0.41	308.0	0.6956	0.0026	0.96	324.5	0.6819	0.0058	2.19
294.0	0.6937	0.0009	0.36	313.0	0.3850	0.0017	1.17	326.8	0.4901	0.0038	1.99
294.0	0.8852	0.0012	0.37	313.0	0.8144	0.0038	1.20	326.8	0.7412	0.0061	2.13
298.5	0.5863	0.0010	0.47	315.5	0.5863	0.0030	1.32	326.9	0.5691	0.0054	2.46
298.5	0.7206	0.0012	0.46	315.5	0.6086	0.0029	1.23	326.9	0.7605	0.0071	2.42
298.5	1.0743	0.0018	0.46	315.5	0.6116	0.0032	1.35	326.9	0.6941	0.0065	2.41
301.6	0.6997	0.0016	0.63	316.6	0.5852	0.0032	1.43	330.4	0.6175	0.0068	2.83
301.6	0.6183	0.0013	0.58	316.6	0.6995	0.0034	1.25	330.4	0.4969	0.0054	2.82
	•	•		$\ln X_2 = (9$	$,86 \pm 0,50)$	) – (5208 ±	= 152)·1/T				
			5-(	4-nitrophe	enyl)-furan	-2-carbox	ylic acid (I	II)			
318.2	0.4842	0.0025	1.33	328.5	0.7986	0.0063	2.05	333.4	0.5463	0.0067	3.17
318.2	0.4970	0.0025	1.29	328.5	0.6513	0.0053	2.09	335.1	0.5791	0.0083	3.70
318.2	0.4759	0.0025	1.35	331.6	0.4512	0.0042	2.39	335.1	0.4886	0.0070	3.68
322.5	0.6562	0.0041	1.61	331.6	0.5093	0.0048	2.42	335.1	0.4417	0.0062	3.63
322.5	0.4347	0.0027	1.63	331.6	0.6344	0.0059	2.41	337.0	0.3587	0.0058	4.15
322.5	0.5529	0.0034	1.61	332.2	0.3651	0.0036	2.53	337.0	0.5723	0.0092	4.13
322.6	0.4914	0.0033	1.73	332.2	0.3302	0.0030	2.34	339.1	0.4610	0.0077	4.29
322.6	0.4251	0.0027	1.66	332.2	0.5830	0.0054	2.40	339.1	0.4593	0.0077	4.33
322.6	0.7458	0.0048	1.67	333.4	0.4088	0.0050	3.17	339.1	0.5062	0.0085	4.30
328.5	0.8195	0.0066	2.07	333.4	0.3740	0.0045	3.12				
$\ln X_2 = (13,6 \pm 1,5) - (6478 \pm 509) \cdot 1/T$											

Temperature dependence of the solubility of the studied acids in propan-2-ol

The thermodynamic solubility parameters  $\Delta_{sol}H$  i  $\Delta_{sol}S$  given in Table 3 characterize, in addition to the process of solution formation, the phase transition of solid 5-(nitrophenol)-furan-2-carboxylic acids into the liquid phase of the solution. Therefore, to calculate the change in enthalpy ( $\Delta_{mix}H$ ) and entropy ( $\Delta_{mix}S$ ) of mixing (solvation), which characterize the interaction of components in solution, it is necessary to take into account the value of enthalpy ( $\Delta_{fus}H$ ) and entropy ( $\Delta_{fus}S$ ) of melting of the studied substances at their average dissolution temperature, equations (2–3).

$$\Delta_{sol}H = \Delta_{fus}H + \Delta_{mix}H \tag{2}$$

$$\Delta_{sol}S = \Delta_{fus}S + \Delta_{mix}S \tag{3}$$

The value of  $\Delta_{fus}$ H of 5-(2-nitrophenyl)-furan-2carboxylic acid was determined in [21] based on the results of the differential thermal method of analysis and is  $33.59 \pm 0.22$  kJ/mol at a melting point (T<sub>fus</sub>) of 491.6  $\pm$  1.0 K. The value of  $\Delta_{fus}$ H of substances (II) and (III) could not be determined experimentally, since according to the data of differential thermal and thermogravimetric methods of analysis, the process of melting acids is accompanied by thermooxidative destruction. In such cases, approximate calculation methods are used to estimate  $\Delta_{fus}H$ , in particular, in [16], the value of  $\Delta_{fus}$ H of 2-methyl-5-(2,5-dichlorophenyl)-furan-3-carboxylic and 2-methyl-5-(2-chloro-5-trifluoro methylphenyl)-furan-3-carboxylic acids were calculated from the specific value of  $\Delta_{fus}S$ , which for phenylfurans is  $0.319 \pm 0.027$  (J/g·K), and in [21] this value was refined and is 0.323  $\pm$  $\pm$  0.026 (J/g·K). Taking into account the above value and the known equation  $\Delta_{fus}S = \Delta_{fus}H/T_{fus}$ , the expression for calculating  $\Delta_{fus}$ H of the studied acids will take the form:

$$\Delta_{fus} H = 0.323 \pm 0.026 \cdot 233.18 \cdot T_{fus} \tag{4}$$

where 233.18 - molar mass of acids, g/mol.

