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N-Sulfinylanilines as Dienes in the Diels–Alder Reaction. Structural Aspects

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Abstract—Reactions of *N*-sulfinylanilines with norbornene and norbornadiene result in the Diels–Alder adducts of benzo-*ortho*-thiazine structure, which was confirmed by the NMR, IR spectroscopy and XRD analysis. In all cases the diene added to the norbornenes bicyclic system at the side of the *endo*-methylene bridge. The methyl group of *meta*-*N*-sulfinyl toluidine directs the norbornene entry into the *para*-position.

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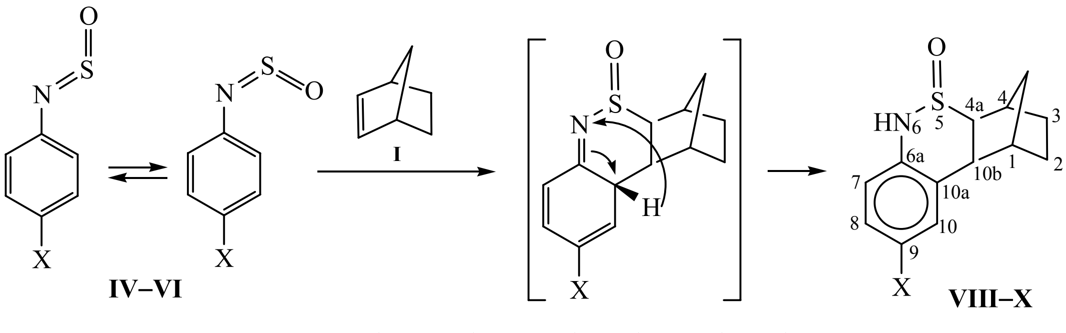
Previously an unusual reactivity of the aromatic *N*-sulfinyl amines has been found in the Diels–Alder reaction where this class of compounds behaves as the heteroatomic dienophiles [1–3] and heteroatomic dienes [4–6]. In the latter case, the aromatic *N*-sulfinylanilines behave like styrenes to form a group of *ortho*-thiazine heterocycles, which are difficultly accessible by the other synthetic methods. The stereochemical behavior and structural orientation of these reactions are unsufficiently studied.

In this regard, we obtained a series of adducts of *N*-sulfinylanilines **III–VII** with norbornene **I** and norbornadiene **II** whose molecular structure was established on the basis of the X-ray diffraction analysis and NMR spectroscopy. The reaction of sulfinyl anilines with norbornene was carried out by mixing the reagents (thionyl aniline:norbornene = 1:1.5) in a sealed ampule at room temperature. The liquid was decanted from the resulting precipitate, the precipitate was washed with petroleum ether and recrystallized from alcohol.

The reactions of *para*-substituted *N*-sulfinylanilines **IV–VI** yielded the adducts **VIII–X** (diene:dienophile = 1:1). Their IR spectra contain characteristic absorption bands in the range of 3175–3150 (N–H) and 1050–1060 cm^{-1} (S=O). The ^{1}H NMR spectra of these adducts are characterized by the presence of proton signals of NH-group in the weak field (7.0–9.0 ppm), the singlet signals of aromatic protons in the range of 6.5–7.0 ppm, and the signals of *AB*-system of the protons of bicyclic fragment at 0.9–3.4 ppm.

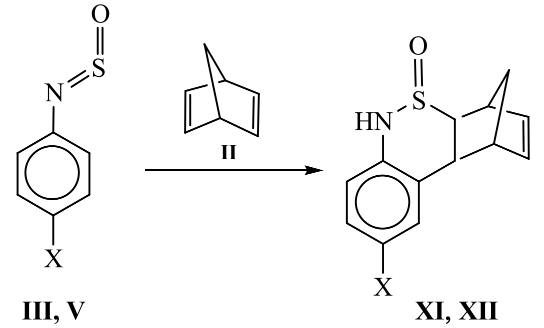
These data are characteristic of the *ortho*-benzothiazine derivatives **VIII–X**.



