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Reaction of *N*-Methylpyrrolidone with 3-Chlorophenyl Isocyanate

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Abstract—3-Chlorophenyl isocyanate forms molecular complex with *N*-methylpyrrolidone.

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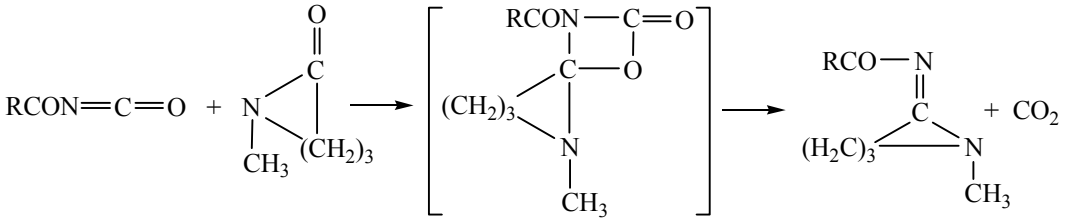
N-Methylpyrrolidone is a simplest and the most widespread representative of the N-substituted lactams. It often is used as a solvent [1], a clarifier for lubricating oils, resins, kerosene, vaseline, and paraffin; as a precipitating agent at producing polyvinyl chloride fiber, as dispersing means for mineral and organic pigments in the manufacture of lacquers and in the process of dyeing [2].

The behavior of the *N*-methylpyrrolidone as a reactive compound in the reactions with benzoyl, trichloroacetyl, triftoracetyl isocyanates has been investigated [3]. Its reactions were found to proceed with the formation of amidines through a stage of oxazetidinone:



R = C_6H_5, CCl_3, CF_3.

Reaction of *N*-methylpyrrolidone with other isocyanates, in particular, with aryl isocyanates, has not been studied. The aim of this work was to study the reaction of *N*-methylpyrrolidone with 3-chlorophenyl isocyanate.

Initially, we investigated the chemical transformations of *N*-methylpyrrolidone and 3-chlorophenyl isocyanate separately. We found that *N*-methylpyrrolidone did not undergo any changes when heated for 70 h at 70°C in the presence of catalytic amounts of triethylamine in toluene. 3-Chlorophenyl isocyanate under these conditions forms a white crystalline powder.

It is known that isocyanates under basic catalysis are capable to form dimers and trimers [4]. In the presence of tertiary amines and catalytic systems "tertiary amine–co-catalyst" trimerization occurs involving NCO groups [5]. Actually, analysis of IR and ^{1}H NMR spectra of the substance obtained by us showed that the 3-chlorophenyl isocyanate under the above conditions formed isocyanurate.

In the IR spectrum of the product of 3-chlorophenyl isocyanate transformation with a catalytic amount of triethylamine a triplet at 1610–1500 cm^{-1} indicates the presence of a benzene ring. The absorption bands at 1654 and 1224 cm^{-1} indicate the presence of O=C–N group. The absorption bands at 1720 and 1420 cm^{-1} correspond to the stretching vibrations of C=O groups at the isocyanurate ring. It should be noted that the spectrum contains an absorption band at 1780 cm^{-1} indicating the presence in the product of traces of dimeric structure.

The results of elemental analysis of the obtained substance confirm the formation of isocyanurate type structure.

Studying the noncatalyzed reaction of *N*-methylpyrrolidone with 3-chlorophenyl isocyanate and transformation of monomers catalyzed by triethylamine we found that in the course of the reaction also a formation of a solid phase occurred. After purification of the solid phase by reprecipitation from acetone solution to hexane were obtained white powder product soluble in acetone, toluene, chloroform, dimethylsulfoxide, acetonitrile, and hot carbon tetrachloride. Yield of the compounds obtained was about 60%.