 $T_{fus}$  of the acids were determined by the capillary method, the values of which are 526.8 and

521.5 K, respectively. The values of  $\Delta_{fus}H$  of compound (**II**) calculated by equation (4) are 39.7 ± ± 3.7 kJ/mol, and (**III**) 39.3 ± 3.7 kJ/mol.  $\Delta_{fus}S$  will be the same as the acids are positional isomers (75.3 ± 7.0 J/mol·K).

Since the values of  $\Delta_{fus}H$  and  $\Delta fusS$  were calculated at  $T_{fus}$ , and the values of  $\Delta_{sol}H$  and  $\Delta_{sol}S$  were calculated in temperature intervals (Table 2), the average values of which are close to 298 K, in order to generalize the results obtained, it was decided to recalculate  $\Delta_{fus}H^{\circ}$  and  $\Delta_{fus}S^{\circ}$  to the generally accepted temperature of 298 K using equations 5 and 6 given in [16].

$$\Delta_{fus} H_{298} = \Delta_{fus} H_{T_{fus}} \quad 1 + \frac{298 - T_{fus}}{1.35 \cdot T_{fus}} \tag{5}$$

$$\Delta_{fus} S_{298} = \Delta_{fus} S_{T_{fus}} \quad 1 + 0.74 \cdot \ln \frac{298}{T_{fus}} \quad (6)$$

The listed values of  $\Delta_{fus}H$  and  $\Delta_{fus}S$  up to 298 K are given in Table 3; the same table also presents the differential values of  $\Delta_{mix}H$  and  $\Delta_{mix}S$  calculated according to equations 2 and 3, which characterize the interaction of components in solution.

The positive values of  $\Delta_{mix}H$  of the studied acids in propan-2-ol in the studied range of concentrations and temperatures indicate that the destruction of intermolecular bonds in individual substances, in particular in acids, requires more energy than is released as a result of the formation of new intermolecular bonds with propan-2-ol. As for the assessment of the effect of isomerization on the value of the mixing enthalpy, it increases in the order meta- (II) < ortho-(I) < para- (III) due to specific intra- and intermolecular interactions. Thus, when dissolving (III), a weaker dipole-dipole interaction with solvent molecules is observed due to a more linear form compared to (I) and (II), which leads to a more endothermic solvation. Since the ortho- and metaisomers are characterized by a more compact structure with stronger interactions, as a result, a lower value of the mixing enthalpy is observed.

Table 3

Solubility thermodynamic functions of the studied acids in propan-2-ol at 298 K

Sub.	$\Delta_{fus}H$ kJ/mol	$\Delta_{fus}S$ J/mol·K	$\Delta_{sol}H$ , kJ/mol	$\Delta_{sol}S,$ J/mol·K	$\Delta_{mix}H$ , kJ/mol	Δ <sub>mix</sub> S, J/mol·K
Ι	23.9±1.1	67.4±2.2	42.6±2.9	89.0±9.1	18.7±3.1	45.7±9.3
II	26.9±4.0	69.9±7.5	43.3±1.3	82.0±4.2	16.4±4.2	38.4±8.6
III	26.8±4.0	70.4±7.5	53.9±4.2	113±12	27.1±5.8	69±15

Table 4

No.	Substance	$X_2 \cdot 10^3$	T <sub>fus</sub> , K	Lit.	№	Substance	$X_2 \cdot 10^3$	T <sub>fus</sub> , K	Lit.
1	4-nitro-1,2- phenylenediamine	1.11	489.1	[22]	7	furan-2-acrylic acid	67.7±1.0	413.2	[14]
2	2-methyl-3- nitrobenzoic acid	24.3	456.6	[23]	8	3-methyl-4-nitrobenzoic acid	2.11	489.1	[24]
3	furan-2-carboxylic acid	215.2±1.0	402.4	[14]	9	2-methyl-5-phenylfuran-3- carboxylic acid	16.34±1.0	458.1	[15]
4	5-(2-nitrophenyl)- furan-2-carboxylic acid	1.49±0.97	491.6	_	10	2-methyl-5-(4- methylphenyl)-furan-3- carboxylic acid	1.85±0.99	507.2	[15]
5	5-(3-nitrophenyl)- furan-2-carboxylic acid	0.49±0.98	526.8	-	11	2-methyl-5-(2-chloro-5- trifluoro-methylphenyl)- furan-3-carboxylic acid	1.56±0.98	517.6	[16]
6	5-(4-nitrophenyl)- furan-2-carboxylic acid	0.29±0.98	521.5	_	12	2-methyl-5-(2,5- dichlorophenyl)-furan-3- carboxylic acid	0.26±0.99	556.1	[16]

