1710 *Russian Chemical Bulletin, International Edition, Vol. 54, No. 7, pp. 1710—1714, July, 2005*

Synthesis and thermal decomposition of ditetrazol-5-ylamine

V. V. Nedel´ko,* A. V. Shastin, B. L. Korsunskii, N. V. Chukanov, T. S. Larikova, and A. I. Kazakov

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588. E-mail: vnedelko@icp.ac.ru

Ditetrazol-5-ylamine (DTA) was synthesized from cyanuric chloride in four steps. The thermal decomposition of DTA in the solid state was studied by thermogravimetry, volumetry, mass spectrometry, IR spectroscopy, and calorimetry. Under isothermal conditions at 200—242 °C, thermal decomposition obeys the first order autocatalytic kinetics. The kinetic and activation parameters of DTA decomposition were determined. The composition of gaseous reaction products and the structure of condensed residue were studied. The thermal effect of thermal DTA decomposition is 281.4 kJ mol^{-1}. The nitrogen content in a mixture of gaseous products formed by the reaction in a temperature interval of 200—242 °C exceeds 97 vol.%.

Key words: ditetrazol-5-ylamine, synthesis, thermal decomposition, kinetics, products, IR spectroscopy, mass spectrometry, reaction mechanism.

Tetrazoles are considered as promising energy-capacity compounds with a high nitrogen content. Some tetrazoles in mixtures with oxidizing agents are shown[1—3] to form efficient gas-generating systems, which can be used for the development of new facilities of individual protection in transport (for instance, airbags for motorists). Gas-generating systems based on tetrazoles and their salts excel the presently used azide generators in the whole series of parameters.[3] It should be mentioned that the nitrogen content in ditetrazol-5-ylamine exceeds 82 wt.%. Ditetrazol-5-ylamine (DTA) is interesting in the scientific respect as a model compound revealing the mechanism of thermal opening of the tetrazole ring. Specific features of the structure of a DTA molecule make it possible to estimate the mutual influence of tetrazole rings through the bridging NH group on the thermal stability of this compound. An ability of tetrazoles to form π-complexes with metals[4] is of interest for syntheses of DTA-based coordination compounds, which can be used as medicines and catalysts for combustion. The thermal decomposition of DTA has not been studied. The kinetic study of thermal decomposition and composition of destruction products and the estimation of thermal effects of the reaction, conditions of ignition, and other specific features of the behavior of DTA under heating seem necessary for practical use of DTA and its safe operation. Although DTA is described,[5] no detailed procedure of its synthesis was published.

Results and Discussion

Synthesis of DTA. Ditetrazol-5-ylamine was synthesized starting from cyanuric chloride (**1**) through intermediate 2,4,6-tris(methoxy)-1,3,5-triazine (**2**), 2,4-bis(hydrazino)-6-methoxy-1,3,5-triazine (**3**), and 2,4-bis(azido)-6-methoxy-1,3,5-triazine (**4**) (Scheme 1).

Kinetics of DTA thermal decomposition. The kinetic curves of weight loss by the DTA samples under linear heating conditions in air with a rate of 1.5 °C min^{-1} are shown in Fig. 1. The hydrated form of DTA eliminates an H_2O molecule in the 120—150 °C temperature interval (curve *1*). The intensely developed process of formation of volatile decomposition products occurs at temperatures >215 °C, while at 248 °C the sample ignites. The preliminary total dehydration of DTA at 120 °C *in vacuo* for 1 h does not change its thermal stability (see Fig. 1, curve *2*), and the ignition temperature of the anhydrous

