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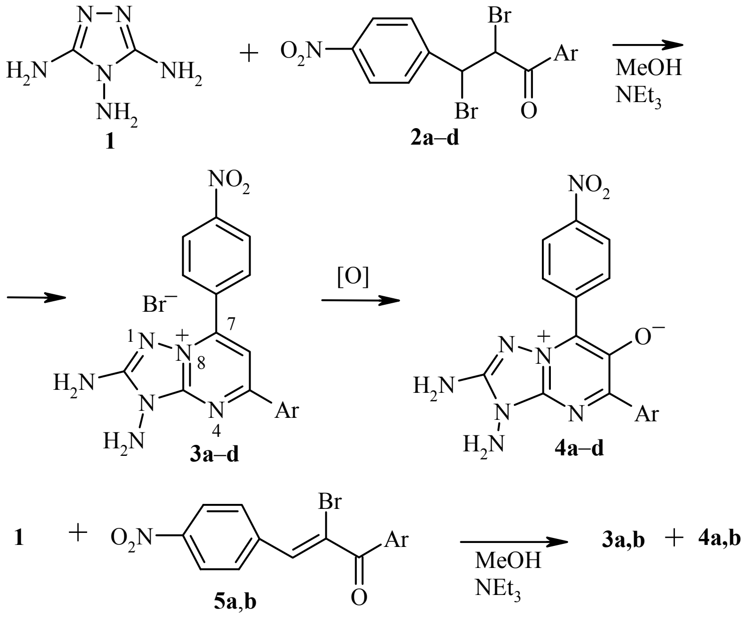
# 2,3-DIAMINO-5-ARYL-7-(4-NITROPHENYL)-1,2,4-TRIAZOLO[1,5-*a*]PYRIMIDINIUM-6-OLATES

**N. N. Kolos, V. D. Orlov, B. V. Paponov, and O. V. Shishkin**

*The corresponding triazolopyrimidinium salts and 1,2,4-triazolo[1,5-a]pyrimidinium-6-olates were formed from the reaction of 3,4,5-triamino-1,2,4-triazole and 1-aryl-3-(4-nitrophenyl)-2,3-dibromopropanones. The structure of one of the latter has been established by X-ray crystallography.*

**Keywords:** mesoionic compounds, olate, triazole, chalcone dibromide, resonance structure, X-ray crystallography.

We have obtained [1] triazolopyrimidinium salts **3a-d** by the reaction of 3,4,5-triamino-1,2,4-triazole (**1**) with 1-aryl-2,3-dibromo-3-(4-nitrophenyl)propanones **2a-d**. In the present work it is shown that 1,2,4-triazolo[1,5-*a*]pyrimidiniumolates **4a-d** are formed along with the mentioned salts and that the yields of **4a-d** increase with increasing duration of refluxing of the reaction mixture. When α-bromochalcones **5a,b** are used in the reaction instead of dibromides **2** the yield of the required products **4a,b** is somewhat increased.



**2–5 a** Ar = Ph, **b** Ar = $C_6H_4Cl$-*p*; **c** Ar = $C_6H_4Br$-*p*; **d** Ar = $C_6H_4NO_2$-*p*

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TABLE 1. Physico-chemical Characteristics of Compounds **3b-d** and **4a-d**

