5. M. M. Sokolova, V. V. Mel'nikov, V. A. Ostrovskii, G. I. Koldovskii, A. A. Mel'nikov, and B. V. Gidaspov, Zh. Org. Khim., 11, 1744 (1975).
6. M. I. Ermakova and N. I. Latosh, Zh. Obshch. Khim., 38, 2390 (1968).
7. I. A. Shikhova, in: Formazans. Proceedings of the Institute of Chemistry of the Ural Scientific Center of the Academy of Sciences of the USSR [in Russian], Vol. 30, Sverdlovsk (1974), p. 18.
8. M. I. Ermakova, N. L. Vasil'eva, and I. Ya. Postovskii, Zh. Anal. Khim., 16, 8 (1961).
9. E. Wedekind, Ber., 36, 2995 (1897).
10. R. Wizinger and V. Biro, Helv. Chem. Acta, 32, 901 (1949).

SYNTHESIS AND ABSORPTION SPECTRA OF 3,5-DIARYL-1,2,4-TRIAZOLES

V. A. Lopyrev, N. N. Chipanina, L. G. Rozinova, G. I. Sarapulova, R. G. Sultangareev, and M. G. Voronkov

UDC 543.422.4.6:547.792.1.07

1,2,4-Triazoles with symmetrical tolyl substituents were obtained from the corresponding 1,3,4-oxadiazoles by reaction with formamide and subsequent hydrolysis of the resulting formyl derivatives; 1,2,4-triazoles with unsymmetrical substituents were obtained from iminoesters and hydrazides of acids. A set of bands of the triazole ring at 1470-1480, 1390, 1270-1290, 1140-1150, and 725-750 cm^{-1} and of NH vibrations at 2400-3200, 1580-1620, and 830-900 cm^{-1} are characteristic for the IR spectra of these triazoles. The UV spectra of the triazoles are characterized by phenyl ring absorption at about 200 nm and a band of electron transitions between the phenyl and triazole rings at 230-290 nm.

1,2,4-Triazole derivatives with various substituents (halo, nitro, amino, alkyl, and other groups) attached to the carbon atoms and one of the nitrogen atoms have been sufficiently adequately studied [1-4]. Not enough study has been devoted to triazoles with aromatic substituents attached to the heteroring carbon atoms.

We have synthesized a number of triazoles (Ia-p) with aromatic substituents in the 3 and 5 positions (Table 1). 3,5-Ditolyl-1,2,4-triazoles Ia,b were obtained by reaction of the easily accessible ditolyloxadiazoles [5, 6] with formamide and subsequent hydrolysis of the formyl derivatives [7]. We were unable to obtain 3,5-di(o-tolyl)-1,2,4-triazole by this method, possibly because of steric hindrance. Triazoles Ic-e were obtained by the method in [8]. Oxidation of the corresponding triazoles was used for the synthesis of 3,5-bis(carboxyphenyl)-1,2,4-triazoles If,g. Partial decomposition of the starting triazoles to give iso- or terephthalic acids occurs during the oxidation (they are the principal products in acidic media). Pure acids If,g were obtained by saponification of their esters (Ih-j). The dihydrazides (In,o) of the acids were also synthesized.

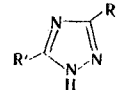
We investigated the IR and UV spectra of the synthesized compounds. The results of calculations of the vibrational spectra of triazole and its 3-chloro and bromo derivatives [4] and data from the spectroscopic studies of C-halogen-substituted triazoles and their potassium salts [9] were taken into account in the assignment of the frequencies in the IR spectra of the triazoles.

The bands of the NH stretching vibrations in the spectra of the investigated triazoles are found over a wide range of frequencies (2400-3200 cm^{-1}); this is due to the strong intermolecular association of these compounds. The bands at 1580-1620 and 830-900 cm^{-1} correspond to the NH deformation vibrations. A small long-wave shift of these bands is observed in the spectra of the N-deuterated products.

The heteroring vibrations are represented by an intense band at 1470-1480 cm^{-1}, absorption of medium intensity at 1390 cm^{-1}, and the most intense band at 1270-1290 cm^{-1}, which is

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1682-1685, December, 1977. Original article submitted December 3, 1976.