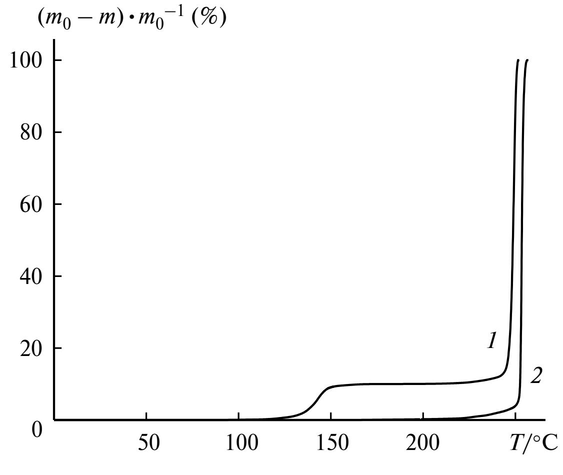
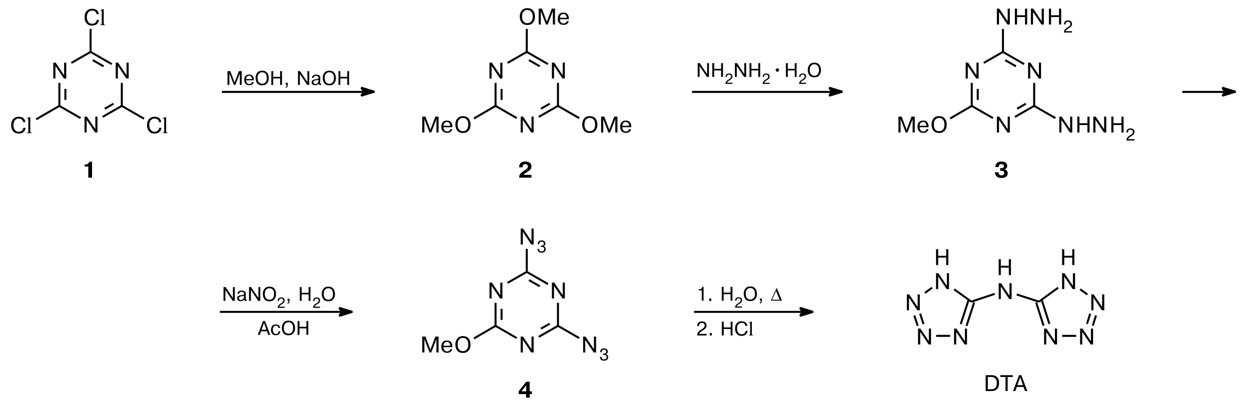


Fig. 1. Nonisothermal kinetics of decomposition of DTA monohydrate (*1*) and dehydrated DTA (*2*) in air (weighed sample 10 mg, heating rate 1.5 deg min^{-1}).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1660—1664, July, 2005.

Scheme 1



sample increases to 254 °C. As known,[6] if the dehydration of solid substances is endothermic, the sample cools down and its temperature becomes lower than the temperature of a heater. Perhaps, this is a reason for somewhat higher ignition temperature of the preliminary dehydrated sample. Replacement of air with argon exerts virtually no effect on the kinetics of DTA decomposition and does not change its ignition temperature in the linear heating regime, which indicates the absence of a noticeable contribution of thermal oxidation. The contribution of DTA evaporation is observed under dynamic vacuum conditions (permanent evacuation of volatile thermolysis products from the reaction zone) at temperatures above 180 °C.

Thermal decomposition of dehydrated DTA under isothermal conditions was studied in air in the temperature interval 201—242 °C. The total weight loss corresponding to complete DTA decomposition is close to 45 wt.%. The kinetic curves (Fig. 2) are S-shaped, and the process is satisfactorily described by the first order autocatalysis equation

$$d\alpha/dt = k_1(1 - \alpha) + k_2\alpha(1 - \alpha), \qquad (1)$$

where α is the conversion of the substance under study, and k_1 and k_2 are the rate constants of noncatalytic and catalytic reactions, respectively. Transformation of Eq. (1) into the equation

$$(d\alpha/dt)/(1 - \alpha) = k_1dt + k_2\alpha dt \qquad (2)$$

makes it possible to determine the absolute values of k_1 and k_2 at different experimental temperatures. These data are given in Table 1.