X = CH_3 (**IV, VIII**), OCH_3 (**V, IX**), NO_2 (**VI, X**).

The structure of the adduct **VIII** was established by the XRD analysis (Fig. 1). According to the XRD data, the addition of *N*-sulfinylaniline as a diene to the norbornene system proceeds at the side of the *endo*-methylene bridge. The C^4–C^{12} and S^5–N^6 bonds, as well as the C^4–C^{12} and S^5=O^5 bonds form the *trans*-configuration of the respective fragments. Characteristically, the relative configuration of the sulfoxide center can be provided by either the *endo*- or *exo*-orientation of the addends in the *Z*- and *E*-forms of *N*-sulfinylaniline, respectively. The choice in favor of a transition state structure of this reaction cannot be done yet, because the problem of spatial isomerism of *N*-sulfinyl amines is still open [7, 8].

The reactions of *N*-sulfinylanilines **III** and **V** with norbornadiene **II** were performed in a similar conditions to give the adducts **XI** and **XII** of 1:1 composition. Their IR spectra contain the characteristic absorption bands in the range of 3222–3227 (N–H) and 1055–1062 cm^{-1} (S=O). In the ^{1}H NMR spectra of these adducts there are the signals of aromatic protons in the region of 6.5–7.0 ppm, the signals of two olefinic protons in the region of 6.0–6.3 ppm, a singlet of the methoxy group of **XII** at 3.73 ppm, and a system of the proton signals of the bicycloheptene fragment at 0.8–3.1 ppm.



III, V **XI, XII**

X = H (**III, XI**), OCH_3 (**V, XII**).

The structure of **XII** was determined by the XRD analysis (Fig. 2). Like in compound **VIII**, in this case the *endo*-junction of thionylaniline **V** to norbornadiene from the side of its *endo*-methylene bridge was found. The C^4–C^{12} and S^5–N^6 bonds, as well as the C^4–C^{12} and S^5=O^5 bonds form the *trans*-configurations of the corresponding fragments.

To determine the structural orientation in these reactions we investigated the reaction of *meta*-*N*-sulfinyltoluidine with norbornene under the conditions similar to those of the above reactions. The IR spectra of the resulting adduct **XIII** (1:1) contain the characteristic absorption bands at 3162 (N–H), 1041 and 1050 cm^{-1} (S=O). In the ^{1}H NMR spectra there are the signals of aromatic protons in the region of 6.65–7.15 ppm and the signals of bicycloheptane protons in the range of 1.0–3.5 ppm. Generally, the ^{1}H NMR spectrum of **XIII** is represented by a double set of the signals with the same splitting. Most likely, these data suggest that the adduct **XIII** consists of two stereoisomers (but not structural isomers). To solve this dilemma the adduct **XIII** was oxidized to the corresponding sulfone **XIV**. In its IR spectrum there are the characteristic absorption bands at 3215 (N–H), 1135, and 1299 cm^{-1} (SO_2). The aromatic protons of sulfone **XIV** are manifested as a singlet (1H) and *AB*-system (2H) at 6.60–7.10 ppm alongside a simplified set of the proton signals of the saturated groups of bicycloheptane fragment confirming the structures **XIII** and **XIV**.

