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STABLE 1,2,4-TRIAZOLO[1,5-*a*]-PYRIMIDINIUM SALTS

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2,3-Diamino-5,7-diaryl-1,2,4-triazolo[1,5-a]pyrimidinium salts have been synthesized by the cyclocondensation of 3,4,5-triamino-1,2,4-triazole with 1,3-diaryl-2,3-propanes, and their structures and chemical properties have been studied.

In a continuation of our investigations concerning the reactivity of heterocyclic *o*-diamines containing a hydrazine amino group [1], the reactions of 3,4,5-triamino-1,2,4-triazole (I) with 1,3-diaryl-2,3-dibromopropanes (IIa-j) have been studied. The reactions were carried out by boiling equimolecular quantities of the substances in methanol in the presence of triethylamine or N-methylmorpholine. Bright yellow or orange crystals of compounds IIIa-j were isolated.

It has been shown previously [2] that reaction of the triamine I with chalcones occurs with elimination of a molecule of ammonia to give 2-amino-1,2,4-triazolo[1,5-*a*]pyrimidine derivatives. However ketones of type II can react with heterocyclic diamines to form annelated 1,5-diazepins [2,3].

To judge from their characteristics, compounds IIIa-j cannot have either of the above structures. For example in their ^{1}H NMR spectra (see experimental) there are two singlets with intensities corresponding to two protons. Both signals are extinguished on the addition of deuteromethanol which indicates that compounds IIIa-j retain two amino groups. In the same spectra the aromatic *o*-protons appear as quartets shifted to weak field and there is also an aromatic multiplet. In the IR spectra, intense absorption bands, sensitive to the nature of R, are observed at 1630-1537 cm^{-1}, and there are also bands in the 3200-3400 cm^{-1} which can be assigned to stretching vibrations of the amino groups (Table 1). The electronic absorption spectra of compounds IIIa-j are characterized by the presence of 3 or 4 bands which are not very sensitive to the electronic character of the substituents R and R^1. The longest wavelength band lies in the 430-466 nm region, i.e., it is much further to long wavelength than in the spectra described for triazolopyrimidines [2]. The mass spectra of compounds IIIa,c,e with *m/z* ([M]$^+$ - Br) 303, 338 and 348 and their fragmentation products do not correspond with the fragmentation of diazepin systems. Hence the structures of molecules IIIa-j cannot be established unambiguously from their spectra. Therefor an X-ray diffraction study was carried out for compound IIIe which showed that this compound is 2,3-diamino-7-(*p*-nitrophenyl)-5-phenyl-1,2,4-triazolo[1,5-*a*]pyrimidinium bromide. The bond lengths and valence angles of molecule IIIe are given in Tables 2 and 3.

In the crystal salt IIIe exists as a 1:1 solvate with DMF (Fig. 1). The bond lengths in the triazolopyrimidine fragment are equalized to a considerable extent which indicates delocalization of the electron density. The nitrogen atom $N_{(5)}$ has planar trigonal coordination and the bond length $C_{(1)}$–$N_{(5)}$ of 1.36 Å indicates strong conjugation between the π-system of the bicycle and the unshared electron pair of the amino group. The hydrazine amino group is prevented from conjugation by rotation around the $N_{(4)}$–$N_{(6)}$ bond and has a pyramidal structure. The angle between the plane of the bicycle and the line passing through the hydrogen atoms on $N_{(6)}$ is 78°. The length of the

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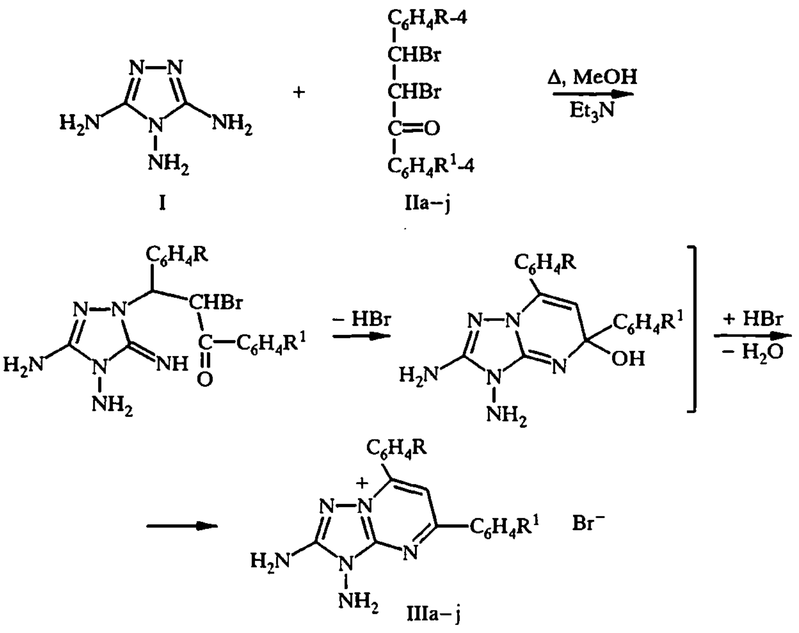
TABLE 1. Physicochemical Characteristics of Compounds IIIa-j