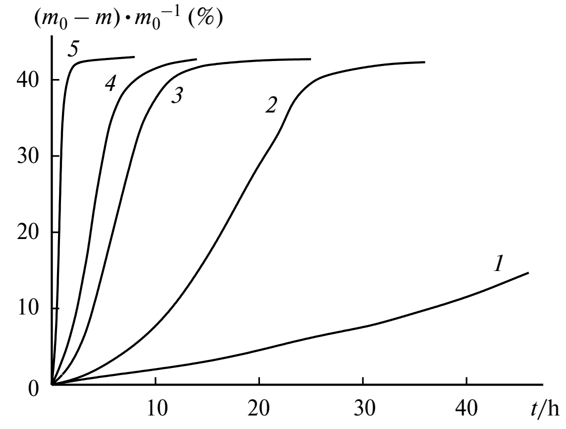


Fig. 2. Kinetics of thermal decomposition of dehydrated DTA (weighed sample 10 mg) in air at 201 (*1*), 211 (*2*), 223 (*3*), 231 (*4*), and 242 °C (*5*).

The temperature plots for the rate constants k_1 and k_2 in the coordinates of the Arrhenius equation are shown in Fig. 3. They are described by the equations

$$k_1 = 10^{15.6\pm0.5}\exp[-(197\pm5)/(RT)], \qquad (3)$$

$$k_2 = 10^{17.5\pm0.7}\exp[-(201\pm7)/(RT)], \qquad (4)$$

where k_1 and k_2 have a dimensionality of s^{-1}, and R is of kJ mol^{-1} K^{-1}. The values of the pre-exponential factor

Table 1. Rate constants of the noncatalytic (k_1) and catalytic (k_2) routes of thermal decomposition of dehydrated DTA at different temperatures from the data of thermogravimetry (weighed sample 10 mg) and calorimetry

Thermogravimetry			Calorimetry		
T/°C	$k_1 \cdot 10^7$	$k_2 \cdot 10^5$	T/°C	$k_1 \cdot 10^7$	$k_2 \cdot 10^6$
	s^{-1}			s^{-1}	
201	6.8±0.4	1.6±0.2	210	6.0±0.5	1.0±0.1
211	19±3	5.6±0.5	217	23±2	2.6±0.2
223	55±6	16±2	225	33±2	6.6±0.4
231	140±15	39±3	235	170±12	13±2
242	360±30	97±7			

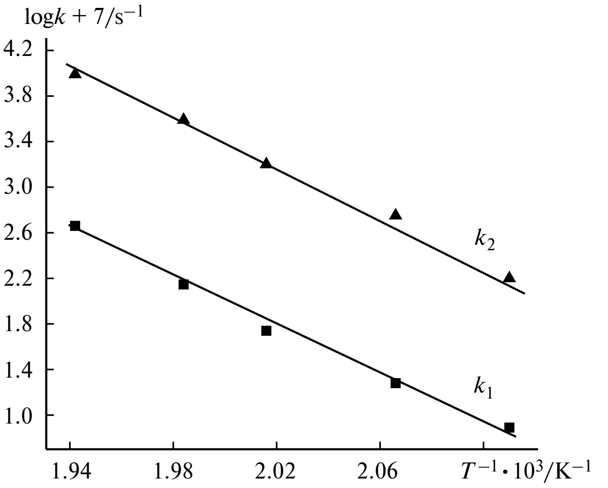


Fig. 3. Arrhenius plots of the rate constants of the noncatalytic (k_1) and catalytic (k_2) routes of thermal decomposition of dehydrated DTA in air (weighed sample 10 mg).

($10^{15.6}$ s^{-1}) and activation energy (197 kJ mol^{-1}) of the noncatalytic reaction are characteristic of thermal decomposition of tetrazoles.[7]

The relation of the heat release rate dQ/dt to the conversion of DTA η obeys the first order autocatalysis equation

$$dQ/dt\ (\text{J mol}^{-1}\ \text{s}^{-1}) = k_1Q_f(1-\eta) + k_2Q_f(1-\eta)\eta, \qquad (5)$$

where $\eta = Q/Q_f$, Q is the heat released to the certain time moment, and Q_f is the total heat of the process. The heats Q and Q_f were determined by numerical integration of the experimental time plot of the heat release rate.