Study of structure and properties of the synthesized compounds by IR, ^1H NMR spectroscopy, and differential scanning calorimetry (DSC) showed that the presence of triethylamine in the reaction mixture does not affect the chemical structure of substances. The IR spectra of all products obtained are identical. They contain an absorption band at 1720 cm^{-1} corresponding to the stretching vibrations of C=O; at 1420 cm^{-1} vibrations of isocyanurate ring appear. There is an absorption band at 1650 cm^{-1} characteristic of O=C–N group. The presence in the structures of the obtained compounds of benzene ring is indicated by a triplet in the region of 1610–1500 cm^{-1}. However, unlike the infrared spectrum of the isocyanurate from 3-chlorophenyl isocyanate, in the IR spectra of the reaction products of methylpyrrolidone with 3-chlorophenyl isocyanate, we detected absorption bands at 2850–3000 cm^{-1}, which corresponded to the stretching vibrations of CH_2. In addition, the IR spectra of the product contain absorption bands at 1780 and 1680 cm^{-1}, which correspond to the C=O group in N-substituted lactams.

Analysis of DSC curves showed that in all cases the reaction products of *N*-methylpyrrolidone with 3-chlorophenyl isocyanate give identical curves, with

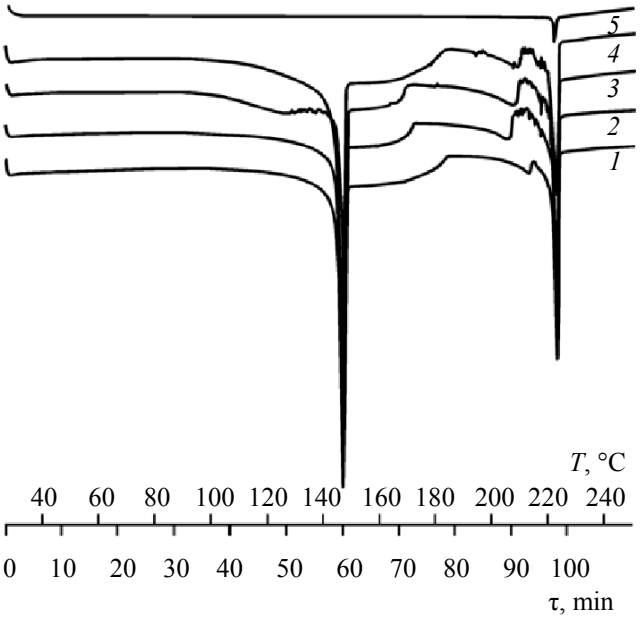


Fig. 1. Differential scanning calorimetry curves of the products of interaction of *N*-methylpyrrolidone with 3-chlorophenyl isocyanate at a concentration of triethylamine (*1*) 0, (*2*) 1.59×10^{-3}, (*3*) 3.18×10^{-3}, and (*4*) 1.59×10^{-2} mol l^{-1}, and (*5*) of isocyanurate from 3-chlorophenyl isocyanate.

endo-peaks at the temperatures 148 and 223ºC (curves *1–4*, Fig. 1). The nature of the curves is consistent with the fact that upon increase in temperature melting initially occurs of the molecular complex of the isocyanurate formed from 3-chlorophenyl isocyanate with *N*-methylpyrrolidone. Then at evaporation of *N*-methylpyrrolidone crystallization occurs of the isocyanurate formed from 3-chlorophenyl isocyanate alone. This leads to appearance on the DSC curves of an *exo*-effect. At further increase in temperature melting of the isocyanurate occurs.

Thus, the data of IR, ^1H NMR spectroscopy and DSC indicate that the molecular structure of the synthesized compounds corresponds to the complex of *N*-methylpyrrolidone with the isocyanurate formed from 3-chlorophenyl isocyanate.

In order to confirm the formation of molecular complex of isocyanurate and *N*-methylpyrrolidone, we have grown single crystals of the product of reaction of *N*-methylpyrrolidone with 3-chlorophenyl isocyanate in the presence of triethylamine with the concentration 1.59×10^{-3} mol l^{-1}, and analyzed it by X-ray diffraction. The performed study of the crystal showed that it contains two molecules of *N*-methylpyrrolidone per a molecule of isocyanurate from 3-chlorophenyl