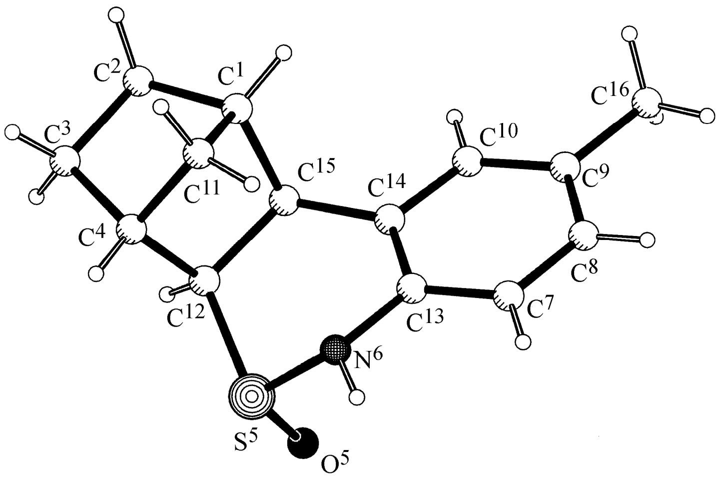


Fig. 1. Geometry of adduct **VIII** of *p*-*N*-sulfinyltoluidine with norbornene in a crystal.

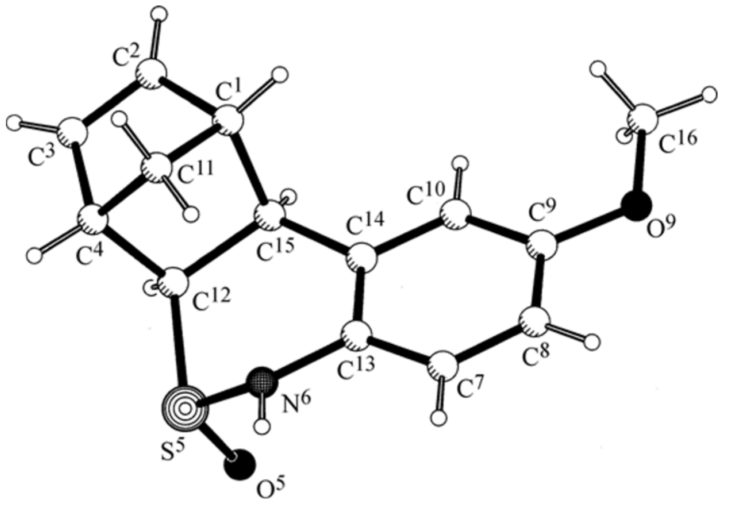


Fig. 2. Geometry of adduct **XII** of *p*-*N*-sylfinylanisidine with norbornadiene in a crystal.

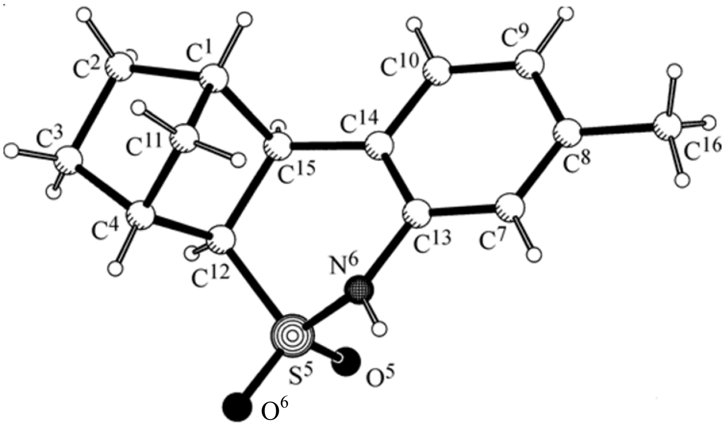
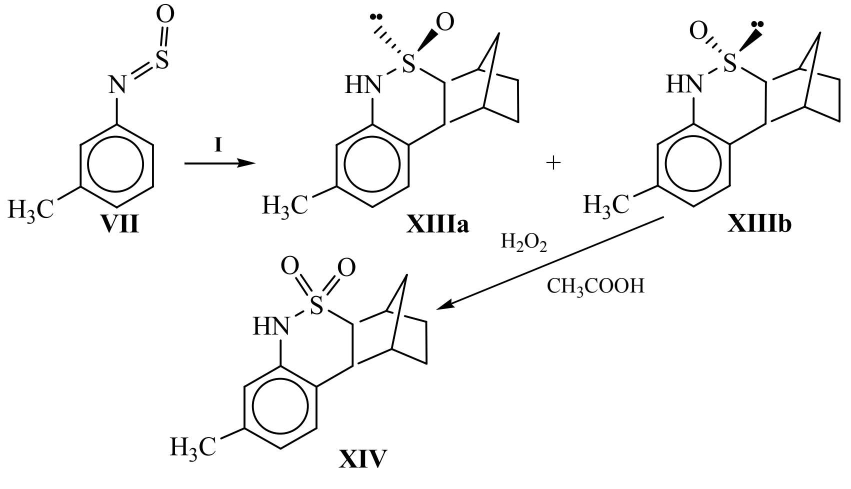