The values determined for k_1 and k_2 are presented in Table 1.

The heat release rates and thermal effects for DTA thermal decomposition were measured by calorimetry under conditions of spontaneous escape of volatile reaction products at temperatures 210—235 °C. The processing of the heat release curves for DTA thermal decomposition confirmed that the kinetic law of the first-order catalytic process was fulfilled. The activation parameters of the catalytic reaction calculated from the calorimetric data (pre-exponential factor and activation energy are $10^{16.2\pm1.3}$ s^{-1} and 205±14 kJ mol^{-1}, respectively) are close to the values measured by thermogravimetry. Despite considerable discrepancies of the activation parameters for the noncatalytic reaction determined by calorimetry ($10^{23.0\pm1.6}$ s^{-1} and 270±15 kJ mol^{-1}) and thermogravimetry ($10^{15.6}$ s^{-1} and 197 kJ mol^{-1}), the values obtained for rate constants of the noncatalytic route can be explained by methodical difficulties associated with exact determination of the rate constants k_1, which are lower than k_2, especially for calorimetric measurements. It can be assumed that the activation parameters of the noncatalytic reaction determined by thermogravimetry are more reliable, because they are close (see above) to the activation parameters of thermal decomposition of tetrazoles according to the first order kinetics (without self-acceleration).[7] The thermal effect of thermal DTA decomposition is equal to 282±19 kJ mol^{-1}.

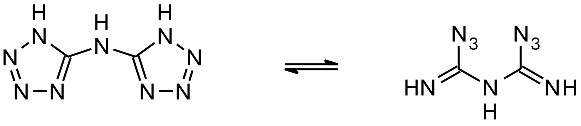
The volumetric data showed that each DTA molecule eliminates two N_2 molecules upon its complete decomposition in the temperature interval 201—242 °C. The volume fraction of nitrogen in a mixture of gaseous decomposition products is close to 97.5%. Purity of the evolved nitrogen was confirmed by mass spectrometry. The mass spectrum of the gaseous products of thermal DTA decomposition obtained at 235 °C, reaction time 1 h, and 100% decomposition depth indicates the formation of nitrogen as a predominant gaseous product, small amount of hydrocyanic acid (peaks with m/z 27, 26, and 25), and traces of H_2O (~0.2 vol.%) and CO_2 (<0.1 vol.%). The N_2 : HCN ratio is estimated as close to 50 : 1 (vol/vol). For deeper two-step DTA heating (235 °C, 1 h, and 450 °C), the qualitative composition of the gaseous decomposition products remains unchanged. However, in the case of high-temperature thermolysis of DTA, the yield of hydrocyanic acid increases noticeably (N_2 : HCN = 7 : 1 vol/vol). The two-stage regime of DTA heating to 450 °C is necessary, because the substance cannot be heated to temperatures higher than 250 °C because of its ignition.

The IR spectrum of the solid residue after complete thermal DTA decomposition (240 °C, 0.5 h) is characterized by broad bands at 600—800 and 1200—1650 cm^{-1}. Similar spectra with a ratio of stretching and bending vibration frequencies of 2 : 1 are characteristic of disordered structures formed by planar networks (for instance, for turbostrate boron nitride, layered aluminosilicates, and some other). The basic NH groups that form weak hydrogen bonds in a DTA molecule disappear during thermal DTA decomposition (as indicated by the absence of an absorption band at 3450 cm^{-1}). The acidic NH groups also disappear (no absorption bands are observed at 2400—2500 cm^{-1}). The solid decomposition product contains the NH_2 groups (two bands at 3100—3300 cm^{-1} and a δ(NH_2) band at 1630 cm^{-1}) and the NH groups forming strong hydrogen bonds (perhaps, Ar=N—H, where Ar is the conjugated heterocycle). The intense bands of stretching vibrations at 1400—1600 and 1040 cm^{-1} and bending vibration bands at 700—800 cm^{-1} indicate a possible presence of triazole rings.[8]