| Compound | Empirical formula | Found N, % / Calculated N, % | mp, °C | Electronic absorption spectra, $\lambda_{max}$, nm ($\varepsilon_{max} \cdot 10^{-3}$) | IR spectra, ν, cm$^{-1}$ |  | Yield, %, by method A (B) |
|---|---|---|---|---|---|---|---|
|  |  |  |  |  | νC=C, C=N | $\nu NH_2$ |  |
| **3b** | $C_{17}H_{13}BrClN_7O_2 \cdot H_2O$ | 20.3<br>20.4 | 227-228 | 276 (17.2), 349 (11.1), 468 (4.9) | 1652, 1629 | 3437, 3300, 3107 | 56 |
| **3c** | $C_{17}H_{13}Br_2N_7O_2 \cdot H_2O$ | 18.9<br>18.7 | 246-247 | 279 (17.3), 347 (10.8), 471 (4.8) | 1669, 1627 | 3476, 3337, 3103 | 62 |
| **3d** | $C_{17}H_{13}BrN_8O_4 \cdot H_2O$ | 22.9<br>22.8 | 253-254 | 293 (17.4), 356 (11.7), 477 (6.1) | 1653, 1638 | 3453, 3330, 3130 | 54 |
| **4a** | $C_{17}H_{13}N_7O_3 \cdot C_3H_7NO$ | 25.9<br>25.7 | 280-281 | 248 (12.9), 332 (11.2), 469 (9.3) | 1669, 1632 | 3430, 3350, 3103 | 53 (67) |
| **4b** | $C_{17}H_{12}ClN_7O_3$ | 24.6<br>24.6 | 303-304 | 251 (13.9), 334 (12.2), 470 (8.1) | 1664, 1637 | 3436, 3376, 3136 | 56 (65) |
| **4c** | $C_{17}H_{12}BrN_7O_3$ | 22.1<br>22.2 | 307-308 | 252 (12.6), 331 (13.4), 471 (11.0) | 1669,1632 | 3403, 3377, 3153 | 54 |
| **4d** | $C_{17}H_{12}N_8O_5$ | 27.3<br>27.4 | 295-297 | 255 (12.8), 341 (13.2), 474 (9.8) | 1650, 1626 | 3433, 3353, 3103 | 57 |

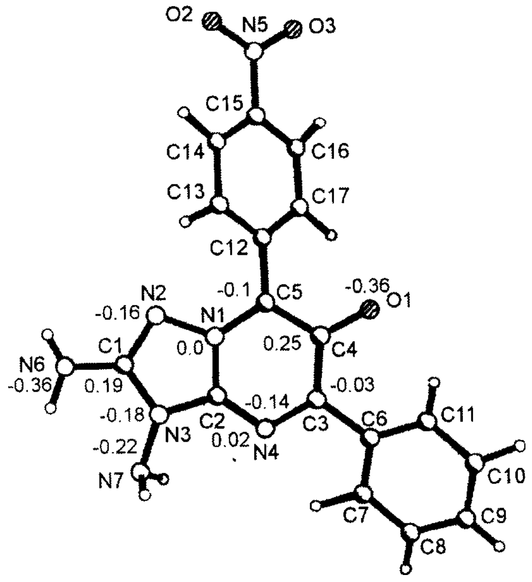


Fig. 1. Charge distribution (in fractions of the electron *e* charge) in the molecule of **4a**.

Salts **3** were washed out of the precipitated reaction products with hot methanol, while the zwitterions **4** were isolated by crystallization from the residue in dimethylformamide.

Compound **3a** was identical to a sample described previously [1] (mp, IR and UV spectra). The structures of products **3b-d** and **4a-d** agreed with the results of elemental analysis, and their $^1$H NMR, UV and IR spectral data. The spatial and molecular structure of compound **4a** was established by X-ray crystallography.

The IR spectra of compounds **4a-d** reveal a group of bands at 3430, 3350, and 3100 cm$^{-1}$ assigned to amino group vibrations of the triazole ring and also bands at 1670 and 1630 cm$^{-1}$ resulting from overlap of the C=C and C=N vibrations of the pyrimidine and triazole rings (Table 1). The $^1$H NMR spectra of compounds **4a-d** are characterized by a broad singlet of the 2-NH$_2$ group in the 6.00 ppm region, a weakly splitted doublet of the 3-NH$_2$ group in low field, and also proton signals of the aryl and the nitrophenyl substituents (Table. 2). According to the X-ray crystallographic data, in crystals molecules **4a** form a 1:1 solvate with DMF.

The amino group at C(1) is planar (sum of the bond angles at nitrogen is 359.7°) and almost coplanar with the plane of the triazole ring (torsion angle N(2)–C(1)–N(6)-H(6NB) 15°). The NH$_2$ group at N(3) has a pyramidal structure (sum of the bond angles at N(7) is 332.7°) and is practically perpendicular to the plane of the azole ring (torsion angle C(1)–N(3)–N(7)–H(7NA) is 115°). In this case the hydrogen atoms are directed towards the pyrimidine ring.

