ISSN 1070-4280, Russian Journal of Organic Chemistry, 2013, Vol. 49, No. 6, pp. 895–903. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © A.S. Morkovnik, T.A. Kuz'menko, L.N. Divaeva, G.S. Borodkin, 2013, published in Zhurnal Organicheskoi Khimii, 2013, Vol. 49, No. 6, pp. 909–917.

2-Aryl(hetaryl)-4*H*-[1,2,4]triazolo[1,5-*a*]benzimidazoles

A. S. Morkovnik, T. A. Kuz'menko, L. N. Divaeva, and G. S. Borodkin

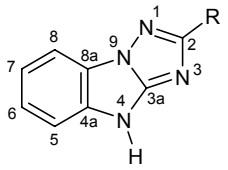
Research Institute of Physical and Organic Chemistry, Southern Federal University,
pr. Stachki 194/2, Rostov-on-Don, 344090, Russia
e-mail: asmork2@ipoc.rsu.ru

Received September 19, 2012

Abstract—2-(4-Methylphenyl)-4*H*-[1,2,4]triazolo[1,5-*a*]benzimidazole and its previously unknown 2-(2-furyl)- and 2-(2-thienyl)-substituted analogs were synthesized by cyclization of benzimidazole-1,2-diamine with the corresponding carboxylic acid chlorides. The IR, ^{1}H, ^{13}C, and ^{15}N NMR, and mass spectra of the cyclization products in combination with the results of quantum-chemical calculations of NMR chemical shifts showed radical differences of [1,2,4]triazolo[1,5-*a*]benzimidazoles having no substituent on N^4 from the recently reported low-melting products of oxidation of 2-amino-1-arylmethylideneaminobenzimidazoles with (diacetoxy-λ^3-iodanyl)benzene, which, as we believe, were erroneously assigned analogous structure.

DOI: 10.1134/S107042801306016X

Kumar et al. [1] recently reported on the oxidation of 2-amino-1-(arylmethylideneamino)benzimidazoles with (diacetoxy-λ^3-iodanyl)benzene; the oxidation products were assigned the structure of 2-aryl[1,2,4]-triazolo[1,5-*a*]benzimidazoles **Ia**–**Id** on the basis of their IR, ^{1}H and ^{13}C NMR, and mass spectra.



Ia–Id

R = 4-MeC_6H_4 (**a**), 4-$MeOC_6H_4$ (**b**), 4-ClC_6H_4 (**c**), 4-BrC_6H_4 (**d**).

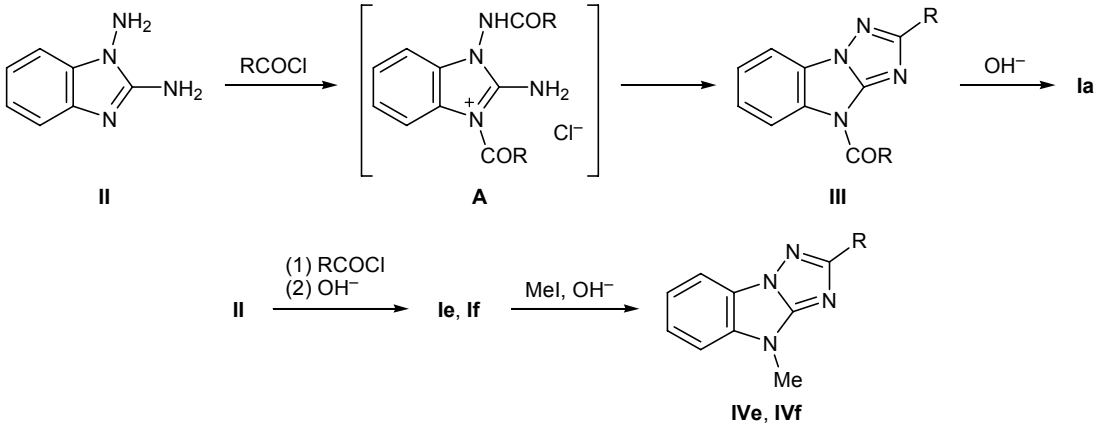
However, these compounds had unexpectedly low melting points (116–143°C, depending on the aryl substituent [1]), which were lower by approximately 200°C than those of structurally identical compounds obtained by pyrolysis of 2-tetrazolylbenzimidazoles [2]. The parent compound of this series, [1,2,4]triazolo[1,5-*a*]benzimidazole and its 2-methyl- and 2-phenyl-substituted derivatives [3, 4] synthesized by cyclization of benzimidazole-1,2-diamine (**II**) with carboxylic acid derivatives are characterized by fairly high melting points. Furthermore, it is well known that structurally related *N*-unsubstituted [1,2,4]triazolo-[4,3-*a*]benzimidazoles [5], pyrazolo[1,5-*a*]benzimidazoles [6, 7], and imidazo[1,2-*a*]benzimidazoles [8] are high-melting substances, which may be due to their ability to form H-dimers [9].

Nevertheless, despite citing the data of [2–4], no comments were given in [1] on so evident inconsistency between the most important physical characteristic of the synthesized compounds and those of known analogs. The present communication is anticipated to clarify the problem which properties are in fact intrinsic to triazolobenzimidazoles **I**.

For this purpose, we synthesized 2-(4-methylphenyl)[1,2,4]triazolo[1,5-*a*]benzimidazole (**Ia**), which was differently characterized in [1, 2], by an independent method, cyclization of diamine **II** with *p*-toluoyl chloride. This reaction, as well as the reaction with carboxylic acid anhydrides [4], is likely to involve intermediate formation of quaternary salt **A**, since the primary product was 4-acyl derivative **III** (Scheme 1). The subsequent hydrolysis of **III** gave the corresponding *N*-unsubstituted triazolobenzimidazole **Ia** with mp 317–318°C, which is consistent with the data of [2]. Unlike low-melting compound described in [1], which was readily soluble in chloroform and in hexane–ethyl acetate (9:1), the cyclization product synthesized by us was poorly soluble in most organic solvents and was purified by recrystallization from DMF.

With a view to extend the substrate series, by reaction of diamine **II** with 2-furoyl and 2-thenoyl chlorides we synthesized previously unknown 2-hetaryl [1,2,4]triazolo[1,5-*a*]benzimidazoles **Ie** and **If** which

Scheme 1.



III, R = 4-MeC_6H_4; **I**, **IV**, R = 2-furyl (**e**), 2-thienyl (**f**).

also melted at high temperature and, like other triazolo[1,5-*a*]benzimidazoles [4], were smoothly alkylated with methyl iodide in alkaline medium to produce 4-methyl derivatives **IVe** and **IVf**.