Fig. 3. Geometry of sulfone **XIV** in a crystal.

The XRD data for the oxidation product **XIV** support the assumption that the adduct **XIII** contains two diastereomers **XIIIa** and **XIIIb**.

As in the cases of **VIII** and **XII**, the XRD data for product **XIV** (Fig. 3) indicate that thionylaniline **VII** is attached to norbornene **I** at the side of the *endo*-



methylene bridge. The $C^4–C^{12}$ and $S^5–N^6$ bonds form fragments of the *trans*-configuration.

The regularities of the addition of thionylaniline dienes to the norbornene dienophile we have found are of the same nature as the reaction of these dienophiles with other dienes [9, 10].

EXPERIMENTAL

The elemental analysis was performed on a CHNS-analyzer CHNS-EuroEA 3000. The IR spectra were recorded on a Bruker Vertex 70 FTIR spectrometer from KBr pellets. The NMR spectra were measured on a Varian Unity spectrometer (300 MHz). The melting points were measured on a Digital Mel-Temp 3.0 digital melting point analyzer.

The X-ray diffraction studies of the crystals of **VIII**, **XII**, and **XIV** were carried out on a Bruker SMART Apex II diffractometer [graphite monochromator, $\lambda(\mathrm{Mo}K_\alpha)$ 0.71073]. The extinction was semi-empirically accounted for by a SADABS software [11]. The structure was solved by the direct method using a SHELXS software [12]. The nonhydrogen atoms were refined in the isotropic and then anisotropic approximations by a SHELXL-97 program [13]. The hydrogen atoms linked to the carbon atoms were placed into the calculated position and refined by a *rider* model. The NH-hydrogen atoms were identified from the difference Fourier series. On the final stage their positions were refined in the isotropic approximation. All calculations were performed using the WinGX [14] and APEX2 software packages [15]. The drawings were made using a PLATON software [16].

The X-ray diffraction data for compounds **VIII**, **XII**, and **XIV** are deposited in the Cambridge Structural Database (CCDC 828 931, 828 933, and 828 932, respectively).

The crystals of compound **VIII** are monoclinic, $C_{14}H_{17}NOS$; at 20°C: *a* 28.904(6), *b* 5.8092(13), *c* 15.807(4) Å; β 108.987(2)°, *V* 2509.7(10) Å^3, *Z* 8, d_{calc} 1.309 g cm^{-3}, space group *C*2/*c*, μMo 2.41 cm^{-1}. The intensities of 9720 reflections were measured, 2277 of which were with $I \geq 2\sigma$. The final values of the divergence factors are *R* 0.0381, *Rw* 0.1085.

The crystals of compound **XII** are rhombic, $C_{14}H_{15}\cdot NO_2S$; at 20°C: *a* 13.183(3), *b* 7.2820(14), 26.024(5) Å; *V* 2498.3(9) Å^3, *Z* 8, d_{calc} 1.390 g cm^{-3}, space group *Pbca*, μMo 2.52 cm^{-1}. The intensities of 17371 reflections were measured, 1927 of which were of $I \geq 2\sigma$. The final values of the divergence factors are *R* 0.0422, *Rw* 0.1167.