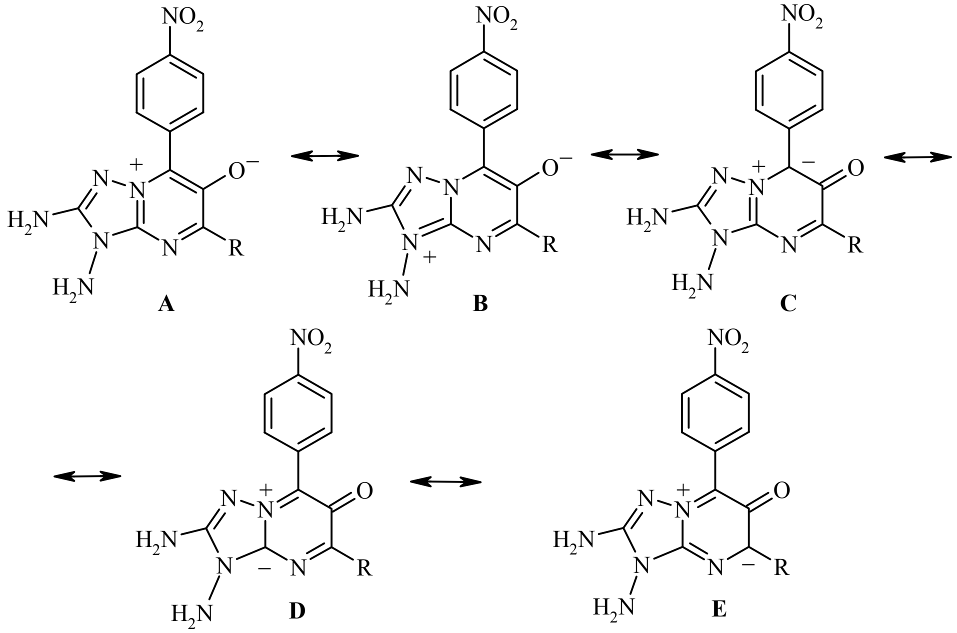
TABLE 2. $^1$H NMR Spectra of Compounds **4a,b,d**; δ, ppm (coupling constants, *J*, Hz).

| Compound | 2-NH$_2$, br. s | 3-NH$_2$, d ($J$ = 7.5) | 5-Ar | 7-C$_6$H$_4$NO$_2$ |
|---|---|---|---|---|
| **4a** | 6.01 | 8.77 | 7.40 m | 8.28 d ($J$ = 7.8);<br>8.49 d ($J$ = 8.0) |
| **4b** | 6.01 | 8.88 | 7.38 d ($J$ = 8.0);<br>7.51 d ($J$ = 8.0) | 8.29 d ($J$ = 7.8);<br>8.49 d ($J$ = 8.0) |
| **4d** | 5.99 | 9.09 | 8.57 d ($J$ = 8.0);<br>8.78 d ($J$ = 8.0) | 8.27 d ($J$ = 7.8);<br>8.56 d ($J$ = 8.0) |

This orientation is probably explained by the unfavorable non-valence interactions with the neighboring amino group which is shown in particular by the short intramolecular contact H(6NA)···N(7) of 2.54 Å (the sum of the van der Waals radii is 2.66 Å [2]). Repulsion of the hydrogen atoms in the *ortho* positions of the phenyl substituents at C(3) and C(5) with the atoms O(1), C(4), N(4), and N(2) (shortened contacts H(7)...N(4) 2.40 Å, H(11)···O(1) 2.39 Å (2.45 Å), H(17)···O(1) 2.22 Å, H(17)···C(4) 2.68 Å, (2.77 Å), H(13)···N(2) 2.55 Å) lead to rotation of the phenyl groups by 25.9(5)° and 37.9(4)° respectively (torsion angles N(4)–C(3)–C(6)–C(7) and N(1)–C(5)–C(12)–C(13)). The nitro group is practically coplanar with the benzene ring C(12)···C(17): the torsion angle C(14)–C(15)–N(5)–O(2) is 10.1(5)°.