The solid product of complete thermal DTA decomposition at 200—242 °C is thermally stable at temperatures up to 300 °C. Deeper heating of the solid product (450 °C, 1 h) is accompanied by the formation of comparable amounts of N_2 and HCN and, as a consequence, the N_2 : HCN ratio decreases from 50 : 1 to 7 : 1 (vol/vol). When the solid product is deeply heated, its IR spectrum changes noticeably. The IR spectrum of the solid product obtained by the two-stage DTA thermolysis (235 °C, 1 h and 450 °C, 1 h) has no absorption bands of the NH, while the basic NH groups with strong hydrogen bonds are retained. The latter is indicated by broad bands at 3325 and 3190 cm^{-1} in the spectrum. The weak bands at 2176—2228 cm^{-1} can be assigned to vibrations of the C≡N bonds.

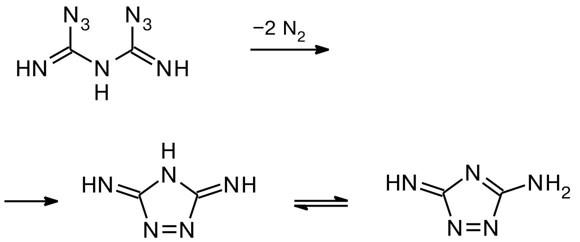
The following mechanism of DTA decomposition can be proposed based on the data of kinetic measurements, mass spectrometry, and IR spectroscopy. In the studied temperature interval from 200 to 240 °C, the decomposition of DTA is preceded by its thermal tautomeric rearrangement to the azidoazomethine form (Scheme 2).

Scheme 2



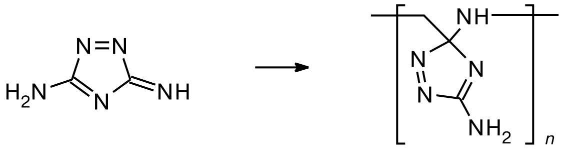
Such a thermal rearrangement with tetrazole ring opening is characteristic of *C*-substituted tetrazoles.[9] The elimination of two nitrogen molecules from intermediate diazide can produce isomeric triazoles (Scheme 3).

Scheme 3



Aminotriazole contains the N=CH bond, which is capable of thermal polymerization, and can transform into polymeric triazole (Scheme 4).

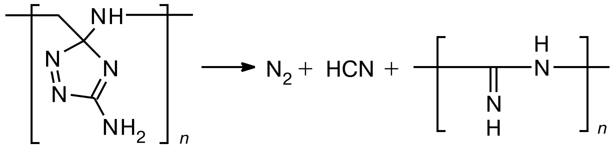
Scheme 4



The formation of polymeric triazoles has been observed earlier[7] for the thermal decomposition of 2-alkyl-5-vinyltetrazole polymers. The structure assumed for polymeric triazole agrees with the IR spectral data.

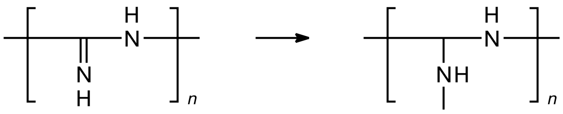
Polymeric triazoles are known to be thermally stable up to 300 °C.[10] The solid product obtained in our experiments by DTA decomposition in a temperature range of 200—240 °C is also stable to 300 °C. Further heating of this product affords comparable amounts of N_2 and HCN. Perhaps, the thermal decomposition of the triazole ring proceeds *via* Scheme 5.

Scheme 5



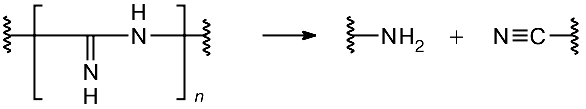
The formation of the network structure (confirmed by the IR spectra) can be due to a deeper thermal polymerization of the linear polymeric product (Scheme 6).