The crystals of compound **XIV** are triclinic, $C_{14}H_{17}\cdot NO_2S$; at 20°C: *a* 7.905(4), *b* 9.431(5), *c* 10.051(6) Å; α 67.431(5), β 73.019(6), γ 87.867(6), *V* 659.4(6) Å^3, *Z* 2, d_{calc} g cm^{-3}, space group *P*-1, μMo 2.39 cm^{-1}. The intensity of 7393 reflections were measured, 2680 of which were with $I \geq 2\sigma$. The final values of the divergence factors are *R* 0.0365, *Rw* 0.1078.

The X-ray diffraction study of compounds **VIII**, **XII**, and **XIV** was performed in the Federal collective spectral analysis center for physical and chemical studies of the structure, composition and properties of substances and materials.

Synthesis of *N*-sulfinylanilines **III**–**VII** was carried out via the reaction of aniline with $SOCl_2$ in benzene according to the procedure [17].

9-Methyl-1,2,3,4,4a,10b-hexahydro-1,4-methano-6*H*-dibenzo[*c*,*e*]-5,6-thiazine-5-oxide (VIII). To 30.6 g (0.2 mol) of *N*-sulfinyltoluidine **IV** was added 2.28 g (0.3 mol) of norbornene **I**. The mixture was placed in a glass ampule, which was sealed and maintained at room temperature for 14 days. When the reagents do not fully dissolve after mixing, the ampule was gently heated until a homogeneous liquid phase appeared. The reaction completing was visually determined by the increasing amount of the crystals formed and a decrease in the amount of the liquid phase in the ampule. The liquid was decanted, the precipitate was washed with petroleum ether and recrystallized from hot ethanol. Yield 46.5 g (94%), mp 185–186°C. IR spectrum, ν, cm^{-1}: 1056 (S=O), 3147 (N–H). ^{1}H NMR spectrum, δ, ppm: 0.95 d (1H, *J* 8.75 Hz), 1.40–1.60 m (4H), 2.10 s (1H), 2.20 s (3H), 2.30 s (1H), 2.50 s (1H), 3.00 d (1H, *J* 8.75 Hz), 3.18 d (1H, *J* 8.75 Hz), 6.67 d (1H, *J* 7.3 Hz), 6.90 d (1H, *J* 7.3 Hz), 6.95 s (1H), 8.85 s (1H). Found, %: C 67.78; H 6.74; N 5.80; S 12.82. $C_{14}H_{17}NSO$. Calculated, %: C 67.98, H 6.93, N 5.66, S 12.96.

9-Methoxy-1,2,3,4,4a,10b-hexahydro-1,4-methano-6*H*-dibenzo[*c*,*e*]-5,6-thiazine-5-oxide (IX) was prepared similarly from 33.8 g (0.2 mol) of *p*-methoxy-*N*-sulfinylaniline **V** and 28.2 g (0.3 mol) of norbornene **I**. Yield 47.9 g (91%), mp 203–204°C. IR spectrum, ν, cm^{-1}: 1058 (S=O), 3179 (N–H). ^{1}H NMR spectrum, δ, ppm: 1.04 d (1H, *J* 10.2 Hz), 1.47 m (2H), 1.72 m (2H), 1.80 d (1H, *J* 10.4 Hz), 2.33 s (1H), 2.48 s (1H), 3.04 d (1H, *J* 8.4 Hz), 3.31 d (1H, *J* 8.5 Hz), 3.76 s (3H), 6.52 s (1H), 6.57 d (1H, *J* 8.4 Hz), 6.67 d (1H, *J* 8.8 Hz), 8.65 s (1H). Found, %: C 63.78; H 6.62; N 5.24; S 12.33. $C_{14}H_{17}NSO_2$. Calculated, %: C 63.85; H 6.51; N 5.32; S 12.18.