 0009-3122/77/1312-1346$07.50

TABLE 1. 3,5-Diaryl-1,2,4-triazoles Ia-p 

Compound I	R	R′	mp. °C	Found, %			Empirical formula	Calc., %			UV spectrum						Yield, %
				C	H	N		C	H	N	λ, nm			$\varepsilon_{max} \cdot 10^{-4}$			
a	*p*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	246	77,4	6,0	16,8	$C_{16}H_{15}N_3$	77,1	6,0	16,8	206	234	258	4,4	3,1	3,2	55
b	*m*-$CH_3C_6H_4$	*m*-$CH_3C_6H_4$	155	71,6	6,4	15,7	$C_{16}H_{15}N_3 \cdot H_2O$	71,9	6,4	15,7	208	244	259	4,2	2,2	2,2	36
c	*o*-$CH_3C_6H_4$	*m*-$CH_3C_6H_4$	71	76,9	5,7	16,7	$C_{16}H_{15}N_3$	77,1	6,0	16,8	203	243	277	3,3	2,2	2,2	72
d	*m*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	164	76,8	5,9	16,7	$C_{16}H_{15}N_3$	—	—	—	205	246	—	2,9	2,0		82
e	*o*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	110	76,8	5,6	16,5	$C_{16}H_{15}N_3$	—	—	—	208	238	259	4,2	3,6	3,7	74
f	*p*-$HOOCC_6H_4$	*p*-$HOOCC_6H_4$	~390	58,4	4,4	12,7	$C_{16}H_9N_3O_4 \cdot H_2O$	58,7	4,0	12,8	201	243	273	Slightly soluble			59
g	*m*-$HOOCC_6H_4$	*m*-$HOOCC_6H_4$	~380	62,6	3,3	13,2	$C_{16}H_9N_3O_4$	62,1	3,5	13,5	—	221	260	Slightly soluble			48
h	*p*-$C_2H_5OCOC_6H_4$	*p*-$C_2H_5OCOC_6H_4$	181	64,3	5,4	11,0	$C_{20}H_{19}N_3O_4$	65,7	5,2	11,5	203	246	284	2,5	2,0	3,1	70
i	*p*-$CH_3OCOC_6H_4$	*p*-$CH_3OCOC_6H_4$	273	63,0	4,4	12,0	$C_{18}H_{15}N_3O_4$	64,0	4,4	12,4	204	244	286	3,5	2,6	3,6	78
j	*m*-$CH_3OCOC_6H_4$	*m*-$CH_3OCOC_6H_4$	196	63,0	4,3	12,5	$C_{18}H_{15}N_3O_4$	—	—	—	—	—	—	—	—	—	63
k	CH_3	*p*-$CH_3C_6H_4$	169	69,1	6,3	24,2	$C_{10}H_{11}N_3$	69,3	6,4	24,3	204	—	274	5,7	—	5,7	77
l [12]	H	C_6H_5	—	—	—	—	$C_8H_7N_3$	—	—	—	—	241	—	—	1,4	—	—
m [8]	C_6H_5	C_6H_5	—	—	—	—	$C_{14}H_{11}N_3$	—	—	—	—	234	255	—	2,2	2,3	—
n	*p*-$NH_2NHCOC_6H_4$	*p*-$NH_2NHCOC_6H_4$	>460	54,5	4,9	26,5	$C_{16}H_{15}N_7O_2$	54,0	4,8	27,5	Insoluble						41
o	*m*-$NH_2NHCOC_6H_4$	*m*-$NH_2NHCOC_6H_4$	>450	—	—	30,0	$C_{16}H_{15}N_7O_2$	—	—	29,1							60
p [10]	*p*-$NO_2C_6H_4$	*p*-$NO_2C_6H_4$	—	—	—	—	$C_{14}H_{19}N_5O_4$	—	—	—							—

often split into two bands. In the spectra of triazoles Ia,m this band retains its position but becomes very weak and unsuitable for identification purposes. The band of ring pulsation vibrations at 1020-1100 cm^{-1} is of high intensity in the spectra of triazoles Ib,d. The symmetry of the orientation of the substituents has a large effect on the frequency of its maximum. Thus it is found at 1020 cm^{-1} in the spectra of symmetrical triazoles Ia,b,m, whereas it is found at 1070 cm^{-1} in the spectra of unsymmetrical Ic-e. In addition, the band at 1140-1150 cm^{-1}, which is frequently assigned to the vibrations of the triazole CH group [9], is associated with the ring stretching vibrations. Calculations show [4] that this vibration is complex and includes ring stretching vibrations and C-H bond deformation vibrations.