Unfortunately, we failed to obtain crystals of **I** and **III** suitable for X-ray analysis, and their structure was studied by IR spectroscopy, mass spectrometry, and one- and two-dimensional ^{1}H, ^{13}C, and ^{15}N NMR techniques. In order to interpret their NMR spectra, the ^{1}H, ^{13}C, and ^{15}N chemical shifts of the 4*H*-tautomers (which were shown [4] to dominate for triazolo[1,5-*a*]-benzimidazoles) of **Ia**, acyl derivative **III**, and two

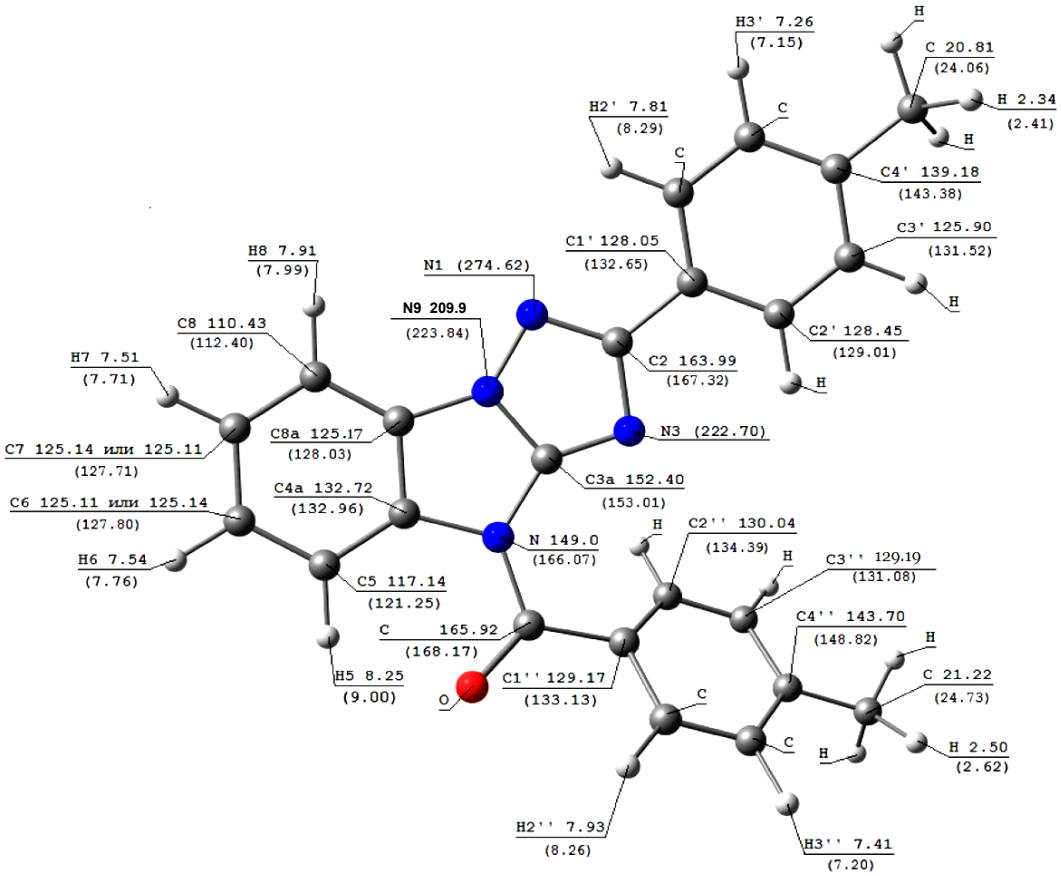
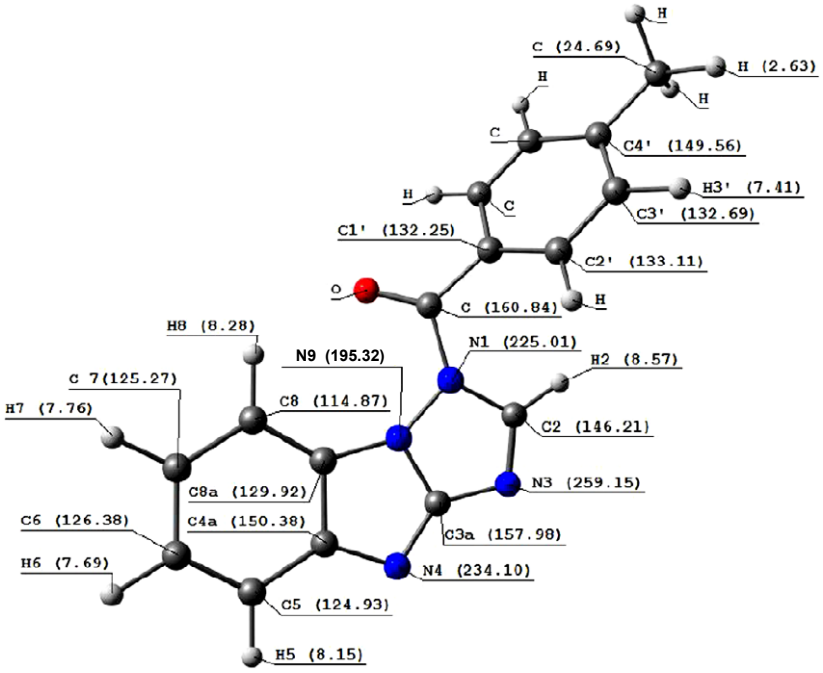
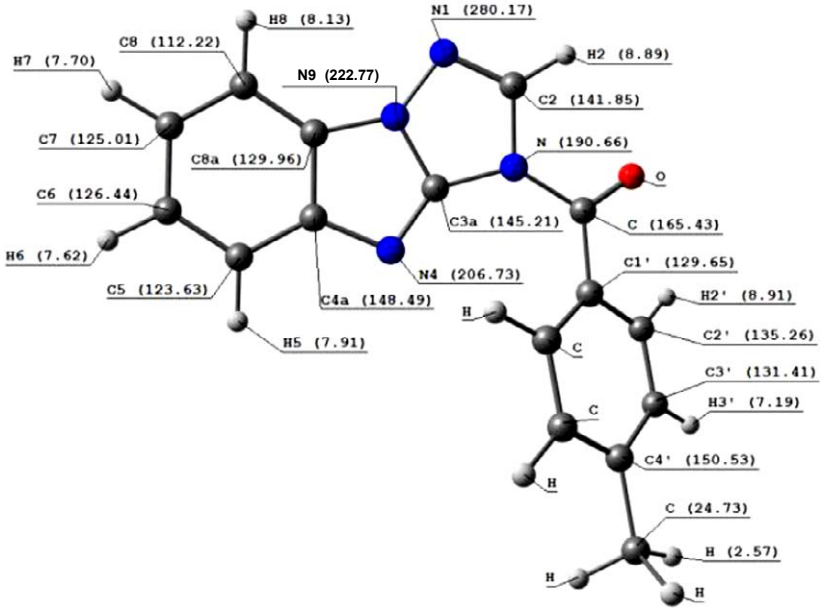


Fig. 1. Experimental and calculated (in parentheses) ^{1}H, ^{13}C, and ^{15}N NMR chemical shifts of 4-(4-methylbenzoyl)-2-(4-methylphenyl)-4*H*-[1,2,4]triazolo[1,5-*a*]benzimidazole (**III**).



