

8. G. A. Shvekhgeimer, V. I. Kelarev, V. I. Shvedov, and L. A. Dyankova, *ZhVKhO*, **32**, 461 (1987).
9. A. Baran'ski, Doctoral Dissertation, I. M. Gubkin Moscow Oil and Gas Institute (1974).
10. R. Hisgen, *J. Org. Chem.*, **41**, 403 (1976).
11. C. Grundmann, *Synthesis*, No. 7, 344 (1970).
12. H. Chikaschita and Y. Morita, *Synth. Commun.*, **15**, 527 (1985).
13. Yu. K. Yur'ev, N. S. Zefirov, and R. A. Ivanova, *Zh. Obshch. Khim.*, **33**, 3512 (1963).

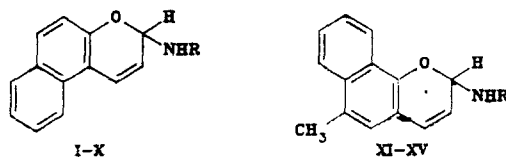
PHOTOCHEMISTRY OF 2-AMINO-2H-BENZOCHROMENES*

A. V. Metelitsa, N. V. Volbushko, and M. I. Knyazhanskii

UDC 547.814+541'651'634'14:543.422

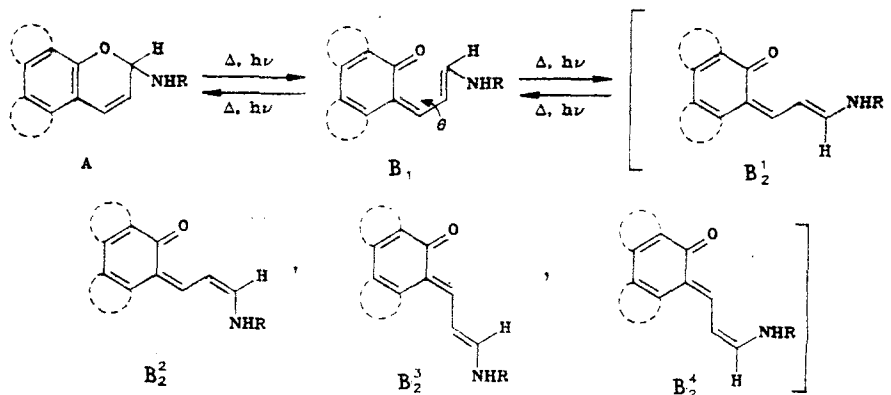
Diabatic photoinduced ring opening of the chromene ring of 2-amino-5,6-benzo-2H-chromenes and 2-amino-6-methyl-7,8-benzo-2H-chromenes leads, in the same way as a thermally induced reaction, to the establishment of ring-chain tautomer equilibrium in the ground electronic state, the position of this equilibrium depending on the polarity of the solvent, the temperature, and structural factors. o-Quinoid tautomers exist as several stable isomeric forms: an acoplanar cis-S-cis-trans-form absorbing in the shortwave region, and S-trans-isomers absorbing in the longwave region of the spectrum. Photoexcitation of the o-quinoid forms in the temperature range 125-190 K initiates mutual conversions of these and the initial 2H-chromene structure. The relative stability of the conformers of the o-quinoid form depends on steric and electronic factors: benzanellation in positions 5,6 leads to stabilization of the cis-S-cis-trans-isomer and in positions 7,8 the S-trans-isomers are more preferred: π -acceptor substituents on the amine component increase the stability of the cis-S-cis-trans isomer and electron-donor substituents stabilize the S-trans-isomer.

Synthetic methods, structure, and tautomeric equilibria in the ground electronic state for 2-amino-2H-benzochromenes, together with some details of the photochemical properties in solution, have been given in [2-4]. In the present work we consider the influence of the aminogroup substituents and the location of annelation on the spectral and photochemical properties of aminochromenes I-XV (Table 1)



For assignment of radicals, see Table 1

In solutions of the 2H-aminochromenes I-XV ring-chain equilibrium is established involving chromene form (A), the acoplanar (in terms of the angle θ) cis-S-cis-trans-isomer (B_1), and the aggregate of S-trans-isomers B_2^i ($i = 1, 2, 3, 4$) [2-4].