Compound	Empirical formula	$\frac{\text{Found, \%}}{\text{Calculated, \%}}$	mp, °C	Electronic spectra			IR spectra, ν, cm^{-1}		Yield, %
				absorption	luminescence		C=N	NH$_2$	
		N		λ_{max}, nm ($\varepsilon_{max}\cdot 10^3$)	λ_{max} (η)	ϕ_f			
IIIa	$C_{17}H_{15}BrN_6\cdot H_2O$	$\frac{21.0}{20.9}$	238-240	243 (18.9), 315 (7.3), 429 (16.1)	521	0.59	1638	3404, 3450	53
IIIb	$C_{18}H_{17}BrN_6O\cdot H_2O$	$\frac{19.5}{19.6}$	269-270	242 (20.4), 326 (7.0), 430 (14.5)	520	0.21	1630	3200, 3303, 3416	56
IIIc	$C_{17}H_{14}BrClN_6\cdot H_2O$	$\frac{19.3}{19.3}$	243-244	243 (29.8), 318 (10.3), 433 (15.9)	525	0.61	1655	3267, 3307, 3367	55
IIId	$C_{17}H_{14}Br_2N_6\cdot H_2O$	$\frac{17.5}{17.6}$	239-240	247 pl 316 (8.1), 433 (18.0)	535	0.73	1648	3334, 3380, 3480	53
IIIe	$C_{17}H_{14}BrN_7O_2\cdot H_2O$	$\frac{18.6}{18.5}$	228-230	250 (16.5), 274 (15.2), 316 (10.2), 455 (8.3)	—	—	1657	3300, 3330, 3436	60
IIIf	$C_{18}H_{17}BrN_6\cdot H_2O$	$\frac{20.2}{20.3}$	237-239	235 (20.8), 322 (7.9), 425 (13.7)	520	0.59	1640	3253, 3315, 3383	54
IIIg	$C_{18}H_{17}BrN_6O\cdot H_2O$	$\frac{19.5}{19.4}$	265-266	238 (19.2), 324 (8.1), 429 (14.6)	517	0.62	1640	3273, 3319, 3390	57
IIIh	$C_{17}H_{14}BrN_7O_2\cdot H_2O$	$\frac{18.4}{18.4}$	241-243	270 (14.7), 330 (8.9), 466 (10.5)	—	—	1630	3347, 3347, 3447	54
IIIi	$C_{17}H_{13}BrCl_2N_6\cdot H_2O$	$\frac{17.9}{17.8}$	270-271	247 (21.8), 322 (8.4), 437 (13.6)	530	0.15	1638	3295, 3395, 3472	52
IIIj	$C_{17}H_{13}Br_3N_6\cdot H_2O$	$\frac{15.0}{15.1}$	221-222	252 (19.0), 320 (12.3), 439 (16.5)	540	0.17	1637	3298, 3386, 3434	56



II, IIIa,e-h R = H, b R = OCH_3, c,i R = Cl, d,j R = Br, e R = NO_2, a-e R^1 = H, f R^1 = CH_3,
g R^1 = OCH_3, h R^1 = NO_2, i R^1 = Cl, j R^1 = Br

$N_{(4)}$–$N_{(6)}$ bond, 1.423(9) Å, indicates the absence of conjugation between the hydrazine amino group and the triazolopyrimidine unit. This orientation of the amino group is also stabilized by the attractive $N_{(6)}\cdots H_{(5B)}$ interaction (interatomic distance 2.56 Å, sum of the van der Waals radii [4] 2.66 Å). The phenyl group at $C_{(3)}$ is coplanar with the bicycle (torsion angle $N_{(1)}$–$C_{(3)}$–$C_{(12)}$–$C_{(13)}$ 2°) despite the shortness of the intramolecular contacts $H_{(13A)}\cdots N_{(1)}$, 2.43 Å, and $H_{(17A)}\cdots H_{(4A)}$, 2.07 Å. The substituent at $C_{(5)}$ is rotated relative to the triazolopyrimidine unit by 41° (torsion angle $C_{(4)}$–$C_{(5)}$–$C_{(6)}$–$C_{(7)}$) probably because of repulsion between atoms $H_{(11A)}$ and $N_{(3)}$ (distance 2.59 Å). The nitro group is almost coplanar with the aromatic ring. The torsion angle $O_{(2)}$–$N_{(7)}$–$C_{(9)}$–$C_{(8)}$ is 9°.