V



VI

Fig. 2. Calculated ^{1}H, ^{13}C, and ^{15}N NMR chemical shifts of model 1- and 3-acyl-substituted 4*H*-[1,2,4]triazolo[1,5-*a*]benzimidazoles **V** and **VI**.

model structures **V** and **VI** with an aroyl group on N^1 and N^3 (Figs. 1–3) were calculated by the density functional-based SOS DFPT method using IGLO-II basis set [10] without considering solvent effects. The geometric parameters were preliminarily optimized at the DFT B3LYP/6-31G** level of theory. To simplify the calculation procedure, only one conformer of each compound was selected among those possible; in particular, such conformer of acyl derivative **III** was that in which the 5-H proton is as close as possible to the C=O group and is therefore deshielded to the strongest extent.

The IR spectrum of *N*-acyl derivative **III** contains a strong carbonyl stretching vibration band at

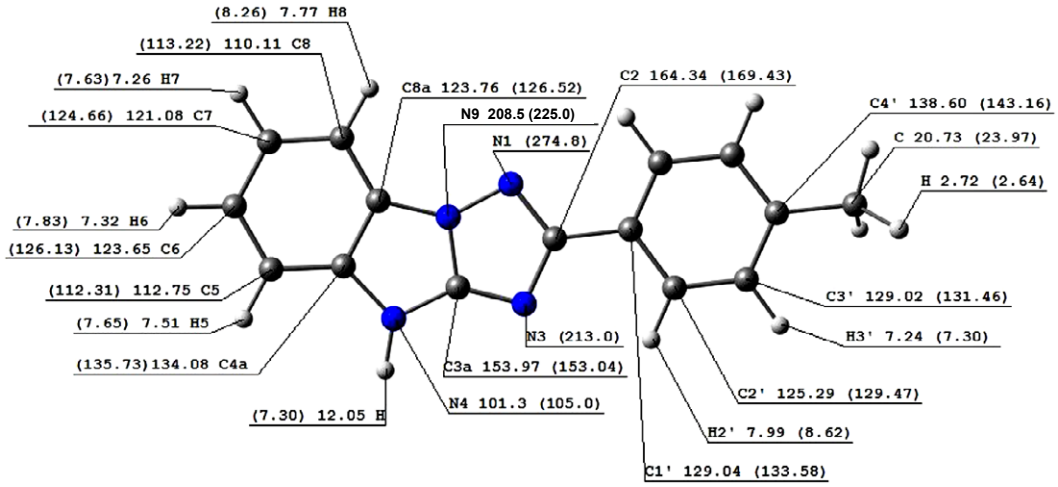


Fig. 3. Experimental and calculated (in parentheses) ^{1}H, ^{13}C, and ^{15}N NMR chemical shifts of 2-(4-methylphenyl)-4*H*-[1,2,4]triazolo-[1,5-*a*]benzimidazole (**Ia**).

1696 cm^{-1}. No such band is present in the spectrum of *N*-unsubstituted triazolobenzimidazole **Ia**, but a broad band is observed in the region 2620–3017 cm^{-1} due to stretching vibrations of the NH group. A signal assignable to the NH proton (δ ~12 ppm) was detected in the ^{1}H NMR spectra of **Ia**, **Ie**, and **If**, whereas Kumar et al. [1] noted the absence of NH signal in the NMR spectra.

The ^{1}H NMR spectrum of 4-(*p*-toluoyl) derivative **III** (Fig. 1) is very similar to the spectrum of known 4-acetyl[1,2,4]triazolo[1,5-*a*]benzimidazole where the position of the acetyl group was reliably determined [4]. Multiplet signals from 6-H and 7-H in the spectrum of **III** (δ 7.54 and 7.51 ppm,* respectively) also overlapped each other, and the 5-H and 8-H signals were displaced downfield due to magnetic anisotropy of the C=O group and N^{1} atom. According to the data of two-dimensional NMR spectroscopy and quantum-chemical calculations, the 5-H proton of **III** and 8-H in **I** and **IV** should resonate in a weaker field.

The calculated chemical shifts of protons in compound **III** differ from the corresponding experimental values by ~0.1–0.2 ppm. Exceptions are 5-H and *ortho* protons in the aryl and aroyl groups, for which δ_{calc} values are overestimated by 0.75, 0.48, and 0.33 ppm, respectively. This may be related to specific features of the selected conformer and slanting potential energy surface of the molecule in the region corresponding to rotation of the tolyl groups about C–C bonds.

* The 6-H and 7-H signals of **III** and **I** were identified taking into account that these protons showed in the ^{15}N–^{1}H HMBC spectra correlations with the ^{15}N nuclei in the *meta* rather than *para* position.

The ^{13}C NMR spectrum of acyl derivative **III** interpreted with account taken of the calculation data and two-dimensional spectra contains 19 expected signals from carbon nuclei (or couples of carbon nuclei) whose chemical shifts were as a rule lower by 2–4 ppm than the calculated values (Fig. 1). The difference may be attributed to errors of the calculation methods and neglect of solvation effects. It was impossible to distinguish between the C^{6} and C^{7} signals at δ_C 125.11 and 125.14 ppm; due to insignificant difference in the chemical shifts, common cross peaks with protons were observed in the two-dimensional spectra, and comparison of the experimental and calculated chemical shifts is rendered incorrect. The calculations also predicted similarity of the chemical shifts of C^{6}/C^{7} and 6-H/7-H in **III**; the corresponding differences Δδ should be 0.09 and 0.05 ppm, respectively (Fig. 1). The C^{2} and C=O carbon atoms (δ_C 163.99 and 165.92 ppm) which do not display cross-peaks with protons in the ^{1}H–^{13}C HMBC spectrum were identified only on the basis of the calculation data. The aromatic carbons atoms in the two aryl substituents were assigned by analysis of the ^{1}H–^{13}C HMBC and ^{1}H–^{1}H COSY spectra.

It was impossible to determine the position of the acyl group in molecule **III** on the basis of two-dimensional ^{13}C–^{1}H and ^{1}H–^{1}H NMR spectra because of the lack of cross-peaks between nuclei in the acyl group and triazolobenzimidazole system. Therefore, the structure of **III** as 4-acyl derivative was confirmed by comparing the experimental ^{1}H, ^{13}C, and ^{15}N chemical shifts with those calculated for structure **III** and model structures **V** and **VI** where the acyl group is