Scheme 6



The appearance of nitrile groups in the solid product of high-temperature decomposition can be due to the thermal destruction of the polymer (Scheme 7).

Scheme 7



Experimental

Ditetrazol-5-ylamine monohydrate was synthesized in four steps from cyanuric chloride in 40% yield. The structure of the synthesized compound was confirmed by the ^{13}C, ^{1}H NMR and IR spectra. The kinetics of thermal DTA decomposition was studied by thermogravimetry on an ATV-14M automated thermobalance,[11] which enabled experiments on both linear heating with different rates and under isothermal conditions in air, vacuum, or inert atmosphere (krypton, argon). The kinetic studies of DTA decomposition by thermal release and measurements of thermal effects of the process were carried out in open glass ampules on a DAK-1 automated dynamic microcalorimeter.[12]

The composition of the gaseous reaction products was determined by mass spectrometry on an MI1201-V instrument and by volumetry. IR spectra of the condensed decomposition products were obtained on a Specord-75IR spectrophotometer in KBr pellets in an frequency region of 400—4000 cm^{-1}.

2,4,6-Tris(methoxy)-1,3,5-triazine (2). Sodium hydroxide (12 g, 0.3 mol) was dissolved in MeOH (100 mL). Cyanuric chloride **1** (18.5 g, 0.1 mol) was added to the resulting mixture with cooling and stirring at such a rate that the temperature would not exceed 30 °C. After compound **1** was added completely, the reaction mixture was stored for 2 h at room temperature. A precipitate of NaCl formed was filtered off, methanol was evaporated, and the residue was recrystallized from water. The yield of **2** was 11.1 g (65%), m.p. 134—135 °C (Ref. 13: 134—136 °C).

2,4-Bis(hydrazino)-6-methoxy-1,3,5-triazine (3). Triazine **2** (6.5 g, 38 mmol) was dissolved in THF (100 mL), and the solution was refluxed with 100% hydrazine hydrate (5.7 g, 114 mmol) for 9 h. A precipitate formed was filtered off and dried in air to constant weight. The yield of **3** was 5.5 g (84%), m.p. 231—232 °C. IR spectrum of **3** (KBr), cm^{-1}: 3325, 3300, 3270, 1600, 1590, 1570, 1555, 1495, 1395, 1355, 1130, 1095, 1070, 1000, 940.

2,4-Bis(azido)-6-methoxy-1,3,5-triazine (4). Compound **3** (3.4 g, 19.8 mmol) was dissolved in an AcOH—H_2O (1 : 1) mixture (20 mL). The resulting solution was cooled in an ice-cold bath, and a saturated aqueous solution of $NaNO_2$ (3.5 g, 50 mmol) was added for 15 min with stirring and cooling. Then cooling was stopped, stirring was continued for 20—25 min, and the mixture was diluted to 50 mL. A precipitate formed was filtered off, washed with a small amount of ice-cold water, and dried on the filter to constant weight. The yield of **4** was 3.4 g (88%), m.p. 61—62 °C. IR (KBr), cm^{-1}: 2175, 2130, 1580, 1560, 1540, 1490, 1450, 1400, 1350, 1210, 1190, 1150.

Ditetrazol-5-ylamine (DTA). Distilled water (250 mL) and compound **4** (3.4 g) were placed in a round-bottom 500-cm^3 flask with a reflux condenser. The mixture was refluxed for 40—48 h until starting compound **4** disappeared (TLC monitoring on Silufol UV 254 plates). The solution was concentrated to 1/2 volume and acidified with hydrochloric acid to acidic pH (litmus). A precipitate formed was filtered off, dried on the filter, recrystallized from water, and dried for 2—3 h at 100 °C. DTA was obtained in 40% yield (1.1 g). The substance decomposes rapidly without melting at temperatures >220 °C, which agrees with published data.[14] ^{13}C NMR (DMSO-d_6), δ: 153.75 (s, N=$\underline{C}$—N). ^1H NMR (DMSO-d_6), δ: 11.57 (br.s, NH of tetrazole and amine). IR (KBr), cm^{-1}: 3440, 3250, 3125, 3025, 2940, 2850 (against a broad absorption band, from 3300 to 2200 cm^{-1}), 1655, 1645, 1620, 1570, 1490, 1480, 1450, 1380, 1350, 1340, 1325, 1280, 1275, 1260, 1245, 1230, 1175, 1130, 1105, 1075, 1050, 1040, 1010, 1000, 860, 810, 750, 730, 725.