The non-hydrogen atoms in the DMF solvent molecule lie in a plane despite the regular intramolecular contact $H_{(18C)}\cdots H_{(21C)}$ of 2.21 Å.

In the crystal the organic cation, the Br^- anion, and the DMF molecule form a three dimensional network on account of the hydrogen bonds $H_{(5B)}\cdots O_{(3)}$ (H···O 2.00 Å, N-H···O 162°), $H_{(6C)}\cdots Br_{(1)}$ (H···Br 2.60 Å, N-H···Br 150°), $H_{(5A)}\cdots O_{(3')}$ (1 - x, 2 - y, -z) (H···O 1.99 Å, N-H···O 164°), $H_{(6B)}\cdots Br_{(Br')}$ (-x, 2 - y, -z) (H···Br 2.63 Å, N-H···Br 163°), and the regular intermolecular contacts $H_{(7A)}\cdots Br_{(1')}$ of 3.09 Å (sum of the van der Walls radii 3.13 Å [4]), $H_{(10A)}\cdots Br_{(1')}$ (0.5 + x, 2.5 - y, -0.5 + z) 3.07 Å, and $H_{(17A)}\cdots Br_{(1')}$ (-x, 3 - y, -z) 2.92 Å.

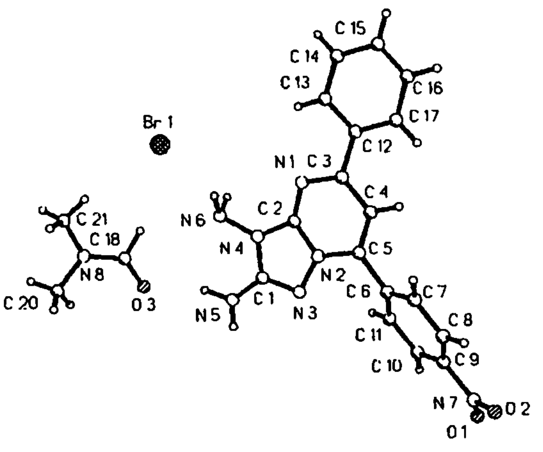


Figure 1. Structure of compound IIIe

TABLE 2. Bond Lengths (Å) in the Molecule of Compound IIIe

Bond	*d*	Bond	*d*
$O_{(1)}-N_{(7)}$	1.211(10)	$C_{(6)}-C_{(11)}$	1.422(11)
$O_{(2)}-N_{(7)}$	1.214(11)	$C_{(7)}-C_{(8)}$	1.382(12)
$N_{(1)}-C_{(2)}$	1.313(11)	$C_{(8)}-C_{(9)}$	1.389(12)
$N_{(1)}-C_{(3)}$	1.363(11)	$C_{(9)}-C_{(10)}$	1.400(13)
$N_{(2)}-C_{(2)}$	1.379(11)	$C_{(10)}-C_{(11)}$	1.403(12)
$N_{(2)}-C_{(5)}$	1.386(11)	$C_{(12)}-C_{(17)}$	1.392(13)
$N_{(2)}-N_{(3)}$	1.393(9)	$C_{(12)}-C_{(13)}$	1.432(12)
$N_{(3)}-C_{(1)}$	1.346(11)	$C_{(13)}-C_{(14)}$	1.392(13)
$N_{(4)}-C_{(2)}$	1.375(11)	$C_{(14)}-C_{(15)}$	1.384(13)
$N_{(4)}-C_{(1)}$	1.391(10)	$C_{(15)}-C_{(16)}$	1.385(13)
$N_{(4)}-N_{(6)}$	1.423(9)	$C_{(16)}-C_{(17)}$	1.389(12)
$N_{(5)}-C_{(1)}$	1.356(11)	$O_{(3)}-C_{(18)}$	1.227(11)
$N_{(7)}-C_{(9)}$	1.495(12)	$N_{(8)}-C_{(18)}$	1.322(11)
$C_{(3)}-C_{(4)}$	1.410(11)	$N_{(8)}-C_{(21)}$	1.441(11)
$C_{(3)}-C_{(12)}$	1.508(12)	$N_{(8)}-C_{(20)}$	1.475(12)
$C_{(4)}-C_{(5)}$	1.395(11)		
$C_{(5)}-C_{(6)}$	1.504(12)		
$C_{(6)}-C_{(7)}$	1.409(12)		

The complete analogy between the conditions for the synthesis of compound and the spectroscopic properties of compound IIIe and compounds IIIa-d,f-j permit the conclusion that they have identical structures.