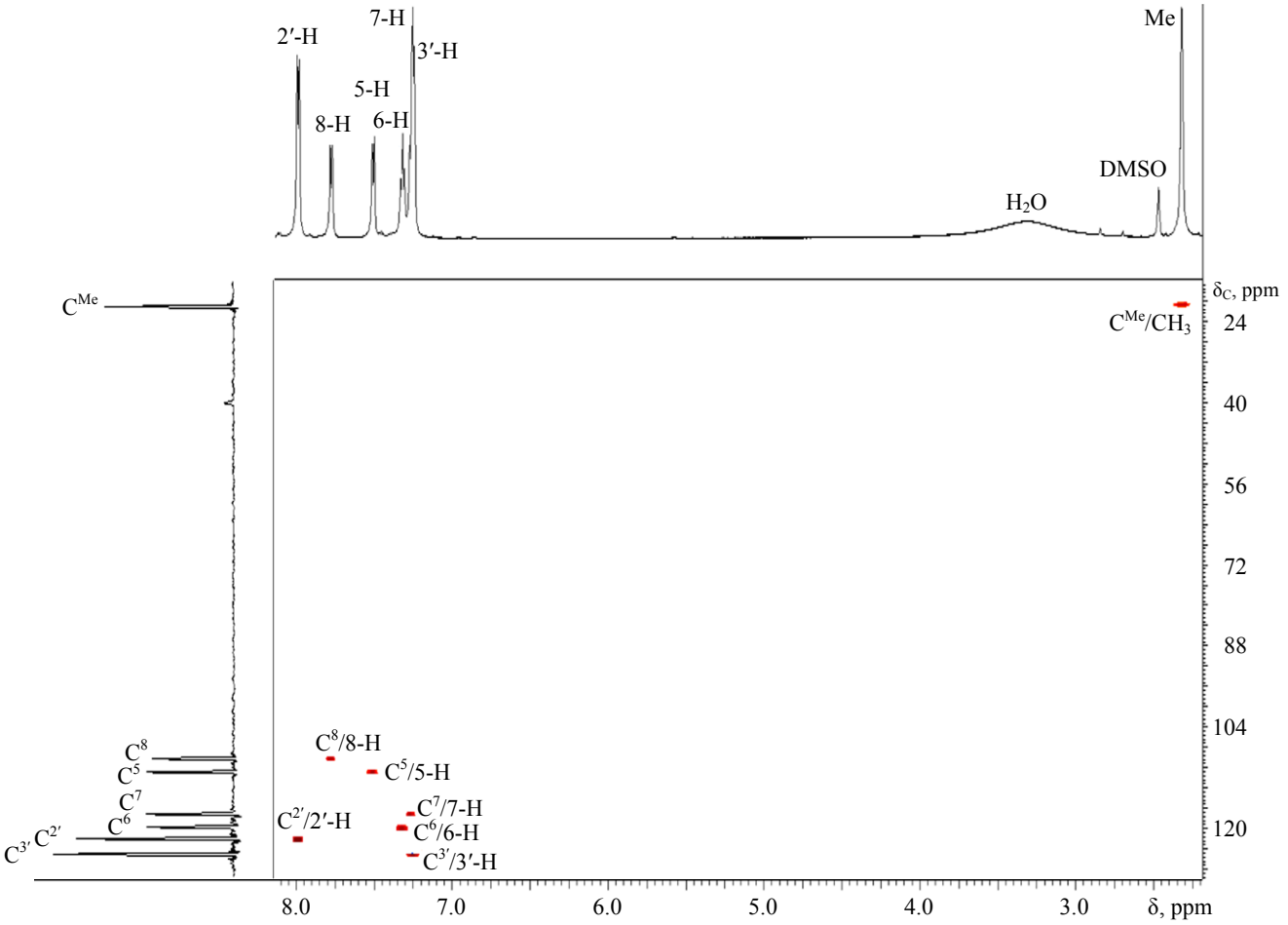


Fig. 4. Two-dimensional ^{1}H–^{13}C HSQC spectrum of 2-(4-methylphenyl)-4*H*-[1,2,4]triazolo[1,5-*a*]benzimidazole (**Ia**).

attached to N^1 and N^3, respectively (Fig. 2). In this respect, the most indicative were the ^{15}N NMR data for N^4. The N^4 atom in 4-substituted triazolobenzimidazoles is sp^3-hybridized, and in 1- and 3-substituted derivatives, sp^2-hybridized. As followed from the ^{15}N–^{1}H HMBC spectrum,** the chemical shift of N^4 is δ_N 149.0 ppm. This value is much closer to that calculated for structure **III** (δ_N 166.1 ppm) than to those found for model 1- and 3-acyl-substituted isomers (δ_N 234.1 and 209.9 ppm, respectively; Fig. 2). In this case, the reduced accuracy of the calculations may be rationalized by strong effect of solvation on the chemical shifts of nitrogen nuclei [11], which is untypical of carbon nuclei.

The cyclization product of 1,2-bis(triphenyl-λ^5-phosphanylideneamino)benzimidazole with *p*-toluoyl chloride, which was assigned previously [12] the structure of 1- or 3-(4-methylbenzoyl)-2-(4-methylphenyl)-[1,2,4]triazolo[1,5-*a*]benzimidazole, is most likely to be 4-acyl derivative **III**, for it is characterized by the same melting point and almost identical IR and ^{1}H and ^{13}C NMR spectra.

Unlike 4-acyl derivative **III**, *N*-unsubstituted compounds **I** displayed larger differences in the chemical shifts of 6-H and 7-H and especially of C^6 and C^7; e.g., for **Ia**: $\Delta\delta$(6-H/7-H) = 0.06, $\Delta\delta(C^6/C^7)$ = 2.57 ppm. In this case, signals from 6-H and 7-H with similar multiplicities and spin–spin coupling constants, as well as signals from C^6 and C^7, can be readily identified using the two-dimensional HSQC (Fig. 4) and HMBC techniques. The C^{4a}/6-H cross-peak in the ^{13}C–^{1}H HMBC spectrum was much more intense than the cross-peak of C^{4a} with more distant 7-H proton, and the ^{15}N–^{1}H HMBC spectrum contained N^4/6-H and N^9/7-H cross peaks, whereas neither N^4/7-H nor N^9/6-H coupling was observed.

Comparison of the NMR spectra of triazolo[1,5-*a*]-benzimidazoles **I** synthesized in the present work with

** The spectrum contained only signals of N^4 and N^9 whose cross-peaks with protons were considerably stronger than those of more distant N^1 and N^3 nuclei.

the spectra of compounds described in [1] revealed considerable differences in the spectral regions corresponding directly to the heterocyclic system. The ^{1}H NMR spectra of our samples lacked aromatic proton signals downfield from δ 7.9 ppm (Fig. 4), whereas the compounds described in [1] displayed two signals in the region δ 8.1–8.5 ppm, which were assigned to 5-H and 8-H. So strong downfield shift of signals from protons in the benzimidazole fragment was observed for neither known triazolobenzimidazoles [4, 12, 13] nor structurally related 2-arylpyrazolo[1,5-*a*]benzimidazoles [7] and imidazo[1,2-*a*]benzimidazoles [9].