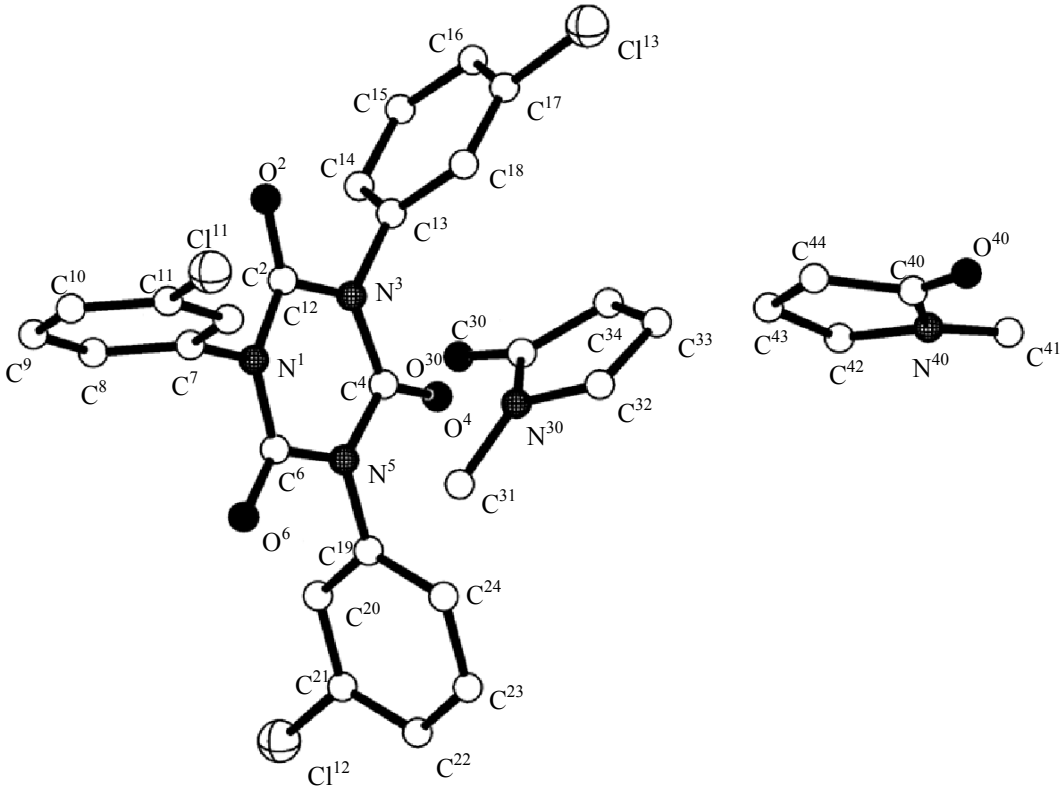


Fig. 2. The geometry of the molecular complex of 1,3,5-(3-chlorophenyl)isocyanurate with *N*-methylpyrrolidone in the crystal and the scheme of numbering of atoms. Hydrogen atoms are not shown.

isocyanate. The geometry of the molecules is shown in Fig. 2.

In the molecule of 1,3,5-(3-chlorophenyl)isocyanurate the chlorophenyl substituents are almost perpendicular to the isocyanurate ring: the dihedral angles between the plane of the isocyanurate ring and the planes of chlorophenyl substituents C^7–C^{12}, C^{13}–C^{18} and C^{19}–C^{24} are 80.9°, 80.6°, and about 89.1°, respectively.

In the crystal of the compound the intermolecular interactions are registered of C–H···O, CH···π, and C–O···π types. Due to the C–H···O interactions the molecules of isocyanurate from 3-chlorophenyl isocyanate in the crystals are connected into infinite chains along the 0*a* axis. The parameters of interaction C^4–O^4···$H^{10'}$ (symmetry operation –1 + *x*, *y*, *z*) between the oxygen of the carbonyl group in the isocyanurate ring and a hydrogen atom of the chlorophenyl ring are the following: O^4···$H^{10'}$ 2.61 Å, O^4···$C^{10'}$ 3.29(1) Å, angle O^4···$H^{10'}$–$C^{10'}$ 131°. The distances between the oxygen atoms O^6, O^2 of two other carbonyl groups in the isocyanurate ring and the corresponding hydrogen atoms H^{16}, H^{22}, respectively, in the neighboring molecules are somewhat larger than the sum of their van der Waals radii and are equal to 2.80 and 2.76 Å, respectively. However, these chains are linked together by C–H···π type contacts between the electron systems of chlorophenyl substituents and hydrogen atoms of the same substituents in the neighboring molecules, that leads to the formation of layers of isocyanurate molecules parallel to the 0*ab* plane (Fig. 3).