The formation of the triazolopyrimidine salts IIIa-j occurs as a result of alkylation of the triamine I by the corresponding α-bromoketone, formed by elimination of HBr from molecules IIa-j [2, 5] with subsequent dehydrobromination and dehydration. Thus in its reactions with the ketones IIa-j the diamine I behaves as a typical 1,3-dinucleophile.

The synthetic scheme was confirmed by the formation of the perchlorate IIIe' in the reaction of the triamine I with 4-nitro-α-bromochalcone in the presence of a catalytic amount of $HClO_4$. The strong acid effectively catalyzes the dehydration and the perchlorate IIIe' is formed in 0.5 h.

Compounds IIIa-j precipitate from the reaction mixture as solvates containing one molecule of water; on recrystallization from DMF trans-solvation occurs and is accompanied by a hypsochromic effect ($\Delta\lambda = 60$ nm).

The chemical properties of salts IIIa-j were studied using compounds IIIa,e as examples. Thus acylation of salts IIIa,e with acetic anhydride in pyridine gave the monoacetyl derivatives IVa,e with loss of hydrazine amino group. Reaction of salts IIIa,e with *p*-nitrobenzaldehyde gave the *p*-nitrobenzylidene derivatives Va,e.

Heating salt IIIa in chloroform gave compound VIa, ^{1}H NMR spectrum contained a singlet for the amino group at $\Delta = 6.42$ ppm, quartets for the *o*-protons with chemical shifts of 8.48 and 8.25 ppm respectively, and a multiplet for the aromatic protons at 7.60-7.78 ppm. A singlet at 8.07 ppm was assigned to the C–H proton of the pyrimidine ring shifted to weak field under the influence of the aryl radicals. The mass spectrum of compound VIa contained a molecular ion peak with *m/z* 287. Electron impact fragmentation gave rise to peaks with *m/z* 247, 232, 204, and 205. The peaks at *m/z* 232 and 247 arose by thermolysis as indicated by the mass fragmentogram. Compound VIa was assigned the structure 2-amino-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidine on the basis of these data. It was also identified by comparison with a sample prepared by a known method [6]. Using compound IIIe as an example, loss of the hydrazine amino group was observed when an attempt was made to prepare the diazonium salt: triazolo[1,5-*a*]pyrimidine, VIe, was isolated. A similar elimination has been recorded for N-aminothionazoles [7].

All of the salts IIIa-j are quite stable when their ethanol solutions were stored in the dark and stability increased when a nitrophenyl group was present at position 5 of the bicycle. At the same time it was noted that compounds IIIa and IIIc underwent rapid photodestruction in sunlight to give compound VII. The ^{1}H NMR spectrum of compound VII contained amino group singlets at 5.44 and 5.55 ppm and aromatic proton signals at 8.13-8.20 (2H, quartet, *o*-protons) and 7.42-7.46 ppm (3H, m). The mass spectrum included a molecular ion at *m/z*