Bands of deformation vibrations of the CH group, the position of which is determined by the character of the substitution in the aromatic ring, are found at 600-900 cm^{-1}.

The most intense band in the spectra of the investigated triazoles is the band at 725-750 cm^{-1}, which is due to ring γ-deformation vibrations. Deuteration of triazole Ia leads to an increase in its frequency from 725 to 755 cm^{-1}. This band is of lower intensity in the spectra of triazole itself (697 cm^{-1}) and its C-halogen-substituted derivatives (715 cm^{-1}) [11].

The bands that characterize the triazole ring vibrations are also weak in the spectra of triazoles If-j, which contain carboxyl and carbalkoxy groups in the aromatic ring: the absorption of the ring γ vibrations at 720-750 cm^{-1} remains the most intense absorption in the spectra. The stretching vibrations of the OH groups in these compounds appear with a considerable increase in the absorption intensity in the left-hand wing of the broad band of stretching vibrations of the NH groups of the triazole ring (2500-2800 cm^{-1}). The bands of the stretching vibrations of the $NHNH_2$ groups of 3,5-bis(p-carboxyhydrazidophenyl)triazole In are overlapped by heteroring NH bands. The bands at 1630, 1552, and 780 cm^{-1} correspond to the NH deformation vibrations of the hydrazide grouping of this compound. This assignment was made on the basis of a comparison of the spectra of p-toluic acid hydrazide and its N-deuterated analog.

Short-wave absorption at 200 nm (ε_{max} $2.5-5\cdot10^4$) and long-wave absorption at 230-290 nm (ε_{max} $1.4-3.7\cdot10^4$) are observed in the electronic spectra of all of the investigated compounds (Table 1).

In addition to the band at about 200 nm, the spectra of monophenyl-substituted triazoles [10] and 3-amino-5-phenyltriazole [11] contain a broad band at 240-260 nm (ε_{max} 100-140 nm). Quantum-chemical calculations show that the first band is associated primarily with electron transitions in the phenyl group and that the long-wave absorption is due to two electron transitions between the phenyl and triazole rings [12]. The introduction of a methyl group in the benzene ring does not affect the extinction of the second band in the spectrum of 3-amino-5-phenyltriazole but increases it to $2\cdot10^4$ in the spectrum of 3-chloro-5-phenyltriazole. The largest absorption coefficient is observed in the spectrum of triazole Ik. The spectrum of Im contains two bands (at 234 and 255 nm), the extinction of each of which is $2.2\cdot10^4$ and corresponds to the overall absorption of two phenyl groups. A hyperchromic effect for both maxima is observed in the spectra of Ia,e,i.

The observed changes in the extinctions of the long-wave absorption of mono- and diphenyl-substituted triazoles I constitute evidence for different degrees of conjugation between the benzene and triazole rings.

EXPERIMENTAL

The unsymmetrically substituted triazoles were obtained by reaction of the iminoesters and hydrazides of the corresponding acids by the method in [8]. The physical constants and the results of elementary analysis of some of the triazoles were previously described in [12]; the data for the remaining compounds are presented in the present paper (Table 1). The IR spectra of KBr pellets and Nujol suspensions of the compounds were obtained with a UR-20 spectrometer at 400-3700 cm^{-1}. The electronic absorption spectra of ethanol solutions of the compounds were obtained with a Specord UV-vis spectrophotometer with quartz cuvettes. The purity of the substances was monitored by repeated recrystallization from suitable solvents and by determination of the melting points.

3,5-Ditolyl-1,2,4-triazoles (Ia,b). A mixture of 30 mmole of the corresponding 2,5-ditolyl-1,3,4-oxadiazole [5] and 70 ml of formamide was heated with stirring to 170-180°C

for 8 h, after which it was cooled. The mixture began to crystallize as it was cooled. It was treated with water, and the precipitate was removed by filtration, washed with water, and refluxed with 10% HCl. It was washed once again with water, dried, and recrystallized from Methyl Cellosolve.