The chemical shifts of C^5 and C^8 in the compounds under comparison were also considerably different. According to the calculations, the C^5 and C^8 nuclei in triazolo[1,5-*a*]benzimidazoles should experience enhanced shielding, and their signals should therefore be shifted appreciably upfield. In particular, the calculated chemical shifts of C^5 and C^8 in **Ia** are δ_C 112.75 and 113.22 ppm, respectively; these values are considerably lower than the next following calculated chemical shift of C^7 (δ_C 121.08 ppm). The theoretical predictions are completely confirmed by the experimental data not only for compounds **I** and **IV** but also for other triazolobenzimidazoles reported previously [12, 14]. In the molecule of triazolobenzimidazole **Ia**, the most shielded carbon nuclei are C^8 (δ_C 110.11 ppm), C^5 (112.75), and C^7 (121.08), and the carbon chemical shifts in known 2-methylaminotriazolobenzimidazole [12] increase in the series (δ_C, ppm): C^8 (108.28) < C^5 (111.95) < C^6 (120.56) < C^7 (121.23) < C^{8a} (124.52) < C^{4a} (132.49) < C^{3a} (152.87) < C^2 (168.32), which almost coincides with that observed for compounds **I** and **IV**. No increased shielding of carbon nuclei was noted for the compounds described in [1]. The two most upfield carbon signals from the heteroaromatic system, which were not assigned in [1], were located at about δ_C 128 ppm, closely to signals from other carbon nuclei (δ_C ~129 ppm).

The structure of compounds **I** as 2-substituted triazolobenzimidazoles is also convincingly confirmed by the mass spectrum of **Ia**. The spectrum contains a strong molecular ion peak with *m*/*z* 248 (100%) and fragment ion peaks corresponding to protonated and nonprotonated nitrile species which are typical of nitrogen-containing heterocycles with an endocyclic N–N bond [15].

Thus, analysis of published data on [1,2,4]triazolo-[1,5-*a*]benzimidazoles and the results of our present study convincingly demonstrate erroneous assignment of the triazolobenzimidazole structure to the products obtained by oxidation of 2-amino-1-arylmethylideneaminobenzimidazoles with (diacetoxy-λ^3-iodanyl)benzene [1]. Therefore, further study on the structure of these compounds seems to be intriguing.

EXPERIMENTAL

The IR spectra were recorded on a Varian Excalibur 3100 FT-IR spectrometer from solid samples. The ^{1}H NMR spectra of **Ie** and **IVf** were obtained on a Varian Unity-300 spectrometer (300 MHz), and the ^{1}H, ^{13}C (with decoupling from protons), and ^{15}N NMR spectra of the other compounds were measured on a Bruker Avance 600 instrument; DMSO-d_6 was used as solvent and reference (for ^{1}H and ^{13}C). The ^{15}N chemical shifts are given relative to ammonia. Signals in the NMR spectra were assigned using ^{1}H–^{1}H COSY [16, 17], ^{1}H–^{13}C HSQC (hsqcetgp) [18], and HMBC (^{1}H–^{13}C and ^{1}H–^{15}N; hmbcgpndqf) techniques [19, 20]; sample concentration 0.1 M, operating frequencies 600 (^{1}H), 150 (^{13}C), and 60 MHz (^{15}N); PABBO *Z*-gradient probe; temperature 303 K; the data were acquired using standard multipulse sequences. The mass spectrum of **Ia** (electron impact, 70 eV) was recorded on a Finnigan MAT INCOS 50 mass spectrometer with direct sample admission into the ion source.

The progress of reactions was monitored, and the purity of the products was checked, by TLC on aluminum oxide plates (activity grade III) using chloroform as eluent; spots were visualized by treatment with iodine vapor.

The geometric parameters of molecules **III**, **V**, and **VI** were optimized using Firefly 7.1G program [21] partly based on the Gamess code [22]. The energy minima were localized by calculating force constant matrices. The chemical shifts were calculated using DeMon 2K 1.0.4 and DeMonMAG [23] with the PW91PW91 functional and IGLO-II basis set.

1*H*-Benzimidazole-1,2-diamine (**II**) was synthesized according to the procedure described in [4]; carboxylic acid chlorides were commercial products (Aldrich).

(4-Methylphenyl)[2-(4-methylphenyl)-4*H*-[1,2,4]-triazolo[1,5-*a*]benzimidazol-4-yl]methanone (III). A mixture of 0.75 g (5 mmol) of compound **II** and 2.7 ml (20 mmol) of *p*-toluoyl chloride was heated for 2 h at 160°C. The mixture was cooled, treated with 25 ml of water, and left to stand for 4–5 h. The precipitate was filtered off and washed on a filter with water,

a small amount of alcohol, and diethyl ether (to remove excess *p*-toluic acid). Yield 1.60 g (87%), colorless crystals, mp 234–235°C (from toluene). IR spectrum, ν, cm^{-1}: 1696 s (C=O), 1554 m, 1425 s, 1309 v.s, 1074 s, 754 v.s, 737 v.s. ^{1}H NMR spectrum,*** δ, ppm: 2.34 s (3H, 4′-CH_3), 2.48 s (3H, 4″-CH_3), 7.25–7.27 m (2H, 3′-H, 5′-H), 7.39–7.43 m (2H, 3″-H, 5″-H), 7.51 t.d (1H, 7-H, *J* = 7.8, 1.5 Hz), 7.54 t.d (1H, 6-H, *J* = 7.7, 1.3 Hz), 7.80–7.82 m (2H, 2′-H, 6′-H), 7.91 d.d.d (1H, 8-H, *J* = 7.8, 1.6, 0.8 Hz), 7.94–7.98 m (2H, 2″-H, 6″-H), 8.25 d.d.d (1H, 5-H, *J* = 7.9, 1.3, 0.7 Hz). Two-dimensional HMBC spectra, δ, ppm (intensity,**** cross-peak): ^{13}C–^{1}H: 21.03, 7.26 (638, 4′-CH_3/3′-H); 21.44, 7.41 (484, 4″-CH_3/3″-H); 110.33, 7.51 (20, C^8/7-H); 110.50, 7.54 (125, C^8/6-H); 117.30, 7.54 (7.8, C^5/7-H); 117.31, 7.51 (1.0 C^5/6-H); 125.12, 7.51 (495, C^7/6-H); 125.12, 8.24 (1245, C^7/5-H, C^6/5-H, C^{8a}/5-H, common peak); 125.13, 7.54 (23, C^6/7-H, C^{8a}/7-H); 125.13, 7.92 (36, C^6/8-H, C^7/8-H, C^{8a}/8-H); 125.90, 7.80 (473, $C^{3'}$/2′-H); 125.95, 7.80 (473, C^{8a}/7-H); 128.40, 2.48 (38123, $C^{3''}$/4″-CH_3); 128.40, 7.26 (2920, $C^{1'}$/3′-H); 129.18, 7.41 (2954, $C^{1''}$/3″-H); 129.20, 2.34 (34967, $C^{3'}$/4′-CH_3); 132.72, 7.52 (920, C^{4a}/6-H, C^{4a}/7-H); 132.82, 7.92 (95, C^{4a}/8-H); 139.15, 7.81 (4016, $C^{4'}$/2′-H); 139.29, 2.34 (21559, $C^{4'}$/4′-CH_3); 143.75, 7.93 (3514, $C^{4''}$/2″-H); 143.86, 2.48 (23225, $C^{4''}$/4″-CH_3); 164.08, 7.81 (2154, C^2/2′-H); 165.54, 7.92 (2464, C=O/2″-H); ^{15}N–^{1}H: 148.21, 7.51 (3.5, N^4/6-H); 209.60, 7.91 (1.0, N^9/8-H); 209.82, 7.55 (1.2, N^9/7-H). Found, %: C 75.27; H 4.83; N 15.45. $C_{23}H_{18}N_4O$. Calculated, %: C 75.39; H 4.95; N 15.29.