TABLE 3. Bond Angles (deg) in Molecule of Compound IIIe

Angle	ω	Angle	ω
$C_{(2)}-N_{(1)}-C_{(3)}$	112.9(9)	$C_{(4)}-C_{(5)}-C_{(6)}$	125.4(10)
$C_{(2)}-N_{(2)}-C_{(5)}$	118.5(8)	$C_{(7)}-C_{(6)}-C_{(11)}$	119.4(9)
$C_{(2)}-N_{(2)}-N_{(3)}$	114.4(8)	$C_{(7)}-C_{(6)}-C_{(5)}$	119.5(9)
$C_{(5)}-N_{(2)}-N_{(3)}$	127.0(8)	$C_{(11)}-C_{(6)}-C_{(5)}$	121.0(9)
$C_{(1)}-N_{(3)}-N_{(2)}$	101.6(7)	$C_{(8)}-C_{(7)}-C_{(6)}$	120.7(9)
$C_{(2)}-N_{(4)}-C_{(1)}$	108.0(8)	$C_{(7)}-C_{(8)}-C_{(9)}$	119.0(10)
$C_{(2)}-N_{(4)}-N_{(6)}$	130.5(8)	$C_{(8)}-C_{(9)}-C_{(10)}$	122.8(9)
$C_{(1)}-N_{(4)}-N_{(6)}$	121.5(8)	$C_{(8)}-C_{(9)}-N_{(7)}$	119.0(11)
$O_{(1)}-N_{(7)}-O_{(2)}$	125.9(11)	$C_{(10)}-C_{(9)}-N_{(7)}$	118.2(10)
$O_{(1)}-N_{(7)}-C_{(9)}$	117.7(11)	$C_{(9)}-C_{(10)}-C_{(11)}$	118.1(9)
$O_{(2)}-N_{(7)}-C_{(9)}$	116.3(11)	$C_{(10)}-C_{(11)}-C_{(6)}$	120.1(9)
$N_{(3)}-C_{(1)}-N_{(5)}$	125.9(9)	$C_{(17)}-C_{(12)}-C_{(13)}$	118.3(9)
$N_{(3)}-C_{(1)}-N_{(4)}$	112.5(8)	$C_{(17)}-C_{(12)}-C_{(3)}$	123.3(10)
$N_{(5)}-C_{(1)}-N_{(4)}$	121.5(9)	$C_{(13)}-C_{(12)}-C_{(3)}$	118.4(9)
$N_{(1)}-C_{(2)}-N_{(4)}$	127.5(10)	$C_{(14)}-C_{(13)}-C_{(12)}$	118.9(10)
$N_{(1)}-C_{(2)}-N_{(2)}$	129.0(10)	$C_{(15)}-C_{(14)}-C_{(13)}$	122.4(11)
$N_{(4)}-C_{(2)}-N_{(2)}$	103.4(9)	$C_{(14)}-C_{(15)}-C_{(16)}$	118.0(11)
$N_{(1)}-C_{(3)}-C_{(4)}$	123.2(9)	$C_{(15)}-C_{(16)}-C_{(17)}$	121.7(11)
$N_{(1)}-C_{(3)}-C_{(12)}$	115.9(10)	$C_{(16)}-C_{(17)}-C_{(12)}$	120.7(10)
$C_{(4)}-C_{(3)}-C_{(12)}$	120.9(10)	$C_{(18)}-N_{(8)}-C_{(21)}$	122.6(10)
$C_{(5)}-C_{(4)}-C_{(3)}$	120.8(9)	$C_{(18)}-N_{(8)}-C_{(20)}$	120.1(9)
$N_{(2)}-C_{(5)}-C_{(4)}$	115.6(9)	$C_{(21)}-N_{(8)}-C_{(20)}$	117.2(10)
$N_{(2)}-C_{(5)}-C_{(6)}$	119.0(9)	$O_{(3)}-C_{(18)}-N_{(8)}$	127.9(10)

218. The IR spectrum (KBr disk) contained absorptions at 1668 cm^{-1} ($\nu_{C=O}$), 3243 and 3350 cm^{-1} (N-H bond). All of the experimental results indicate photolysis to give 3,4-diamino-5-(N-benzoyl)-1,2,4-triazole. Photodestruction was not observed when an ethanolic solution of compound IIIe was irradiated.

The amino groups in compounds IIIa-j have low nucleophilicity and did not react with phenacyl bromides and chalcones even under vigorous conditions.

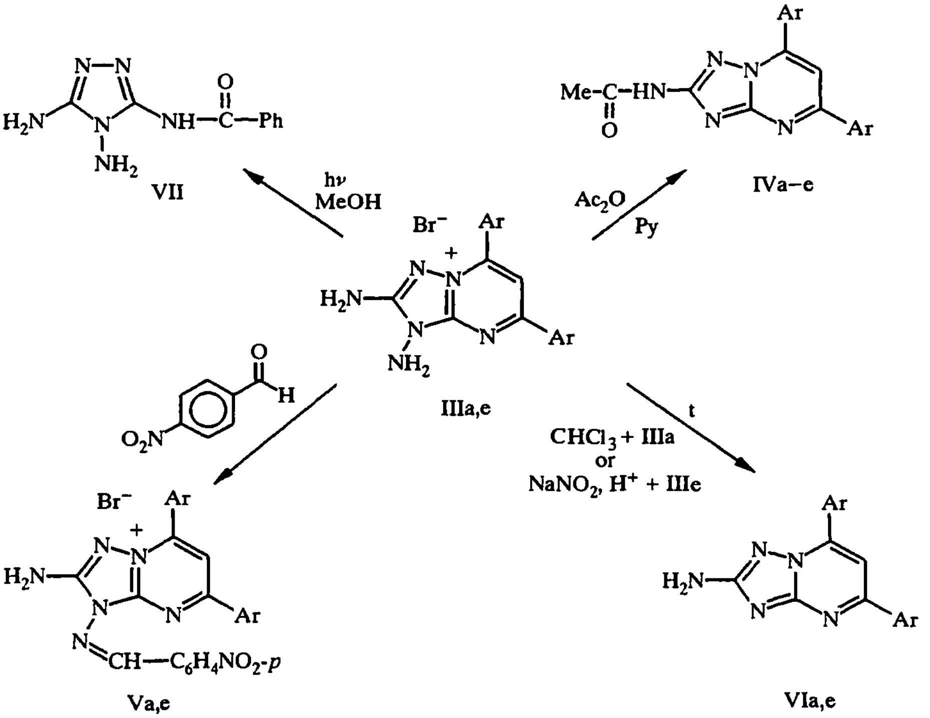


TABLE 4. Spectral Characteristics of Compound IIIa in Solvents of Varying Polarity