9-Nitro-1,2,3,4,4a,10b-hexahydro-1,4-methano-6*H*-dibenzo[*c*,*e*]-5,6-thiazine-5-oxide (X) was prepared similarly from 36.8 g (0.2 mol) of *p*-nitro-*N*-sulfinylaniline **VI** and 28.2 g (0.3 mol) of norbornene **I**. Reaction time was 28 days. Yield 49.0 g (88%), mp 250°C (decomp.). IR spectrum, ν, cm^{-1}: 1050 (S=O), 3166 (N–H). ^1H NMR spectrum, δ, ppm: 1.13 d (1H, *J* 10.9 Hz), 1.50–1.80 m (5H), 2.38 s (1H), 2.55 s (1H), 3.16 d (1H, *J* 8.9 Hz), 3.46 d (1H, *J* 8.3 Hz), 6.80 d (1H, *J* 8.7 Hz), 7.02 s (1H), 7.98 d (1H, *J* 8.7 Hz), 8.10 s (1H). Found, %: C 55.92; H 5.15; N 10.16; S 11.41. $C_{13}H_{14}N_2SO_3$. Calculated, %: C 56.10; H 5.07; N 10.06; S 11.52.

1,4,4a,10b-Tetrahydro-1,4-methano-6*H*-dibenzo-[*c*,*e*]-5,6-thiazine-5-oxide (XI) was prepared similarly from 28.5 g (0.2 mol) of *N*-sulfinylaniline **III** and 27.6 g (0.3 mol) of norbornadiene **II**. Yield 41.6 g (90%), mp 187–188°C. IR spectrum, ν, cm^{-1}: 1054 (S=O), 3165 (N–H). ^1H NMR spectrum, δ, ppm: 0.80 d (1H, *J* 8.8 Hz), 1.45 d (1H, *J* 9.2 Hz), 2.16 m (2H), 2.42 s (1H), 2.74 s (1H), 6.02 m (2H), 6.50 d (1H, *J* 7.9 Hz), 6.65 t (1H, *J* 7.5 Hz), 6.79 t (1H, *J* 7.2 Hz), 6.91 d (1H, *J* 7.2 Hz), 8.70 s (1H). Found, %: C 67.69; H 5.55; N 6.13; S 13.71. $C_{13}H_{13}NSO$. Calculated, %: C 67.50; H 5.66; N 6.06; S 13.86.

9-Methoxy-1,4,4a,10b-tetrahydro-1,4-methano-6*H*-dibenzo[*c*,*e*]-5,6-thiazine-5-dioxide (XII) was prepared similarly from 33.8 g (0.2 mol) of *p*-methoxy-*N*-sulfinylaniline **V** and 27.6 g (0.3 mol) of norbornadiene **II**. Yield 47.6 g (91%), mp 195– 196°C. IR spectrum, ν, cm^{-1}: 1031, 1055 (S=O), 3222 (N–H). ^1H NMR spectrum, δ, ppm: 1.15 d (1H, *J* 8.9 Hz), 1.80 d (1H, *J* 8.8 Hz), 2.73 d (1H, *J* 9.8 Hz), 2.81 s (1H), 3.04 m (2H), 3.35 s (1H), 3.72 s (3H), 6.35 m (2H), 6.73 d. d (1H, *J* 8.7, 2.7 Hz), 6.78 d (1H, *J* 8.5 Hz), 6.86 d (1H, *J* 2.4 Hz). Found, %: C 64.20; H 5.60; N 6.53; S 12.11. $C_{14}H_{15}NSO$. Calculated, %: C 64.34; H 5.79; N 5.36; S 12.27.

8-Methyl-1,2,3,4,4a,10b-hexahydro-1,4-methano-6*H*-dibenzo[*c*,*e*]-5,6-thiazine-5-oxide (XIII) was prepared similarly from 33.8 g (0.2 mol) of *meta*-*N*-sulfinyltoluidine **VII** and 28.2 g (0.3 mol) of norbornene **I**. Yield 45.5 g (92%), mp 223–224°C. IR spectrum, ν, cm^{-1}: 1041, 1050 (S=O), 3162 (N–H). Found, %: C 67.80; H 6.79; N 5.73; S 12.78. $C_{14}H_{17}NSO$. Calculated, %: C 67.98; H 6.93; N 5.66; S 12.96.