2-(4-Methylphenyl)-4*H*-[1,2,4]triazolo[1,5-*a*]-benzimidazole (Ia). A suspension of 1.10 g (3 mmol) of 4-acyl derivative **III** in 30 ml of a 10% solution of sodium hydroxide was heated for 0.5 h under reflux until it became homogeneous. The solution was cooled and acidified with concentrated aqueous HCl to pH 3–4, and the precipitate was filtered off and thoroughly washed with water. Yield 0.68 g (92%), colorless fiber-like crystals, mp 317–318°C (from DMF); published data: mp 116–118°C [1], 330–331°C [2]. The product was sparingly soluble in alcohol, chloroform, and water. IR spectrum, ν, cm^{-1}: 3017–2620 w (NH), 1602 s, 1468 s, 1225 m, 1107 m, 819 s, 741 v.s. ^{1}H NMR spectrum, δ, ppm: 2.32 s (3H, Me), 7.24 d (2H, 3′-H, 5′-H, *J* = 8.0 Hz), 7.26 t (1H, 7-H, *J* = 7.7 Hz), 7.32 t (1H, 6-H, *J* = 7.7 Hz), 7.51 d (1H, 5-H, *J* = 8.1 Hz), 7.77 d (1H, 8-H, *J* = 8.1 Hz), 7.99 d (2H, 2′-H, 6′-H, *J* = 8.0 Hz), 12.05 br.s (1H, NH). Two-dimensional HMBC spectra, δ, ppm (intensity, cross-peak), ^{13}C–^{1}H: 20.62, 7.99 (1.5, 4′-CH_3/2′-H); 20.90, 7.26 (85.3, 4′-CH_3/3′-H); 110.33, 7.51 (6.7, C^8/5-H); 110.50, 7.33 (76.6, C^8/6-H); 110.65, 7.26 (15.1, C^8/7-H); 113.04, 7.27 (83.5, C^5/7-H); 113.05, 7.32 (13.2, C^5/6-H); 113.07, 7.78 (3.8, C^5/8-H); 121.50, 7.51 (67.2, C^7/5-H); 121.51, 7.32 (3.9, C^7/6-H); 124.02, 7.78 (57.5, C^6/8-H); 124.04, 7.32 (10.4, C^{8a}/6-H); 124.06, 7.51 (74.4, C^6/5-H); 124.11, 7.26 (77.0, C^6/7-H, C^{8a}/7-H); 126.30, 2.32 (11.4, $C^{2'}$/4′-CH_3); 126.31, 7.25 (13.2, $C^{2'}$/3′-H); 129.04, 7.25 (244.4, $C^{1'}$/3′-H); 129.38, 7.98 (9.8, $C^{3'}$/2′-H); 129.39, 2.32 (898.4, $C^{3'}$/4′-CH_3); 134.12, 7.26 (7.0, C^{4a}/7-H); 134.41, 7.33 (67.5, C^{4a}/6-H); 134.42, 7.78 (61.2, C^{4a}/8-H); 138.93, 2.32 (595.8, $C^{4'}$/4′-CH_3); 138.95, 7.99 (117.5, $C^{4'}$/2′-H); 138.98, 7.25 (1.0, $C^{4'}$/3′-H); C^{3a} showed no cross-peaks; 164.61, 7.99 (80.9, C^2/2′-H); 164.75, 2.32 (6.2, C^2/4′-CH_3); 164.76, 7.25 (1.6, C^2/3′-H); ^{15}N–^{1}H: 101.29, 7.51 (15.5, N^4/5-H); 101.30, 7.32 (1.0, N^4/6-H); 208.45, 7.26 (2.2, N^9/7-H); 208.45, 7.77 (19.1, N^9/8-H); 208.98, 7.51 (3.3, N^9/5-H). Mass spectrum, *m*/*z* (I_{rel}, %): 248 (100) $[M]^+$, 222 (1.7) $[M - CH{\equiv}CH]^+$, 208 (0.8) $[M - Me{-}C{\equiv}CH]^+$, 182 (0.2) $[M - CH{\equiv}CH - MeC{\equiv}CH]^+$, 158 (0.8) $[M - p\text{-}MeC_6H_4]^+$, 144 (1.7) $[M - C_6H_4N_2]^+$, 131 (8.3) $[M - p\text{-}MeC_6H_4\text{-}CN]^+$, 118 (10.0) $[p\text{-}MeC_6H_4C{\equiv}NH]^+$, 116 (4.2) $[NCC_6H_4CH_2]^+$, 104 (5.0) $[C_6H_4N_2]^+$, 102 (4.9) $[PhNC]^+$, 91 (4.2) $[C_7H_7]^+$, 90 (4.1) $[C_7H_6]^+$, 77 (3.3) $[Ph]^+$, 65 (1.7) $[C_5H_5]^+$, 51 (1.7) $[C_4H_3]^+$. Found, %: C 72.61; H 4.73; N 22.38. $C_{15}H_{12}N_4$. Calculated, %: C 72.56; H 4.87; N 22.57.

2-(2-Furyl)-4*H*-[1,2,4]triazolo[1,5-*a*]benzimidazole (Ie). A mixture of 0.75 g of diamine **II** and 2 ml (20 mmol) of 2-furoyl chloride was fused for 2 h at 150–160°C. The melt was cooled and treated with 25 ml of 10% aqueous sodium hydroxide, the mixture was heated for 15–20 min under reflux until it became homogeneous, 0.1 g of activated charcoal was added, and the mixture was heated for 5–7 min under reflux and filtered while hot. The filtrate was cooled and acidified with concentrated aqueous HCl to pH 3–4, and the precipitate (a mixture of compound **Ie** and 2-furoic acid) was thoroughly washed on a filter with water, 3–5 ml of cold alcohol, and diethyl ether. Yield 0.95 g (85%), mp 295–296°C (from EtOH). IR spectrum, ν, cm^{-1}: 3140–2530 br (NH), 1602 w, 1585 s, 1513 m, 1310 s, 1223 s, 1170 s, 738 v.s. ^{1}H NMR spectrum, δ, ppm: 6.55 d.d (1H, 4′-H, *J* = 3.3, 1.8 Hz),

*** Hereinafter, primed locants refer to the substituent on C^2, and double-primed, to the substituent on N^4.

**** Given are intensities relative to the weakest cross-peak.

6.93 d.d (1H, 3′-H, J = 3.3, 0.9 Hz), 7.22–7.32 m (2H, 6-H, 7-H), 7.47 d (1H, 5-H, J = 7.5 Hz), 7.65 d.d (1H, 5′-H, J = 1.8, 0.9 Hz), 7.74 d (1H, 8-H, J = 7.8 Hz), 12.25 s (1H, NH). Found, %: C 64.35; H 3.72; N 24.78. $C_{12}H_8N_4O$. Calculated, %: C 64.28; H 3.60; N 24.99.