Solvent	ν_{abs}, cm^{-1}	ν_{flu}, cm^{-1}	$\Delta\nu$, cm^{-1}
Dioxane	20040	18760	1280
Acetone	20440	18940	1500
Acetonitrile	21300	19080	2220
Methanol	23680	19100	4580
Water	24940	19820	5120

The synthesized compounds IIIa-j have intense yellow-green fluorescence in polar solvents. A comparison of their fluorescence characteristics showed that substituents at positions 5 and 7 have insignificant effect on the fluorescence. The absorption and fluorescence of compound IIIa have been measured in various solvents. Attention is drawn to the increase in the Stoke's shift on going from a nonpolar aprotic solvent (dioxane) to a polar protic solvent (water) (Table 4) which indicates that the polarity of compound IIIa increases on going to the excited state.

TABLE 5. Coordinates ($E \times 10^4$) and Equivalent Isotropic Thermal Parameters ($E^2 \times 10^3$) for the Non-hydrogen Atoms in Molecule of Compound IIIe

Atom	x	y	z	$U_{(eq)}$
$Br_{(1)}$	209(1)	10954(1)	1387(1)	65(1)
$O_{(1)}$	5050(7)	17584(8)	-2853(4)	83(3)
$O_{(2)}$	4894(9)	19133(10)	-2161(5)	111 (4)
$N_{(1)}$	-23(7)	13294(9)	-583(4)	33(2)
$N_{(2)}$	1850(7)	13671(8)	-940(4)	33(2)
$N_{(3)}$	2943(7)	13049(8)	-923(4)	42(2)
$N_{(4)}$	1688(7)	11856(8)	-431(4)	38(2)
$N_{(5)}$	3622(7)	10962(9)	-454(4)	58(2)
$N_{(6)}$	1366(6)	10765(8)	-77(4)	50(2)
$N_{(7)}$	4691(8)	18042(11)	-2386(5)	57(3)
$C_{(1)}$	2807(9)	11939(11)	-597(5)	35(3)
$C_{(2)}$	1054(10)	12966(10)	-658(5)	34(3)
$C_{(3)}$	-359(9)	14507(11)	-824(5)	37(3)
$C_{(4)}$	391(9)	15330(9)	-1106(4)	36(3)
$C_{(5)}$	1521(9)	14912(11)	-1178(5)	39(3)
$C_{(6)}$	2387(8)	15699(9)	-1477(5)	31(3)
$C_{(7)}$	2536(9)	17034(10)	-1325(5)	48(3)
$C_{(8)}$	3285(9)	17792(10)	-1617(5)	49(3)
$C_{(9)}$	3878(8)	17223(12)	-2071(5)	40(3)
$C_{(10)}$	3739(8)	15910(12)	-2255(4)	40(3)
$C_{(11)}$	2996(9)	15137(10)	-1948(5)	44(3)
$C_{(12)}$	-1607(9)	14930(11)	-779(5)	35(3)
$C_{(13)}$	-2343(9)	14036(11)	-509(4)	45(3)
$C_{(14)}$	-3498(10)	14415(13)	-467(5)	61(4)
$C_{(15)}$	-3953(10)	15636(15)	-665(6)	64(4)
$C_{(16)}$	-3229(10)	16493(11)	-922(5)	52(3)
$C_{(17)}$	-2073(9)	16156(11)	-976(5)	51(3)
$O_{(3)}$	3960(6)	9036(8)	638(4)	70(2)
$N_{(8)}$	3648(8)	8381(8)	1661(5)	51(3)
$C_{(18)}$	3363(9)	8971(11)	1071(7)	50(3)
$C_{(20)}$	4826(10)	7736(11)	1875(6)	80(4)
$C_{(21)}$	2885(10)	8420(12)	2140(6)	94(5)

Fluorescence of compounds of type III is characterized by satisfactorily high quantum yields (Table 1); a substantial decrease in quantum yield was only observed for compounds containing heavy atoms (compounds IIIi and IIIj).