In the crystal the molecules of **4a** form a three dimensional network via hydrogen bonds H(6NA)...O(1)' (-*x*, -0.5 + *y*, 2.5 - *z*), (O···H 1.79 Å, O···H–N 156.7°), H(7NA)···O(1S)' (1 - *x*, -0.5 + *y*), 2.5 - *z*)(O···H 2.18 Å, O···N–H 136.9°), H(7NB)···O(1)' (*x*, 1.5 + *y*, -0.5 + *z*)(O···H 1.88 Å, O···H–N 165°) and the shortened intermolecular contact H(17)···N(7)' (-*x*, 0.5 + *y*, 2.5 - *z*) 2.50 Å.

The structure of molecule **4a** may be described by a set of basic resonance structures A–E:



The contributions of these structures was analyzed by calculating the charges and bond orders (Fig. 1 and 2) with the molecular geometry determined by X-ray crystallography. In comparison with bond C(2)–N(4) the bond C(2)–N(3) is significantly longer (1.363(4) Å) and has a smaller bond order which shows that it is a single bond which omits the resonance structure B.

The bond order of the C(4)–O(1) (Fig. 2) shows that it is basically a double bond, and the C(3)–C(4) and C(4)–C(5) bonds are single. The similar bond lengths and bond orders of N(4)–C(3) and N(4)–C(2) indicate considerable electron density delocalisation in this fragment. Analogous delocalisation is observed in the fragment C(2)–N(1)–C(5), but with a noticeably smaller bond orders. This analysis permits the conclusion that structures C-E provide the basic contributions to the structure. The existence of the pyrimidine ring in a strongly compressed boat conformation supports this conclusion. Atoms C(2) and C(4) deviate from the plane of the other atoms of the ring by -0.05 and -0.07 Å respectively.

The formation of mesoionic compounds in the reactions of aminoazoles with polarizable olefins has been described in [3], where the contributions of olate and oxo-forms in a similar structures were discussed on the basis of IR spectroscopic data. 6-Hydroxy derivatives of azolopyrimidine systems were obtained by the present authors [4, 5], but the formation of mesoionic compounds by oxidation of the corresponding

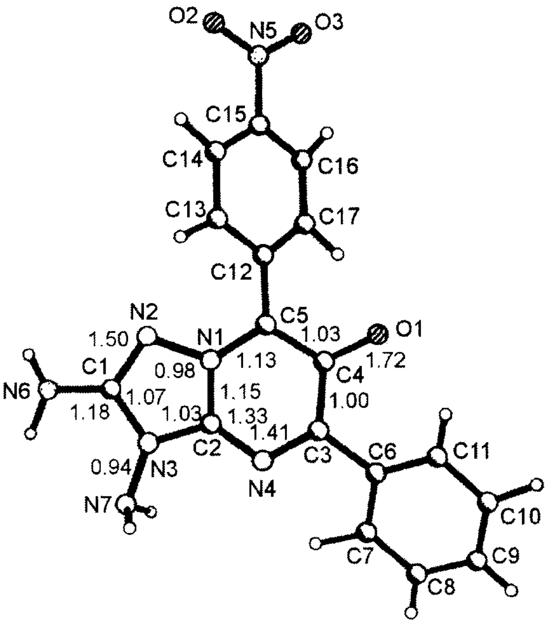


Fig. 2. Bond orders in the molecule **4a**

pyrimidinium salts was not described. We propose that the conversion of the salts **3a-d** into compounds **4a-d** occurs analogously to the processes described in these papers with air oxygen as the oxidant. The oxidation of salt **3a** into the mesoionic compound **4a** by keeping it in a DMSO solution for 40 h on a boiling water bath in the air supports this idea.