2-(2-Thienyl)-4*H*-[1,2,4]triazolo[1,5-*a*]benzimidazole (If) was synthesized as described above for **Ie** from diamine **II** and 2-thenoyl chloride. Yield 82%, light yellow crystals, mp 336–337°C (from DMF). ^{1}H NMR spectrum, δ, ppm: 7.17 d.d (1H, 3′-H, J = 5.0, 3.6 Hz), 7.30 distorted d.d.d (1H, 7-H, J = 7.9 Hz), 7.36 distorted d.d.d (1H, 6-H, J = 7.7 Hz), 7.55 d (1H, 5-H, J = 8.0 Hz), 7.63 d.d (1H, 2′-H, J = 5.0, 1.2 Hz), 7.69 d.d (1H, 4′-H, J = 3.6, 1.2 Hz), 7.82 d (1H, 8-H, J = 7.8 Hz), 12.41 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 110.34 (C^8), 112.96 (C^5), 121.37 (C^7), 123.64 (C^{8a}), 123.94 (C^6), 126.13 ($C^{3'}$), 127.28 ($C^{5'}$), 127.90 ($C^{4'}$), 134.08 (C^{4a}), 134.58 ($C^{2'}$), 153.74 (C^{3a}), 160.23 (C^2). Two-dimensional HMBC spectra, δ, ppm: ^{13}C–^{1}H: 110.31, 7.55 (18.9, C^8/5-H); 110.51, 7.37 (185.4, C^8/6-H); 110.69, 7.30 (51.3, C^8/7-H); 112.95, 7.37 (55.4, C^5/6-H); 113.01, 7.30 (204.2, C^5/7-H); 113.01, 7.82 (10.1, C^5/8-H); 121.34, 7.55 (149.8, C^7/5-H); 121.57, 7.37 (7.7, C^7/6-H); 123.64, 7.37 (37.1, C^{8a}/6-H); 123.72, 7.30 (150.7, C^{8a}/7-H); 123.73, 7.55 (138.7, C^{8a}/5-H); 123.98, 7.82 (120.1, C^6/8-H); 124.16, 7.30 (11.6, C^6/7-H); 124.16, 7.55 (11.8, C^6/5-H); 126.22, 7.17 (80.5, $C^{3'}$/4′-H); 126.23, 7.63 (66.5, $C^{3'}$/5′-H); 127.36, 7.17 (99.4, $C^{5'}$/4′-H); 127.36, 7.69 (69.8, $C^{5'}$/3′-H); 127.92, 7.63 (40.2, $C^{4'}$/5′-H); 127.98, 7.69 (28.0, $C^{4'}$/3′-H); 134.13, 7.82 (121.3, C^{4a}/8-H); 134.16, 7.37 (164.8, C^{4a}/6-H); 134.21, 7.30 (7.7, C^{4a}/7-H); 134.62, 7.17 (230.1, $C^{2'}$/4′-H); 134.63, 7.63 (62.7, $C^{2'}$/5′-H); 134.66, 7.69 (87.3, $C^{2'}$/3′-H); C^{3a} showed no cross peaks; 160.27, 7.17 (1.6, C^2/4′-H); 160.28, 7.63 (1.3, C^2/5′-H); 160.34, 7.69 (63.3, C^2/3′-H); ^{15}N–^{1}H: 99.87, 7.36 (232.4, N^4/6-H); no N^4/7-H peak; 99.87, 7.55 (206.7, N^4/5-H); 99.90, 7.82 (1.0, N^4/8-H); 192.90, 7.63 (2.9, N^3/4′-H); 192.90, 7.69 (1.5, N^3/2′-H); 193.60, 7.17 (62.6, N^3/3′-H); 208.70, 7.30 (203.7, N^9/7-H); 208.70, 7.55 (70.5, N^9/5-H); 208.70, 7.82 (345.1, N^9/8-H); 253.10, 7.17 (219.5, N^1/3′-H); 253.10, 7.69 (21.8, N^1/2′-H). Found, %: C 59.78; H 3.47; N 23.54; S 13.17. $C_{12}H_8N_4S$. Calculated, %: C 59.98; H 3.36; N 23.32; S 13.34.

2-(2-Furyl)-4-methyl-4*H*-[1,2,4]triazolo[1,5-*a*]benzimidazole (IVe). A solution of 0.67 g (3 mmol) of triazolobenzimidazole **Ie** and 0.22 g (4 mmol) of potassium hydroxide in 1.5 ml of water was evaporated to dryness, the residue was dispersed in 10 ml of acetone, and 0.25 ml (4 mmol) of methyl iodide was added. The mixture was stirred for 2 h at 20–25°C and evaporated, the residue was treated with 15 ml of chloroform, and the solution was passed through a column charged with Al_2O_3 (10×1.5 cm) using chloroform as eluent. A fraction with R_f 0.7 was collected. Yield 0.54 g (76%), colorless crystals which darkened on storage, mp 139–140°C (from EtOAc). ^{1}H NMR spectrum, δ, ppm: 3.83 s (3H, Me), 6.66 d.d (1H, 4′-H, J = 3.4, 1.8 Hz), 7.04 d.d (1H, 3H, J = 3.4, 0.8 Hz), 7.34 d.d.d (1H, 7-H, J = 8.1, 7.3, 1.1 Hz), 7.43 d.d.d (1H, 6-H, J = 8.3, 7.83, 1.2 Hz), 7.69 d.m (1H, 5-H, J = 8.1 Hz), 7.83 d.d (1H, 5′-H, J = 1.8, 0.8 Hz), 7.83 d.d.d (1H, 8-H, J = 8.0, 1.2, 0.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 29.65 (Me), 109.77 ($C^{3'}$), 110.29 (C^8), 111.34 (C^5), 111.73 ($C^{4'}$), 121.48 (C^7), 123.23 (C^{8a}), 123.86 (C^6), 135.25 (C^{4a}), 143.93 ($C^{5'}$), 146.55 ($C^{2'}$), 154.17 (C^{3a}), 157.05 (C^2). Two-dimensional HMBC spectra, δ, ppm: ^{13}C–^{1}H: 109.85, 6.66 (112.4, $C^{3'}$/4′-H); 110.01, 7.83 (132.9, $C^{3'}$/5-H); 110.41, 7.42 (304.2, C^8/6-H); 110.58, 7.33 (93.3, C^8/7-H); 111.31, 7.42 (61.3, C^5/6-H); 111.31, 7.83 (279.6, C^5/8-H); 111.34, 7.33 (374.4, C^5/7-H); 111.79, 7.03 (145.7, $C^{4'}$/3′-H); 121.67, 7.69 (264.0, C^7/5-H); 121.82, 7.42 (36.1, C^7/6-H); 123.00, 7.69 (382.7, C^{8a}/5-H); 123.02, 7.42 (71.2, C^{8a}/6-H); 123.20, 7.83 (9.9, C^{8a}/8-H); 123.34, 7.33 (310.4, C^{8a}/7-H); 123.76, 7.69 (8.1, C^6/5-H); 123.80, 7.83 (202.1, C^6/8-H); 135.27, 3.82 (1811.5, C^{4a}/4-CH_3); 135.27, 7.42 (279.5, C^{4a}/6-H); 135.29, 7.83 (227.3, C^{4a}/8-H); 135.41, 7.33 (73.0, C^{4a}/7-H); 144.05, 6.66 (195.9, $C^{5'}$/4′-H); 146.33, 7.03 (448.8, $C^{2'}$/3′-H); 146.53, 6.66 (318.3, $C^{2'}$/4′-H); 146.64, 7.83 (163.9, $C^{2'}$/5′-H); 154.24, 3.82 (2181.9, C^{3a}/4-CH_3); 157.06, 6.66 (1.0, C^2/4-H); 157.06, 7.04 (27.5, C^2/3-H); 157.13, 7.83 (11.2, C^2/8-H); ^{15}N–^{1}H: 94.19, 3.82 (705.4, N^4/4-CH_3); 94.19, 7.42 (5.1, N^4/6-H); 94.19, 7.69 (49.4, N^4/5-H); 94.19, 7.83 (1.0, N^4/8-H); 205.82, 7.33 (7.7, N^9/7-H); 205.82, 7.68 (9.6, N^9/5-H); 205.82, 7.83 (58.7, N^9/8-H). Found, %: C 65.66; H 4.37; N 23.38. $C_{13}H_{10}N_4O$. Calculated, %: C 65.54; H 4.23; N 23.52.