*Communication 20 from the series "Photo- and thermochromic piranes." See [1] for Communication 19.

Scientific-Research Institute for Physical and Organic Chemistry, Rostov State University, Rostov-on-Don. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 4, pp. 453-458, April, 1991. Original article submitted May 3, 1988; revision submitted February 5, 1990.

TABLE 1. Relative quantum Yields (Φ) of the Photoreaction of Aminochromenes in 4:1 Isopentane-Isopropanol

Compound	R	Φ	Compound	R	Φ
I	C ₆ H ₄ Br- <i>p</i>	0,1	VIII	C(CH ₃) ₃	0,3
II	C ₆ H ₅	0,2	IX	CH(CH ₃) ₂	1
III	C ₆ H ₄ CH ₃ - <i>p</i>	0,07	X	C ₅ H ₄ N- α	—
IV	C ₆ H ₂ (CH ₃) ₃ -2,4,6	0,04	XI	C ₆ H ₄ NO ₂ - <i>p</i>	1
V	C ₆ H ₄ OCH ₃ - <i>p</i>	0,03	XII	C ₆ H ₄ Br- <i>p</i>	0,1
VI	C ₆ H ₄ N(CH ₃) ₂ - <i>p</i>	0,07	XIII	C ₆ H ₅	0,01
VII	CH ₂ C ₆ H ₅	0,5	XIV	C ₆ H ₄ OCH ₃ - <i>p</i>	0,03
			XV	CH ₂ C ₆ H ₅	0,04

*Relative quantum yields of compounds I-IX evaluated in terms of product B₁ formed preferentially as a result of photoreaction at 128 K, and of compounds XI-XV in terms of products B₂ formed at 163 K.

TABLE 2. Spectral Regions of the Absorption Bands of Tautomeric Structures.

Form	$\Delta\lambda(S_0 \rightarrow S_1)$, nm	$\Delta\lambda(S_0 \rightarrow S_2)$, nm
A	325 ... 360	280 ... 320
B ₁	345 ... 440	305 ... 340
B ₂	490 ... 650	350 ... 420

Assignment of the bands in the electronic absorption spectra of compounds I-XV to S₀ → S₁ and S₀ → S₂ transitions was made on the basis of comparison of their spectra with the results of UV spectroscopy of model compounds, IR, PMR, and luminescence spectroscopy and quantum chemical calculations (Table 2). It was not possible to use the overlapped absorption bands associated with S₀ → S₁ and S₀ → S₂ transitions of the structures A, B₁, and B₂, to determine the extinctions of the separate bands. The S₀ → S₁ transitions of isomers B₂¹, differing in energy by no more than 800 cm⁻¹ [3], could not be separated spectroscopically and assigned to definite structures. These features stipulated the largely qualitative character of the present studies of photoinduction processes

The equilibrium A = B_{1,2} in the ground states is shifted in the direction of the B form as the polarity of the solvent increases and as the molecular structure varies — change in the position of 5,6 benzannellation to 7,8, and changes in the radical R in the sense of replacement of acceptor substituents by donor or methyl substituents in the aryl ring and of the latter by an alkyl group. At the same time, the equilibrium B₁ = B₂ is very strongly shifted to the right in all 7,8 benzannellated molecules, but in 5,6 benzannellated structures with R = Alk, only at T > 170 K. However, for this same structure with R = Ar, and at T < 170 K and for R = Alk, the prevailing form becomes B₁.

The photochromic properties of all the compounds I-XV are determined exclusively by the photolytically induced change of character for the ground states of the tautomeric equilibrium of A, B₁, and B₂ without the formation of new forms.