TABLE 3. Bond Lengths (*l*) in Structure **4a**

| Bond | *l*, Å | Bond | *l*, Å |
|---|---|---|---|
| N(1)–C(2) | 1.346(4) | C(5)–C(12) | 1.465(5) |
| N(1)–C(5) | 1.370(4) | C(6)–C(7) | 1.391(5) |
| N(1)–N(2) | 1.398(4) | C(6)–C(11) | 1.398(5) |
| N(2)–C(1) | 1.329(4) | C(7)–C(8) | 1.382(6) |
| N(3)–C(2) | 1.365(4) | C(8)–C(9) | 1.371(6) |
| N(3)–C(1) | 1.363(4) | C(9)–C(10) | 1.371(6) |
| N(3)–N(7) | 1.409(4) | C(10)–C(11) | 1.388(5) |
| N(4)–C(2) | 1.315(4) | C(12)–C(13) | 1.396(5) |
| N(4)–C(3) | 1.329(4) | C(12)–C(17) | 1.405(4) |
| N(5)–O(3) | 1.223(4) | C(13)–C(14) | 1.384(5) |
| N(5)–O(2) | 1.230(4) | C(14)–C(15) | 1.378(5) |
| N(5)–C(15) | 1.464(5) | C(15)–C(16) | 1.377(5) |
| N(6)–C(1) | 1.343(4) | C(16)–C(17) | 1.378(6) |
| O(1)–C(4) | 1.276(4) | N(1S)–C(1S) | 1.302(5) |
| C(3)–C(4) | 1.450(5) | N(1S)–C(3S) | 1.447(6) |
| C(3)–C(6) | 1.484(5) | N(1S)–C(2S) | 1.446(6) |
| C(4)–C(5) | 1.438(5) | O(1S)–C(1S) | 1.226(6) |

TABLE 4. Bond Angles (ω) in Structure **4a**

| Angle | ω, deg. | Angle | ω, deg. |
|---|---|---|---|
| C(2)–N(1)–C(5) | 121.5(3) | N(1)–C(5)–C(12) | 120.0(3) |
| C(2)–N(1)–N(2) | 111.1(3) | C(4)–C(5)–C(12) | 123.9(3) |
| C(5)–N(1)–N(2) | 126.9(3) | C(7)–C(6)–C(11) | 119.3(3) |
| C(1)–N(2)–N(1) | 103.3(3) | C(7)–C(6)–C(3) | 118.0(3) |
| C(2)–N(3)–C(1) | 106.8(8) | C(11)–C(6)–C(3) | 122.6(3) |
| C(2)–N(3)–N(7) | 126.4(3) | C(8)–C(7)–C(6) | 119.6(4) |
| C(1)–N(3)–N(7) | 125.9(3) | C(9)–C(8)–C(7) | 121.2(4) |
| C(2)–N(4)–C(3) | 116.6(3) | C(10)–C(9)–C(8) | 119.6(4) |
| O(3)–N(5)–O(2) | 123.5(4) | C(9)–C(10)–C(11) | 120.7(4) |
| O(3)–N(5)–C(15) | 118.4(4) | C(10)–C(11)–C(6) | 119.6(4) |
| O(2)–C(5)–C(15) | 118.1(4) | C(13)–C(12)–C(17) | 119.1(3) |
| N(2)–C(1)–N(6) | 124.8(3) | C(13)–C(12)–C(5) | 121.4(3) |
| N(2)–C(1)–N(3) | 112.3(3) | C(17)–C(12)–C(5) | 119.5(3) |
| N(6)–C(1)–N(3) | 122.9(3) | C(14)–C(13)–C(12) | 120.3(3) |
| N(4)–C(2)–N(1) | 125.6(3) | C(15)–C(14)–C(13) | 118.6(3) |
| N(4)–C(2)–N(3) | 128.0(3) | C(14)–C(15)–C(16) | 123.0(3) |
| N(1)–C(2)–N(3) | 106.4(3) | C(14)–C(15)–N(5) | 118.6(4) |
| N(4)–C(3)–C(4) | 123.0(3) | C(16)–C(15)–N(5) | 118.4(4) |
| N(4)–C(3)–C(6) | 114.5(3) | C(17)–C(16)–C(15) | 118.1(3) |
| C(4)–C(3)–C(6) | 122.5(3) | C(16)–C(17)–C(12) | 121.0(3) |
| O(1)–C(4)–C(5) | 121.7(3) | C(1S)–N(1S)–C(3S) | 121.3(5) |
| O(1)–C(4)–C(3) | 121.4(3) | C(1S)–N(1S)–C(2S) | 118.9(5) |
| C(5)–C(4)–C(3) | 116.9(3) | C(3S)–N(1S)–C(2S) | 119.7(5) |
| N(1)–C(5)–C(4) | 116.0(3) | O(1S)–C(1S)–N(1S) | 127.4(5) |