Literature data[5]: ^{13}C NMR (DMSO-d_6), δ: 153.46 (s, N=$\underline{C}$—N); the IR spectrum contains a series of typical bands at 700—800, 900—1100, and 1500—1600 cm^{-1}.

This work was financially supported by the Grants of Council of the President of the Russian Federation (Program of State Support for Leading Scientific Schools of Russia, Grant NSh 00-15-97451).

References

1. H. Schmidt, N. Eisenreich, A. Baier, J. Neutz, D. Schroter, and V. Weiser, *Propellants, Explosives, Pyrotechnics*, 1999, **24**, 144.
2. T. Matsuzava, K. Sackata, J. Kaneko, J. Zhou Wu, M. Arai, and M. Tamura, *J. Jpn Explos. Soc.*, 1994, **55**, 265.
3. A. Miyake, M. Yukawa, T. Ogawa, A. Kimura, and K. Nishida, *J. Jpn Explos. Soc.*, 1998, **59**, 116.
4. Z. G. Aliev, T. K. Goncharov, V. P. Grachev, and V. P. Roshchupkin, *Koord. Khim.*, 1991, **17**, 1101 [*Sov. J. Coord. Chem.*, 1991, **17** (Engl. Transl.)].
5. Yu. A. Azev, I. P. Loginova, B. V. Golomolzin, I. I. Mudretsova, and V. L. Rusinov, *Khim. Geterotsikl. Soedin.*, 1990, No. 8, 135 [*Chem. Heterocycl. Compd.*, 1990 (Engl. Transl.)].
6. N. Z. Lyakhov and V. V. Boldyrev, *Usp. Khim.*, 1972, **41**, 1960 [*Russ. Chem. Rev.*, 1972, **41** (Engl. Transl.)].
7. V. P. Roshchupkin, V. V. Nedel´ko, T. S. Larikova, and S. V. Kurmaz, *Vysokomol. Soedin.*, *Ser. A*, 1989, **31**, 1726 [*Polym. Sci. USSR, Ser. A*, 1989, **31** (Engl. Transl.)].
8. N. Colthur and L. Daly, *Introduction to Infrared and Raman Spectroscopy*, Acad. Press, New York—London, 1964, 511 p.
9. K. Nishiyama and J. Miyata, *Bull. Chem. Soc. Jpn*, **58**, 2419.
10. V. A. Lopyrev, V. N. Salaurov, V. N. Kurakin, L. A. Tataroval, and T. G. Ermakov, *Vysokomol. Soedin.*, *Ser. B*, 1985, **27**, 145 [*Polym. Sci. USSR, Ser. B*, 1985, **27** (Engl. Transl.)].
11. L. N. Gal´perin and Yu. R. Kolesov, *Izmerit. Tekhnika* [*Measuring Technique*], 1981, No. 4, 23 (in Russian).
12. O. S. Galyuk, Yu. I. Rubtsov, G. S. Malinovskaya, and G. B. Manelis, *Fiz. Khim.* [*Physical Chemistry*], 1965, **39**, 2319 (in Russian).
13. J. Thurston, J. Dudley, D. Kaiser, and F. Shaefer, *J. Am. Chem. Soc.*, 1951, **73**, 72.
14. W. P. Norris and R. A. Henri, *J. Org. Chem.*, 1964, **29**, 650.

Received May 21, 2004;
in revised form October 13, 2004