Thus, in these layers three neighboring molecules of isocyanurate interconnected in the crystal by a second order helical axis, participate in the formation of cyclic C–H···π contacts. The parameters of these contacts are close enough: the distance from the hydro-gen atom to the center of the ring are in the range of 2.72–2.80 Å, the C–H···π contact angle within 140°–144°.

It is interesting to note that each isocyanurate ring of such a layer is involved at both sides in the π-electron interactions with the oxygen atoms of the carbonyl groups of molecules of *N*-methylpyrrolidone (the contacts of C=O···π type) (Fig. 4). The distances from the oxygen atoms to the center of the ring are 2.77Å and 2.83Å, the angles of C–H···π contact are 174° and 167°.

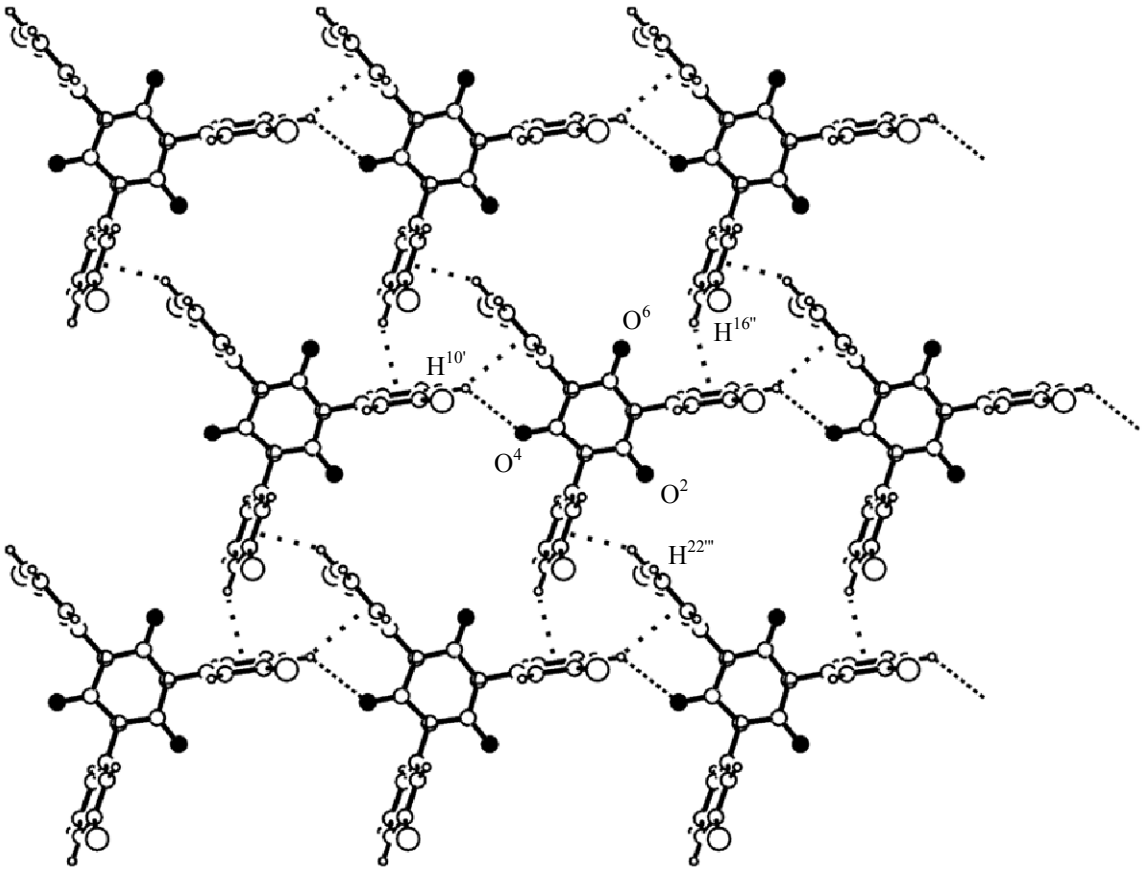


Fig. 3. Formation of a layer of H-bonded molecules of the isocyanurate from 3-chlorophenyl isocyanate in the crystal of the molecular complex. View along the 0*c* axis, the hydrogen bonds C–H···O are shown by the small dotted line, CH···π contacts by large dotted line.