TABLE 5. Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) of Non-hydrogen Atoms in the Structure of **4a**

| Atom | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 |
| N(1) | 97(2) | 6572(2) | 13910(3) | 39(1) |
| N(2) | -675(2) | 5958(2) | 13729(3) | 43(1) |
| N(3) | 503(2) | 5594(2) | 12756(3) | 43(1) |
| N(4) | 1620(2) | 6805(2) | 13309(3) | 45(1) |
| N(5) | -3069(3) | 8273(3) | 16611(4) | 67(1) |
| N(6) | -939(3) | 4682(2) | 12542(3) | 54(1) |
| N(7) | 913(2) | 5175(2) | 11862(3) | 51(1) |
| O(1) | 940(2) | 8648(1) | 14711(3) | 50(1) |
| O(2) | -3448(3) | 7743(2) | 17147(4) | 102(1) |
| O(3) | -3313(2) | 8999(2) | 16561(3) | 84(1) |
| C(1) | -398(3) | 5386(2) | 13003(3) | 43(1) |
| C(2) | 807(3) | 6355(2) | 13326(4) | 41(1) |
| C(3) | 1695(3) | 7559(2) | 13833(4) | 42(1) |
| C(4) | 915(3) | 7894(2) | 14362(3) | 40(1) |
| C(5) | 104(3) | 7341(2) | 14451(3) | 41(1) |
| C(6) | 2622(3) | 8042(2) | 13788(3) | 43(1) |
| C(7) | 3030(3) | 7844(3) | 12763(4) | 62(1) |
| C(8) | 3930(4) | 8252(3) | 12735(5) | 80(1) |
| C(9) | 4444(4) | 8838(3) | 13720(5) | 75(1) |
| C(10) | 4044(3) | 9040(2) | 14731(5) | 67(1) |

TABLE 5 (continued)

| 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|
| C(11) | 3136(3) | 8648(2) | 14781(4) | 54(1) |
| C(12) | -714(3) | 7569(2) | 15018(4) | 40(1) |
| C(13) | -1075(3) | 7011(2) | 15778(3) | 47(1) |
| C(14) | -1853(3) | 7239(2) | 16295(4) | 50(1) |
| C(15) | -2272(3) | 8022(2) | 16026(4) | 51(1) |
| C(16) | -1947(3) | 8590(2) | 15268(4) | 49(1) |
| C(17) | -1161(3) | 8362(2) | 14775(4) | 46(1) |
| N(1S) | 6007(3) | 9244(3) | 10130(5) | 81(1) |
| O(1S) | 6785(3) | 9733(2) | 12357(4) | 101(1) |
| C(1S) | 6159(4) | 9283(3) | 11460(6) | 83(1) |
| C(2S) | 6643(6) | 9767(4) | 9599(7) | 124(2) |
| C(3S) | 5258(5) | 8663(4) | 9197(6) | 121(2) |

## EXPERIMENTAL

IR spectra in KBr pellets were recorded with a Specord IR-75 spectrometer, electronic spectra of methanol solutions were recorded on a Specord M-40 instrument, and $^1$H NMR spectra of DMSO-d$_6$ solutions with TMS as internal standard were recorded on a Gemini-2000 spectrometer.

The purity of the compounds synthesized was checked by TLC on Silufol UV-254 plates with methanol as eluent.

