

# Furan Derivatives. XXIX.

## Polymorphism of 3-(5-Nitro-2-furyl)acrylic Acid

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Received July 22, 1970

By using X-ray diffraction methods and infrared spectroscopy, it has been found that 3-(5-nitro-2-furyl)acrylic acid crystallizes according to the character of solvent in the form of polymorphic modifications.

As stated in the preceding paper [1], 3-(5-nitro-2-furyl)acrylic acid (*I*) prepared by nitration of 3-(2-furyl)acrylic acid is accompanied with considerable amounts of impurities. The search for the criteria of purity of the substance *I* revealed some anomalies concerning the melting point. The melting points of *I* quoted in literature are in the range from 231°C to 238°C [2–8]. On recrystallization from ethanol, the substance *I* prepared by Perkin reaction from 5-nitro-2-furfurylidene diacetate has the melting point of 241–242°C [1]. The attempt to obtain a preparation corresponding to the synthesized standard (m.p. 241–242°C) also from the substance *I* prepared by nitration of 3-(2-furyl)acrylic acid was successful after repeated recrystallization from ethanol. The recrystallization of the prepared substance from acetone caused the melting point to decrease to 238°C. The melting point of the substance *I* was 237°C if tetrahydrofuran was used as solvent. The addition of other substances to *I* brought down the melting point of the system only slightly (235–238°C).

The causes of the melting point depression following recrystallization may be different. Provided the contamination in the course of recrystallization is excluded, some changes either in molecular or crystal structure must have taken place. To find out the cause of melting point depression unambiguously, the substance *I* was prepared in a pure state and afterwards crystallized from different solvents. The crystals thus formed were analyzed and investigated by physicochemical methods.

### Experimental

All melting points are corrected.

3-(5-Nitro-2-furyl)acrylic acid prepared according to [6] was extracted with ethyl ether and washed on a filter with hot ethanol till the filtrate flowing off was bright yellow. The remaining solid substance was several times recrystallized from water and ethanol. After repeated recrystallizations from ethanol, the compound *I* with melting point of 243°C was obtained.

The chromatographic investigation on a thin layer of silica gel cemented with 10% of plaster with solvent system tetrahydrofuran–benzene (1 : 2) showed that the substance gave only one spot with  $R_F = 0.32$  [9].

The portions of the substance *I* thus prepared were recrystallized from water, acetone, tetrahydrofuran and dioxane, respectively. To obtain some better developed and

larger crystals, a portion crystallized from more dilute solutions which had been inoculated with the crystal obtained in the first crystallization. Such crystals suitable for the investigation by single crystal methods were successfully prepared by the crystallization of *I* from water as well as from ethanol and dioxane. All crystals were dried *in vacuo* at room temperature.

The habit of crystals was dependent on the character of solvent used. The crystallization from alcohol yielded bright yellow needles while from dioxane deep yellow scales, from water red-brown needles, and from acetone and tetrahydrofuran yellow scales decomposing by the effect of daily light were obtained.

The crystals prepared from different solvents were analyzed and the temperatures of starting sublimation as well as melting points and infrared absorption spectra were measured. It were the powder diffraction patterns as well as rotation and Weissenberg patterns which were taken from the above crystals. The results of chemical analyses, melting point and sublimation measurements are presented in Table 1.

The infrared absorption spectra were measured with an UR-10 double-beam spectrophotometer (Zeiss, Jena) in the region from 3600 to 700  $\text{cm}^{-1}$  in KBr cell of 0.427 mm width in *nujol* within an accuracy of  $\pm 1 \text{ cm}^{-1}$ . The calibration of instrument was made by means of a polystyrene foil.

The substances were investigated by the X-ray powder method. The pictures were made with a powder diffractograph GON II (Chirana, Prague) under following conditions:  $\text{CuK}\alpha$  radiaton, nickel filter, voltage 36 KV, sensitivity 500, time constant 8, paper drive  $1^\circ \text{ min}^{-1}$ , rotation of sample  $1^\circ \text{ min}^{-1}$ , intensity 3–8 mA according to the height of diffraction maxima. The measured diffraction patterns are in Fig. 1.

The rotation patterns were taken from crystals formed by the crystallization from water, ethanol, and dioxane. Since the crystals prepared by crystallization from water decomposed during photographing, it was possible to use them only for rotation patterns. On the other hand, the crystals prepared by crystallization from ethanol and dioxane were more stable and it was possible to use them for both rotation and Weissenberg patterns. With last samples, only the layers 0, I, and II were photographed. Since these results enabled us to take up unambiguously an attitude towards the question of polymorphism, the photographing of crystals round further crystallographic axis was not more carried out.

Table 1

Characteristics of 3-(5-nitro-2-furyl)acrylic acid crystallized from different solvents

Sample	Solvent	Analysis (found)*			M.p. [°C]	Beginning of sub- limation [°C]	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{O})$	$\gamma(\text{C}-\text{H})^{**}$
		% C	% H	% N					
1	ethanol	45.92	2.70	7.61	243	210	1632	1682	978
2	acetone	45.94	2.69	7.69	241	227	1632	1683	978
3	tetrahydrofuran	45.89	2.75	7.64	241	217	1632	1682	978
4	water	45.92	2.77	7.63	241	—	1632	1682	978
5	dioxane	45.95	2.74	7.64	242	201	1632	1683	978

\* Calculated 45.90% C, 2.73% H, 7.65% N.