EXPERIMENTAL

X-ray Structural Study. Crystals of molecule IIIe ($C_{17}H_{14}N_7O_2^+Br^-\cdot C_3H_7NO$) are monoclinic. At 20°C $a = 11.389(5)$, $b = 10.277(4)$, $c = 20.371(6)$ Å, $\beta = 102.60(3)°$, $V = 2372(2)$ Å^3, $d_{calc} = 1.431$ g/cm^3, space group $P2_1/n$, $Z = 4$. The unit cell parameters and the intensities of 1155 independent reflexions ($R_{int} = 0.034$) were measured with a Siemens P3/PC automatic diffractometer (λMoKα, graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{max} = 50°$). Absorption was calculated by direct integration over the crystal ($T_{min} = 0.7944$, $T_{max} = 0.9497$).

The structure was solved by direct methods using the SHELXTL PLUS suite of programs [8]. The positions of the hydrogen atoms were calculated geometrically and refined using the "riding" model with fixed $U_{iso} = nU_{eq}$ of the non-hydrogen atom bonded to the hydrogen atom ($n = 1.5$ for methyl groups and 1.2 for other hydrogen atoms). Refinement on F^2 by full matrix least squares in the anisotropic approximation for non-hydrogen atoms for 1155 reflexions gave a final $wR_2 = 0.090$ ($R_1 = 0.039$ for 1028 reflexions with $F > 4\sigma(F)$, $S = 1.02$). Coordinates of the nonhydrogen atoms are given in Table 2.

IR spectra of KBr disks were recorded on an IR-75 spectrometer. Electronic spectra of methanol solutions with a concentration of $1.5\cdot10^{-5}$ mol/liter were obtained with a Specord UV-vis machine. Fluorescence spectra of methanol solutions were recorded with a Hitachi F-4010 spectrofluorometer (the standard for calculation of quantum yields was a solution of quinine hydrogen sulfate in 0.1N H_2SO_4). ^{1}H NMR spectra of DMSO-d_6 solutions with TMS as internal standard were measured with A Varian VXR-200 Gemini instrument. Mass spectra were recorded with a Finnigan MAT 4651P instrument under standard conditions. The mass spectrum of compound IIIe was also measured in glycerol with an MI 1201-E machine. Purity of the products was monitored by TLC on Silufol UV-254 strips with a methanol–chloroform (1:10) solvent system.

2,3-Diamino-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidinium Bromide (IIIa). A mixture of ketone IIa (1.84 g, 5 mmol), triamine I (0.6 g, 5 mmol), and triethylamine (1 ml) in methanol (70 ml) was boiled for 2 h when the solution had an intense green luminescence. After evaporation of 2/3 of the solvent salt IIIa (0.75 g, 53%) precipitated and was recrystallized from 1:10 chloroform–methanol. ^{1}H NMR spectrum: 5.95 (2H, s, C-NH_2), 7.30 (2H, s, N–NH_2), 7.38-7.44 (7H, m, arom. CH), 8.02–8.05 (2H, d, arom. CH), 8.76-8.79 ppm (2H, d, arom.CH). Mass spectrum, *m/z* (I_{rel}, %): 303 (100), 286 (45), 205 (12), 200 (52), 199 (36), 103 (80), 102 (73).

Compounds IIIb-j were obtained analogously starting from the dibromides IIb-j. The characteristics of **compounds IIIa-j** are cited in Table 1. The ^{1}H NMR and mass spectra of some of them are given below.

Compound IIIc. ^{1}H NMR spectrum: 6.03 (2H, s, C–NH_2), 7.38 (2H, s, N–NH_2), 7.42-7.47 (5H, m, arom. CH), 8.12–8.14 (2H, d, arom.CH), 8.75-8.77 ppm (2H, d, arom. CH). Mass spectrum, *m/z* (I_{rel},%): 338 (22), 336 (80), 301 (10), 281 (5), 266 (8), 137 (12), 129 (8), 103 (18).

Compound IIIe. ^{1}H NMR spectrum: 6.44 (2H, s, C–NH_2), 7.68-7.70 (3H, m, arom. CH), 8.17 (2H, s, N–NH_2), 8.42-8.50 ppm (7H, m, arom. CH). Mass spectrum, *m/z*, (I_{rel}, %): 348 ([M^+] - Br) (in glycerol). Mass spectrum, *m/z*, (I_{rel}, %): molecular ion peak absent, 332 (28), 331 (7), 283 (5), 244 (6), 190 (10), 188 (10), 161 (49), 160 (100), 158 (51), 82 (60), 81 (80), 80 (70), 79 (92).

Compound IIIe (DMF Solvate). ^{1}H NMR spectrum: 2.73 (3H, s, DMF), 2.89 (3H, s, DMF), 6.44 (2H, s, C–NH_2), 7.68-7.71 (3H, m, arom. CH), 8.07 (1H, s, DMF), 8.12 (2H, s, N–NH_2), 8.42-8.57 ppm (7H, m. arom. CH).