**X-ray Crystallographic Study of Compound 4a**. Crystals of the DMF solvate of triazolopyrimidiniumolate **4a** ($C_{20}H_{20}N_8O_4$) were monoclinic. At 20°C $a$ = 13.354(3), $b$ = 16.298(5), $c$ = 10.246(3) Å; $\beta$ = 112.12(2)°; $V$ = 2066(1) Å$^3$; $d_{calc}$ = 1.403 g/cm$^3$; space group $P2_1/c$; $Z$ = 4. The parameters of the unit cell and the intensities of 3463 independent reflexions were measured on a Siemens P3/PC automatic diffractometer ($\lambda$Mo$K\alpha$, graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{max}$ = 50°). Preliminary evaluation of the experimental data was carried out according to [6]. The structure was solved by direct methods using the SHELXTL PLUS [7]. The positions of the hydrogen atoms were determined by difference syntheses of the electron density and refined using the "riding" model with fixed $U_{iso}$ = 1.2 $U_{eq}$ of the non-hydrogen atom to which the hydrogen atom was bonded. Refinement of 2792 reflexions *via* $F^2$ by the full-matrix least-squares method in the anisotropic approximation for the non-hydrogen atoms gave $wR_2$ = 0.149 ($R_1$ = 0.061 for 1564 reflexions with $F > 4\sigma(F)$, $S$ = 0.97). Coordinates of the non-hydrogen atoms are presented in Table 4.

Samples of compounds **3a-d** were synthesized in 54-64% yield as described in [1].

**2,3-Diamino-7-(*p*-nitrophenyl)-5-phenyl-1,2,4-triazolo[1,5-*a*]pyrimidinium-6-olate (4a). A.** A mixture of ketone **2a** (2.0 g, 4 mmol), triamine **1** (0.5 g, 4 mmol), and triethylamine (1 ml) in methanol (70 ml) was refluxed for 5 h. The precipitate which separated on cooling was filtered off and treated with hot methanol. Compound **4a** (0.76 g) was isolated by crystallization of the residue from dimethylformamide. The methanol solution was reduced to 1/3 on a rotary evaporator, cooled, and filtered to give bromide **3a** (0.3 g, 16%).

**B**. A solution of bromide **3a** (0.5 g, 1.2 mmol) in DMSO (2 ml) was kept on a boiling water bath for 40 h. After cooling, the reaction mixture was filtered to give compound **4a** (o,3 g, 71%).

**C**. Product **4a** was obtained from α-bromochalcone **5a** (1.6 g, 4 mmol) and triamine **1** (0.5 g, 4 mmol) by method **A**. A mixed sample of **4a** prepared by methods **A** and **C** gave no depression of the melting point.

**2,3-Diamino-5-{(*p*-chlorophenyl/*p*-bromophenyl/*p*-nitrophenyl)}-7-(*p*-nitrophenyl)-1,2,4-triazolo-[1,5-*a*]pyrimidinium-6-olates 4b-d** were prepared by method **A** from triamine **1** and ketones **2b-d** respectively. Compound **4b** was also prepared from the α-bromochalcone **5b** by method **B**.

## REFERENCES

1. N. N. Kolos, V. D. Orlov, B. V. Paponov, O. V. Shishkin, S. V. Baumer, and N. A. Kvashnitskaya, *Khim. Geterotsikl. Soedin.,* 796 (1999).
2. Yu. V. Zefirov and P. M. Zorkii, *Usp. Khim.,* **58**, 713 (1989).
3. Yoshiro Matsuda, Yausige Chiyomaru, Kazuki Furano, and Takanobu Nishiyori, *Heterocycles*, **41**, 2777 (1995).
4. S. M. Desenko, V. D. Orlov, V. V. Lipson, O. V. Shishkin, K. A. Potekhin, and Yu. T. Struchkov, *Khim. Geterotsikl. Soedin.,* 109 (1993).
5. S. M. Desenko, V. D. Orlov, V. V. Lipson, O. V. Shishkin, S. V. Lindeman, and Yu. T. Struchkov, *Khim. Geterotsikl. Soedin.,* 688 (1993).
6. R. H. Blessing, *J. Appl. Cryst.,* No. 22, 396 (1989).
7. G. M. Sheldrick, *SHELXTL PLUS. PC Version. A system of computer programs for the determination of crystal structure from X-ray diffraction data.* Rev. 5.02 (1994).