\*\* Deformation non-planar vibrations of C—H bonds in CH=CH groups (*trans*).

### Results and Discussion

The results of organic analysis (Table 1) of the crystals prepared from different solvents are equal within the accuracy of analysis. In all cases the chemical composition of the substance is equal. This conclusion is confirmed by the identity of absorption infrared spectra which show equal absorption bands.

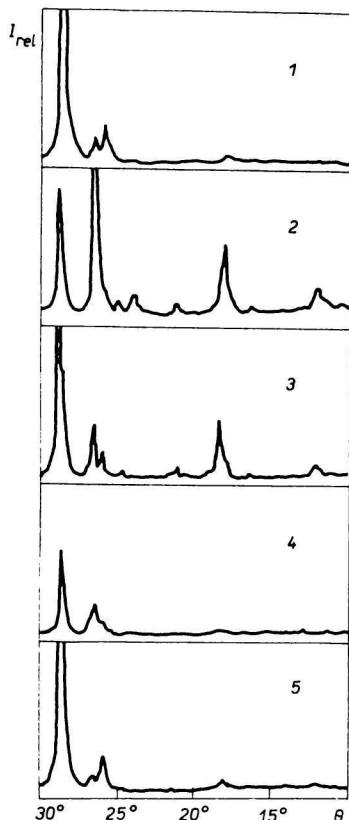


Fig. 1. Powder diffraction patterns of 3-(5-nitro-2-furyl)acrylic acid crystals.

1. ethanol; 2. acetone; 3. tetrahydrofuran; 4. water; 5. dioxane.

From the changes in the molecular structure of *I* which could be able to bring about the melting point depression in the course of recrystallization, it is the change in geometrical isomerism and in molecular conformation which come into consideration. The rearrangements of individual geometrical isomers of *I* have not been investigated yet. It is, however, known that such changes were observed, *e.g.* in the course of the nitration of 3-(2-furyl)acrylic acid [1, 8]. It was necessary to investigate this possibility because in the case of substance *I* prepared in usual way the sublimation was observed already at about 170°C (melting point of the *cis*-isomer *I* is 176°C [8]). The results of the measured infrared spectra enabled us to solve this problem. The *cis*-isomer of *I* has a characteristic absorption band of non-planar deformation vibration  $\gamma(\text{C}-\text{H})$  at 821  $\text{cm}^{-1}$  while the *trans*-isomer has  $\gamma(\text{C}-\text{H})$  at 978  $\text{cm}^{-1}$ . The absorption band of 821  $\text{cm}^{-1}$  did not appear any more and was not found even with the substances obtained by evaporating mother liquors to dryness. Since the

band of  $978\text{ cm}^{-1}$  was present in all spectra measured, all samples may be considered to be *trans*-isomers.

The problem of conformation of the substances investigated is more important. There are four configurations which can theoretically arise: *s-trans s-trans*, *s-trans s-cis*, *s-cis s-trans*, and *s-cis s-cis*. The conformation relations in furan series have hitherto been studied with 2-furaldehyde [10], some ketones, and the derivatives of furancarboxylic acid [11]. It ensues from the paper [10] and from the study of the conformation of benzylidene-acetones [12] that the *s-cis* and *s-trans* conformation isomers show in infrared spectrum two bands differing by  $20\text{ cm}^{-1}$  approximately. There is a single band  $\nu(\text{C}=\text{O})$  at  $1683\text{ cm}^{-1}$  in the infrared spectrum of *I* corresponding to the dimer form of *I* [13], the free rotation of which is hindered to a great extent. The broad complex band  $\nu(\text{C}=\text{O})$  at  $1682\text{ cm}^{-1}$  which is equal in all cases enables us to deduce that the conformation of *I* did not change during crystallization. Equally,  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}-\text{H})$ , and the furan ring vibration are unchanged.

Since the changes in molecular structure of *I* have been excluded, it may be stated with certainty that some changes in crystal structure occurred. Elemental analysis of the crystals as well as the infrared absorption spectra exclude the possibility of building in the solvent into crystal so that the changes observed may be attributed to the polymorphism of *I*. In this respect, the measurement of powder diffraction patterns completed with rotation and Weissenberg patterns provided the preparation of larger crystals was possible, was successful.

The crystals prepared from dioxane and ethanol possess equal structure and monoclinic symmetry (see graphs *I* and *5* in Fig. 1), while the crystals prepared from water have different structure as evident from powder and rotation diffraction patterns. According to X-ray diffraction patterns (Fig. 1), the crystals from acetone and tetrahydrofuran are other polymorphic modifications of 3-(5-nitro-2-furyl)acrylic acid. Since these polymorphic modifications differ in their melting points only slightly it may be concluded that the melting-point measurement refers not only to the crystals obtained from water but also to the sublimated compound. We have not succeeded in determining the crystal structure of the sublimated substance *I* because a partial decomposition takes place and the crystals thus formed are contaminated and not suited for X-ray analysis.

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Translated by R. Domanský