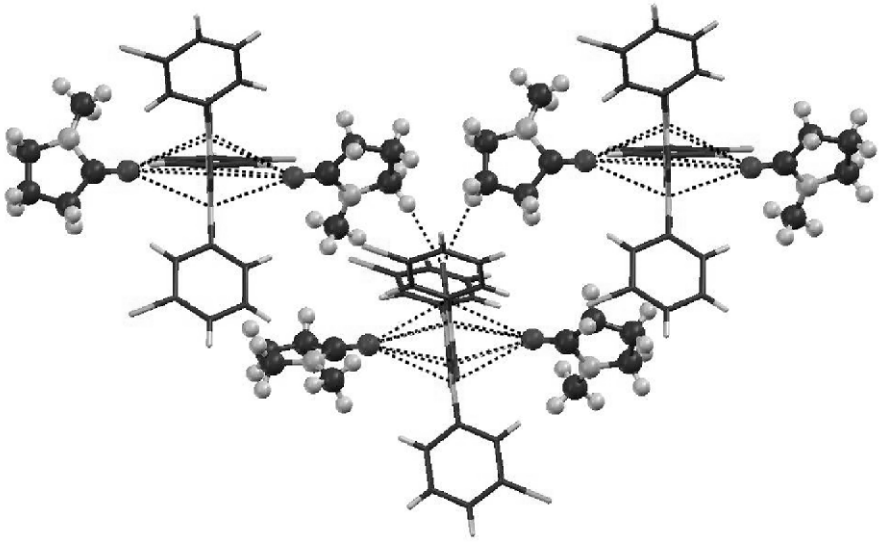


Fig. 4. C–O···π and C–H···O interactions in the crystal of the molecular complex (shown by the dotted line). View along the crystallographic 0*b* axis. Molecules of *N*-methylpyrrolidone are shown in the boll–rod model.

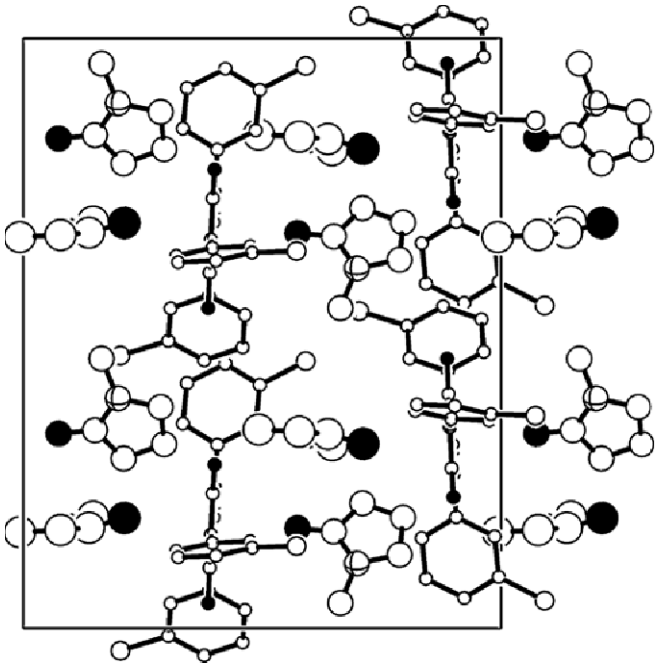


Fig. 5. Packing of molecules in the crystal of the molecular complex. Atoms in the molecules of *N*-methylpyrrolidone are shown as larger spheres. View along the 0*a* axis.

The participation of the methylene hydrogens of two *N*-methylpyrrolidone molecules in a bifurcate hydrogen bond with the oxygen atom O^2 of the carbonyl group binds these layers in three-dimensional molecular lattice (Fig. 5). *N*-Methylpyrrolidone molecules are arranged between the layers of the isocyanurate molecules from 3-chlorophenyl isocyanate. Although at this packing of the molecules the crystal contains almost no cavities potentially available for solvent molecules, the calculated packing coefficient of molecules 64.5% is at the bottom limit of the range (0.65–0.75) typical for the crystals of organic compounds.