Compound IIIf. ^{1}H NMR spectrum (CD_3OD): 2.38 (3H, s, CH_3), 5.20 (2H, s, C–NH_2), 6.56 (2H, s, N–NH_2), 7.23-7.26 (2H, d, arom. CH), 7.46-7.49 (3H, m, arom. CH), 7.87-7.90 (2H, d, arom. CH), 8.40-8.48 ppm (2H, d, arom.CH).

Compound IIIi. ^{1}H NMR spectrum: 6.01 (2H, s, C–NH_2), 7.34 (2H, s, N–NH_2), 7.41-7.45 (5H, m, arom.CH), 8.11-8.14 (2H, q, arom. CH), 8.77-8.80 ppm (2H, d. arom. CH).

2,3-Diamino-7-(4-nitrophenyl)-5-phenyl-1,2,4-triazolo[1,5-*a*]pyrimidinium Perchlorate (IIIe'). A solution of amine I (0.25 g, 2 mmol) and 4-nitro-α-bromochalcone (1.0 g, 2 mmol) in methanol (60 ml) containing concentrated perchloric acid was boiled for 0.5 h. On cooling the perchlorate IIIe' precipitated (0.65 g, 95%); mp 275°C. IR Spectrum: 1672 (C+n), 3405, 3343, 3285 cm^{-1} (N–H). Found, %: N 20.0. $C_{17}H_{14}N_7O_6Cl\cdot H_2O$. Calculated, %: N 21.0.

2-Acetylamino-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidine (IVa). A solution of salt IIIa (0.3 g, 1 mmol) and acetic anhydride (3 ml, 30 mmol) was heated in pyridine (8 ml) for 10 min. After cooling the reaction mixture was poured onto ice and filtered to give yellow crystals of compound IVa (0.3 g, 85%); mp 318-319°C. IR spectrum: 3400 br (N–H), 1636 cm^{-1} (C=O). ^{1}H NMR spectrum: 2.49 (3H, s, CH_3), 7.64-7.67 (3H, m, arom. CH), 8.43-8.55 ppm (7H, m, arom.CH). Found, %: N 21.2. $C_{19}H_{14}N_5O$. Calculated, %: N 21.3.

Compound IVe was prepared analogously. Mp 320-321°C. IR Spectrum: 1642 (C=O), 1518, 1342 cm^{-1} (NO_2). Found,%: N 22.4. $C_{19}H_{14}N_6O_3$. Calculated, %: N 22.5.

2-Amino-3-(*p*-nitrobenzylideneamino)-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidinium Bromide (Va). A mixture of salt IIIa (0.2 g, 0.66 mmol) and 4-nitrobenzaldehyde (0.1 g, 0.66 mmol) was boiled in DMF (5 ml) for 40 min. After cooling the reaction mass was carefully diluted with water and filtered to give compound Va (0.1 g, 35%); mp 225-226°C. IR spectrum: 3425 br (NH_2), 1520, 1338 cm^{-1} (NO_2). Found, %: N 19.1. $C_{24}H_{18}BrN_7O_2$. Calculated, %: N 19.0.

Compound Ve was prepared analogously. Yield 40%; mp 248-249°C. Found, %: N 19.8. $C_{24}H_{17}BrN_8O_4$. Calculated, %: N 20.0.

2-Amino-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidine (VIa). A solution of salt IIIa (0.5 g, 1.6 mmol) was heated in a 4:1 chloroform–methanol mixture (20 ml) for 20 min. After cooling filtration gave 2-amino-5,7-diphenyl-1,2,4-triazolo[1,5-*a*]pyrimidine (VIa) (0.33 g, 27%); mp 233-234°C. Lit. mp 233-234°C [6]. Found, %: N 24.3%. $C_{17}H_{13}N_5$. Calculated, %: N 24.4.

Compound VIe was obtained under conditions for the diazotization of weakly basic amines [9]. Yield 33%; mp 271-272°C. IR spectrum: 3449, 3318 (NH_2), 1649 (C=N), 1510, 1340 cm^{-1}. Found, %: N 25.2. $C_{17}H_{13}N_6O_2$. Calculated, %: N 25.3.

3,4-Diamino-5-(N-benzoylamino)1,2,4-triazole (VII). A. A solution of salt IIIa (0.3 g, 1 mmol) in methanol (30 ml) was irradiated with a mercury lamp for 10 h, after which 2/3 of the solvent was evaporated and compound VII precipitated (0.12 g, 80%); mp 208-209°C. IR spectrum: 3350, 3243 (NH_2), 1688 cm^{-1} (C=O). Found, %: N 38.4. $C_9H_{10}N_6O$. Calculated, %: N 38.5.

B. Compound VII (0.1 g, 75%) was obtained on photoirradiation of compound IIIc (0.25 g).

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