Solubility at 298 K and melting point of substances containing nitro and/or carboxyl groups

Judging by the experimentally determined solubility values (Table 2), the solutions of the studied acids in propan-2-ol can be considered extremely dilute, since the value of  $X_2$  does not exceed 0.01. In this case, it is worth checking the statement "a solid with a high melting point is less soluble than a solid with a low melting point". Since the solubility of only three acids was studied in this work, in order to conduct a more thorough analysis, a number of publications were selected from the literature that investigated the solubility of substances with nitro or carboxyl groups in propan-2-ol, Table 4.

Judging from the values of solubility in propan-2-ol at 298 K (Table 4), their values decrease with increasing  $T_{fus}$ . Plotting these values in the coordinates  $\ln(X_2) = f(1/T_{fus})$ , we obtained a linear dependence in Fig. 2.

After processing the dependence by the method of least squares, we obtained equation (7) with a correlation coefficient of  $\rho = 0.934$ :

$$\ln X_2 = -26.6 + 10069 * 1/T_{fus} \tag{7}$$

This similarity of the dependence indicates the same type of interaction between propan-2-ol and dissolved substances, regardless of their structure. The determined equation (7) makes it possible to estimate the approximate solubility of carboxyl-containing compounds in propan-2-ol by their  $T_{fus}$ .



Fig. 2. Dependence of the logarithm of the mole fraction of dissolved substances in propan-2-ol on the inverse of the melting point:  $\circ$  – values are shown in Table 4

### Conclusion

In this work the temperature dependences of the solubility of positional isomers of 5-(nitrophenyl)-furan-2-carboxylic acids in propan-2-ol were determined at 303.7–334.6 K (isomer I), 292.4– 330.4 K (isomer II) and 318.2–339.1 K (isomer III) temperature ranges. The thermodynamic parameters such as their solubility (I:  $\Delta_{sol}H = 42.6 \pm 2.9$  kJ/mol,  $\Delta_{sol}S = 89.0 \pm 9.1$  J/mol·K; II:  $\Delta_{sol}H = 43.3 \pm 1.3$  kJ/mol,  $\Delta_{sol}S = 82.0 \pm 4.2$  J/mol·K; III:  $\Delta_{sol}H = 53.9$   $\pm$  4.2 kJ/mol,  $\Delta_{sol}S = 113 \pm 12$  J/mol·K) and mixing, i.e. solvation, (I:  $\Delta_{mix}H = 18.7 \pm 3.1$  kJ/mol,  $\Delta_{mix}S = 45.7 \pm 9.3$  J/mol·K; II:  $\Delta_{mix}H = 16.4 \pm 4.2$  kJ/mol;  $\Delta_{mix}S = 38.4 \pm 8.6$  J/mol·K; III:  $\Delta_{mix}H = 27.1 \pm 5.8$  kJ/mol,  $\Delta_{mix}S = 69 \pm 15$  J/mol·K) were calculated at 298 K and could be used as a thermodynamic reference data for further energy consumption estimation at the synthesis and purification stages of these substances.

The dependence of the solubility of carboxylcontaining substances at 298 K in propan-2-ol on  $T_{fus}$ was established, which makes it possible to estimate the approximate solubility of substances in solvent by  $T_{fus}$ .

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# ТЕРМОДИНАМІЧНІ ПАРАМЕТРИ РОЗЧИНІВ 5-(НІТРОФЕНІЛ)-ФУРАН-2-КАРБОНОВИХ КИСЛОТ У ПРОПАН-2-ОЛІ

На основі температурної залежності розчинності 5-(2-нітрофеніл)-фуран-2-карбонової кислоти, 5-(3-нітрофеніл)-фуран-2-карбонової кислоти та 5-(4-нітрофеніл)-фуран-2-карбонової кислоти в пропан-2-олі розраховано ентальпію та ентропію їх розчинення. З урахуванням ентальпії та ентропії плавлення, перерахованих до 298 К, розраховано ентальпії та ентропії змішування. Визначено залежність розчинності карбоксилвмісних речовин при 298 К від їхньої температури плавлення.

Ключові слова: розчинність; ентальпія розчинення; ентальпія змішування; ентальпія плавлення; 5-(2-нітрофеніл)-фуран-2-карбонова кислота; 5-(3-нітрофеніл)-фуран-2-карбонова кислота; 5-(4-нітрофеніл)-фуран-2-карбонова кислота.