Based on these data (atomic coordinates and cell parameters of the crystal of molecular complex) we calculated theoretical diffraction pattern for the molecular complex of isocyanurate from 3-chlorophenyl isocyanate with *N*-methylpyrrolidone, which was compared with the experimental diffraction patterns, in particular, the diffractogram obtained for the product synthesized at concentration of triethylamine 1.59×10^{-3} mol l^{-1} (Fig. 6). It is seen from the figure that the calculated diffraction pattern coincides with the experimental (Fig. 6, curves *1* and *2*, respectively).

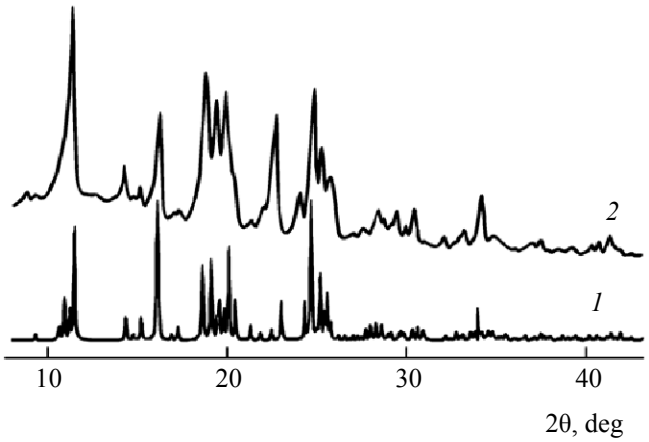


Fig. 6. Diffractograms: (*1*) theoretical, the molecular complex of isocyanurate from 3-chlorophenyl isocyanate and *N*-methylpyrrolidone; (*2*) reaction products of *N*-methylpyrrolidone with 3-chlorophenyl isocyanate in the presence of 1.59×10^{-3} mol l^{-1} of triethylamine.

Thus, at the interaction of *N*-methylpyrrolidone with 3-chlorophenyl isocyanate in the presence of triethylamine, as well as in its absence, a molecular complex is formed between the isocyanurate originating from 3-chlorophenyl isocyanate and *N*-methylpyrrolidone. Interaction of 3-chlorophenyl isocyanate with *N*-methylpyrrolidone differs significantly from the reactions of acyl isocyanates with *N*-methylpyrrolidone. As noted above, acyl isocyanates in these transformations form amidines.

In our view, the fact that at the transformations of isocyanates in the presence of *N*-methylpyrrolidone can be obtained molecular complexes is interesting for syntheses. We suggest that at the polymerization with lactam rings opening in the obtained complexes it is principally possible to obtain polyamides nanostructured with isocyanurates.

EXPERIMENTAL

We used *N*-methylpyrrolidone and 3-chlorophenyl isocyanate from Sigma Aldrich with the content of the main substance 99%. In the synthesis of samples were used freshly distilled 3-chlorophenyl isocyanate, triethylamine, and solvents.

The reaction between 3-methylpyrrolidone and chlorophenyl isocyanate was carried out in argon atmosphere, in sealed ampules. In an ampule was placed 5.77 ml (0.0543 mol) of toluene and 5.70 ml (0.0594 mol) of *N*-methylpyrrolidone. Then to the resulting solution was added catalytic amount of

triethylamine (concentration of the catalyst varied from 0 to 1.59×10^{-2} mol l^{-1}). To the mixture was injected equimolar with *N*-methylpyrrolidone amount of 3-chlorophenyl isocyanate, 7.18 ml (0.0594 mol). Synthesis was carried out at 70ºC for 70 hours. In the course of the reaction of *N*-methylpyrrolidone with 3-chlorophenyl isocyanate a formation in the reaction medium of a solid phase was observed. The precipitate was filtered off. To remove other reagents, it was dissolved in acetone and the reaction product was reprecipitated to hexane. The resulting product was dried in a vacuum at a temperature of 30ºC to a constant weight.

The structure of the products formed was establishes by elemental analysis, IR, ^{1}H NMR spectroscopy, DSC, X-ray analysis and X-ray diffraction.