8-Methyl-1,2,3,4,4a,10b-hexahydro-1,4-methano-6*H*-dibenzo[*c*,*e*]-5,6-thiazine-5-oxide (XIV). To a solution of 13 g (0.05 mol) of adduct **XIII** in a minimal amount of glacial acetic acid was added dropwise ~7 ml of H_2O_2 (30%). The mixture was kept for few days at room temperature. The crystals formed were filtered off and recrystalled from warm ethanol. Yield 10.4 g (75%), mp 201–202°C. IR spectrum, ν, cm^{-1}: 1136 (SO_2), 3215 (N–H). ^1H NMR spectrum, δ, ppm: 1.09 d (1H, *J* 10.1 Hz), 1.40–1.60 m (4H), 1.80 d (1H, *J* 10.0 Hz), 2.21 s (3H), 2.26 s (1H), 2.66 s (1H), 3.40 d. d (2H, *J* 13.65, 8.9 Hz), 6.59 s (1H), 6.83 d (1H, *J* 8.6 Hz), 7.12 d (1H, *J* 8.8 Hz), 9.75 s (1H). Found, %: C 63.98; H 6.72; N 5.19; S 12.32. $C_{14}H_{17}NSO_2$. Calculated, %: C 63.85; H 6.51; N 5.32; S 12.18.

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REFERNCES

1. Kataev, E.G. and Plemenkov, V.V., *Zh. Obshch. Khim.*, 1962, vol. 32, no. 11, p. 3817.
2. Whitesell, J.K., James, D., and Carpenter, J.F., *Chem. Commun.*, 1985, p. 1449.
3. Bayer, A., Endeshaw, M.M., and Gautun, O.R., *J. Org. Chem.*, 2004, vol. 69, p. 7198.
4. Collins, G.R., *J. Org. Chem.*, 1964, vol. 29, p. 1688.
5. Kataev, E.G. and Plemenkov, V.V., *Zh. Org. Khim.*, 1967, vol. 4, no. 6, p. 1094.
6. Hanson, P. and Stone, T.W., *J. Org. Soc.*, 1984, p. 2429.
7. Romano, R.M., Della, Vedova, C.O., and Hildebrandt, P., *J. Mol. Struct.*, 1999, vol. 508, p. 5.
8. Muchall, H.M., *J. Phys. Chem.*, 2001, vol. 105, no. 3, p. 632.
9. Plemenkov, V.V. and Katerinich, L.V., *Zh. Obshch. Khim.*, 1982, vol. 18, no. 4, p. 835.
10. Plemenkov, V.V., *Doctoral (Chem.) Dissertation*, Kazan, 1985.
11. Sheldrick, G.M., *SADABS*, University of Gottingen, Germany, 2004.
12. Sheldrick, G.M., *Acta Crystallogr. A*, 2008, vol. 64, no. 1, p. 112.
13. Sheldrick, G.M., *SHELXL-97 Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.
14. Farrugia, L.J., *J. Appl. Crystallogr.*, 1999, vol. 32, no. 4, p. 837.
15. *APEX (Version 2.1), SAINTPlus, Data Reduction and Correction Program*, Version 7.31A, Bruker Advansed X-Ray Solutsions, BrukerXS Inc., Madison, Wisconsin, USA, 2006.
16. Spek, A.L., *Acta Crystallogr. (A)*, 1990, vol. 46, no. 1, p. 34.
17. Kresze, G., Maschke, A., Albrecht, R., Bederke, K., Patschke, H.P., Smalla, H., and Trede, A., *Angew. Chem.*, 1962, vol. 74, p. 135.