3,5-Bis(carboxyphenyl)-1,2,4-triazoles (If,g). A) A mixture of 12 mmole of triazole Ia or Ib, 56 mmole of $KMnO_4$, 1-2 g of $NaHCO_3$, and 100 ml of H_2O was heated for 8 h, after which the MnO_2 was removed by filtration and washed with hot water. The filtrate and the wash waters were evaporated to 50 ml, and dilute HCl was added with stirring. The resulting precipitate was removed by filtration, washed with water, and dried. The product was reprecipitated from a hot solution in Methyl Cellosolve by the addition of water.

B) The calculated amount of 10% alcoholic KOH was added dropwise in the course of 15-20 min to a hot solution of 20 mmole of triazole Ii or Ij in methanol, after which the mixture was cooled and acidified with HCl. The resulting precipitate was removed by filtration and washed with water.

3,5-Bis(carbalkoxyphenyl)-1,2,4-triazoles (Ih-j). A) A mixture of 13 mmole of acid If or Ig, 15 ml of methanol or ethanol, and 0.5 ml of concentrated H_2SO_4 was refluxed for 4 h, after which it was cooled and neutralized to pH 6-7 with alcoholic KOH solution. The resulting ester was recrystallized from methanol.

B) Excess dry HCl was bubbled into a suspension of 78 mmole of the dipotassium salt of If in 90 ml of methanol, after which the mixture was poured into water, and the precipitate was removed by filtration and washed with water. Ester Ii was recrystallized from methanol.

3,5-Bis(carbohydrazidophenyl)-1,2,4-triazoles (In,o). A mixture of 10 mmole of ester Ii or Ij and 50 ml of hydrazine hydrate was refluxed for 6 h, after which the excess hydrazine hydrate was removed by vacuum distillation. When the residue was cooled, it yielded fine acicular crystals, which were recrystallized from formamide.

LITERATURE CITED

1. V. V. Mel'nikov, V. V. Stolpakova, S. A. Zacheslavskii, M. S. Pevzner, and B. V. Gidaspov, Khim. Geterotsikl. Soedin., No. 10, 1423 (1973).
2. V. V. Mel'nikov, V. V. Stolpakova, and B. V. Gidaspov, Khim. Geterotsikl. Soedin., No. 11, 1567 (1972).
3. V. V. Mel'nikov, V. V. Stolpakova, M. S. Pevzner, and B. V. Gidaspov, Khim. Geterotsikl. Soedin., No. 5, 707 (1973).
4. G. G. Skvortsova, E. S. Domnina, L. P. Makhno, V. K. Voronov,and D. D. Taryashinova, Khim. Geterotsikl. Soedin., No. 11, 1566 (1973).
5. CIBA, Ltd., British Patent No. 896219 (1962); Chem. Abstr., 58, 12574 (1963).
6. Ya. A. Levin and M. S. Skorobogatova, Khim. Geterotsikl. Soedin., No. 6, 1114 (1967).
7. H. Hoegl, US Patent No. 3287116 (1966); Chem. Abstr., 66, 66751 (1967).
8. I. Ya. Postovskii and N. N. Vereshchagina, Zh. Obshch. Khim., 29, 2139 (1959).
9. V. Ya. Grinshtein, A. A. Strazdin', and A. K. Grinval'de, Khim. Geterotsikl. Soedin., No. 2, 248 (1970).
10. K. T. Potts, Chem. Rev., 61, 87 (1961).
11. M. G. Voronkov, V. A. Lopyrev, N. N. Chipanina, V. V. Makarskii, L. V. Sherstyannikova, O. A. Zadyadko, E. F. Shibanova, T. N. Vereshchagina, and Yu. L. Frolov, Khim. Geterotsikl. Soedin., No. 4, 546 (1977).
12. M. G. Voronkov, V. A. Lopyrev, N. N. Chipanina, V. V. Makarskii, O. A. Zasyadko, L. V. Sherstyannikova, E. F. Shibanova, T. N. Vereshchagina, and Yu. L. Frolov, Khim. Geterotsikl. Soedin., No. 5, 698 (1977).