^{1}H NMR spectra were obtained on a Bruker AVANCE spectrometer with operating frequency 400 MHz, 90º pulse, duration 0.5 μs, delay between pulses 10 s, the number of FID scans 16 or 32, solvent acetone-d_6. In the study of the reaction products by ^{1}H NMR the following compounds were identified:

Isocyanurate from 3-chlorophenyl isocyanate, δ, ppm: 7.41–7.55 (12H, arom. protons);

Molecular complex of the isocyanurate from 3-chlorophenyl isocyanate with *N*-methylpyrrolidone, δ, ppm: 1.96 m (2H, CH_2), 2.18 m (2H, CH_2), 2.74 s (3H, CH_3), 3.34 m (2H, CH_2), 7.41–7.56 m (12H, arom. protons).

The IR spectra were obtained on a FT-IR spectrometer Spectrum BX II of Perkin Elmer, Inc. at application of samples on the KBr plates.

Elemental analysis of samples was performed on a CHN-3 analyzer. Found, %: C 56.06, 56.33; H 2.57, 2.73; N 9.30, 9.43; Cl 21.97, 22.19. Calculated, %: C 55.59; H 2.56; N 8.95; Cl 22.68.

DSC curves were obtained on an instrument using a DSC 1 METTLER TOLEDO module, which is a component of the thermal analysis device STAR^e. Temperature of tests was from 25°C to 250°C, sample heating rate 2°C min^{-1}, the crucible of Al.

Single crystals of the product of reaction of 3-methylpyrrolidone with chlorophenyl isocyanate at the concentration of triethylamine 1.59×10^{-3} mol l^{-1} were obtained from the acetone solution of the compound by slow evaporation of the solvent. X-ray analysis of single crystals was carried out on an automatic four-circle diffractometer CAD-4 NONIUS BV at 23ºC. Preliminary treatment of the data was performed using the program MOLEN [6] on a computer AlphaStation 200. Crystals of $C_{21}H_{12}C_{13}N_3O_3\cdot2(C_5H_9NO)$ are monoclinic. At 23°C a = 11.013 (3), b = 19.080 (5), c = 15.464 (2) Å, β = 93.988(5)°, V = 3241.6(13) Å^3, M = 658.95, d_{calc} = 1.35 g cm^{-3}, Z = 4, space group *Cc*. Cell parameters and intensities of 3842 reflections, of which 1954 were independent and 686 with $I \geq 2\sigma$, were measured at 23°C (graphite monochromator, λCuK_α radiation, ω-scanning, $\theta \leq 57.22°$). Decrease in the intensity of three check reflections during the experiment was not observed, the extinction (μCuK_α 29.5 cm^{-1}) was taken into account. The structure was solved by the direct method with program SIR [7] and refined first in isotropic and then in anisotropic approximation using the programs SHLXL-97 [8] and WinGX [9]. Hydrogen atoms were calculated on the basis of stereochemical criteria and refined by the relevant *rider* models. The final values of divergence factors R = 0.0545, R_W = 0.0864 for 686 reflections with $F \geq 2\sigma$. Analysis of intermolecular interactions and images are made using the program PLATON [10]. Atomic coordinates and temperature parameters for the compound are deposited in the Cambridge crystal structure database under the number CCDC 739999.

Powder diffraction patterns were obtained on an automatic X-ray diffractometer Bruker D8 Advance equipped with a Vario unit and a linear coordinate detector Vantec. The CuK_α radiation monochromated by the germanium curved Johansson monochromator was used, the mode of X-ray tube operation was as follows: 40 kV, 40 mA. The experiments were performed at 23°C in Bragg–Brentano geometry with a flat sample. The substance was pre-compressed and used as thin tablets (2–4 mm) on a glass substrate. During the experiment, the sample was rotated at 15 rpm. The diffraction pattern was recorded in the range of scattering angles 2θ from 4° to 70°, with a step 0.0081°, duration of the spectrum acquisition 0.5 s in each point. For each sample were obtained several diffraction patterns in different experimental regimes and with different time of the data acquisition. For the molecular complex of the isocyanurate from 3-chlorophenyl isocyanate with *N*-methylpyrrolidone, whose structure was established by X-ray analysis of a single crystal of the product of interaction of *N*-methylpyrrolidone with 3-chlorophenyl isocyanate at the triethylamine concentration 1.59×10^{-3} mol l^{-1}, was

calculated the powder diffractogram. Comparison of the calculated powder diffraction patterns with the experimental ones allowed the identification of the compounds.

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