4-Methyl-2-(2-thienyl)-4*H*-[1,2,4]triazolo[1,5-*a*]benzimidazole (IVf) was synthesized as described above for compound **IVe** from triazolobenzimidazole **If**. Yield 72%, colorless crystals, mp 130–131°C. ^{1}H NMR spectrum, δ, ppm: 3.88 s (3H, Me), 7.12 d.d (1H, 4′-H, J = 6.9, 3.5 Hz), 7.28–7.41 m (4H, 3′-H, 5-H, 6-H, 7-H), 7.79 d.d (1H, 5′-H, J = 3.5, 1.3 Hz), 7.82 d (1H, 8-H, J = 8.1 Hz). Found, %: C 61.54; H 4.07; N 22.17; S 12.50. $C_{13}H_{10}N_4S$. Calculated, %: C 61.40; H 3.96; N 22.03; S 12.61.

This study was performed using the facilities of "Molecular Spectroscopy" shared research center of the Southern Federal University.

REFERENCES

1. Kumar, A., Parshad, M., Gupta, R.K., and Kumar, D., *Synthesis*, 2009, p. 1663.
2. Rao, J.P. and Reddy, K.K., *Synth. Commun*., 1988, vol. 18, p. 1995.
3. Ho, R.I.-F. and Day, A.R., *J. Org. Chem*., 1973, vol. 38, p. 3084.
4. Kuz'menko, V.V., Kuz'menko, T.A., Pozharskii, A.F., Doron'kin, V.N., Chikina, N.L., and Pozharskaya, S.S., *Khim. Geterotsikl. Soedin*., 1989, p. 209.
5. Badr, M.Z.A., Mahmoud, A.M., Mahgoub, S.A., and Hozien, Z.A., *Bull. Chem. Soc. Jpn*., 1988, vol. 61, p. 1339.
6. Wilde, H., Hauptmann, S., Ostermann, G., and Mann, G., *J. Prakt. Chem*., 1984, vol. 326, p. 829.
7. Kuz'menko, T.A., Divaeva, L.N., and Morkovnik, A.S., *Izv. Akad. Nauk, Ser. Khim*., 2011, p. 535.
8. Ogura, H., Takayanagi, H., Yamazaki, Y., Yonezawa, S., Takagi, H., Kobayashi, S., Kamioka, T., and Kamoshita, K., *J. Med. Chem*., 1972, vol. 15, p. 923; Anisimova, V.A., Simonov, A.M., and Borisova, T.A., *Khim. Geterotsikl. Soedin*., 1973, p. 791; Kuz'menko, T.A., Kuz'menko, V.V., Pozharskii, A.F., and Anisimova, V.A., *Khim. Geterotsikl. Soedin*., 1990, p. 1517.
9. Mas, Th., Claramunt, R.M., Santa María, M.D., Sanz, D., Alarcón, S.H., Pérez-Torralba, M., and Elguero, J., *Arkivoc*, 2002, part (v), p. 48; Catalan, J., de Paz, J.L.G., del Valle, J.C., Claramunt, R.M., and Mas, Th., *Chem. Phys*., 2004, vol. 305, p. 175.
10. Malkin, V.G., Malkina, O.L., Casida, M.E., and Salahub, D.S., *J. Am. Chem. Soc*., 1994, vol. 116, p. 5898.
11. Claramunt, R.M., Alkorta, I., Lopez, C., Elguero, J., Garcıa, M.A., and Denisov, G.S., *New J. Chem*., 2003, vol. 27, p. 734; Witanowski, M., Stefaniak, L., and Webb, G.A., *Annu. Rep. NMR Spectrosc*., 1993, p. 41.
12. Molina, P., Aller, E., and Lorenzo, A., *Heterocycles*, 1994, vol. 37, p. 997.
13. Mohamed, B.G., Hussein, M.A., Abdel-Alim, A.-A.M., and Hashem, M., *Arch. Pharm. Res*., 2006, vol. 29, p. 26.
14. Kuz'menko, T.A., Kuz'menko, V.V., Divaeva, L.N., Morkovnik, A.S., and Borodkin, G.S., *Izv. Akad. Nauk, Ser. Khim*., 2012, p. 1150.
15. Erra-Balsells, R., *Org. Mass Spectrom*., 1991, p. 293; Cotte, J.L., *Org. Mass Spectrom*., 1972, p. 1071.
16. Nagayama, K., Kumar, A., Wuthrich, K., and Ernst, R.R., *J. Magn. Reson*., 1980, vol. 40, p. 321.
17. Aue, W.P., Bartholdi, E., and Ernst, R.R., *J. Chem. Phys*., 1976, vol. 64, p. 2229.
18. Davis, A.L., Keeler, J., Laue, E.D., and Moskau, D., *J. Magn. Reson*., 1992, vol. 98, p. 207.
19. Hurd, R.E. and John, B.K., *J. Magn. Reson*., 1991, vol. 91, p. 648.
20. Willker, W., Leibfritz, D., Kerssebaum, R., and Bermel, W., *Magn. Reson. Chem*., 1993, vol. 31, p. 287.
21. Granovsky, A.A., *www.classic.chem.msu.su/gran/firefly/index.htm*
22. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, Sh., Matsunaga, N., Nguyen, K.A., Su, Sh., Windus, Th.L., Dupuis, M., and Montgomery, J.A., Jr., *J. Comput. Chem*., 1993, vol. 14, p. 1347.
23. Koester, A.M., Flores-Moreno, R., Geudtner, G., Goursot, A., Heine, Th., Reveles, J.U., Patchkovskii, S., Vela, A., and Salahub, D.R., *DeMon Developers, DeMon2K 1.0.4*, NRC, Canada, 2004.