The rate of dark relaxation increases rapidly with increase in temperature: at T < 200 K it is close to zero and the dark concentrations of isomers A and B are determined by the photostationary state. However, at T ≥ 250 K the relaxation rate is already so much greater that stationary photoexcitation does not result in a marked shift in the equilibrium.

In solutions of the 2-amino-5,6-benzo-2H-chromenes I-X in the temperature range 120-200 K in the photostationary state during irradiation in the absorption band of the S₁ ← S₀ transition of form A, the B isomers predominate, dominating also in the tautomeric equilibrium characteristic for the ground state of the given molecular structure at the corresponding temperature. Thus, on photolysis of arylaminochromenes I-VI and X, apart from an insignificant amount of B₂, the photoproduct B₁ is predominantly formed (Fig. 1). At the same time, for the alkylaminochromenes VII-IX, the photoproduct B₂ is mainly formed, but the concentration (relative to B₁) falls with reduction in temperature (see above) (Fig. 2).

At T < 130 K, the effectiveness of the photolytic formation of product B₁ correlates with the dependence of the stability of the quinoid isomers in the ground state on the nature of the substituent R, and is increased on moving from

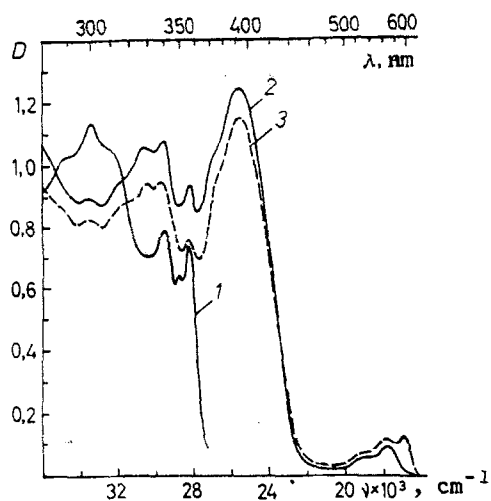


Fig. 1

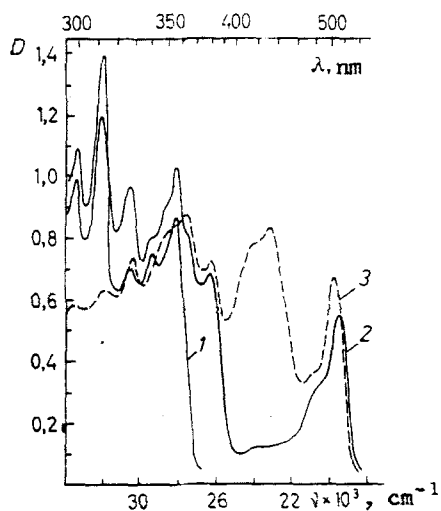


Fig. 2

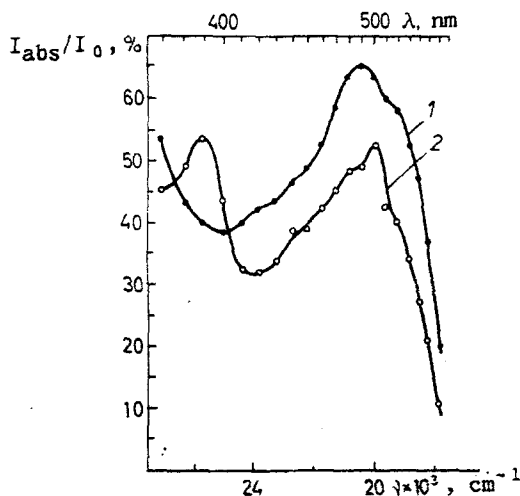


Fig. 3

Fig. 1. Photoinduced change in the absorption spectrum of aminochromene I in 4:1 isopentane-isopropanol. $\lambda_{\text{irr}} = 313 \text{ nm}$: 1, 2) 0 and 40-min irradiation, respectively (163 K, $c = 6 \cdot 10^{-5}$ mole/liter); 3) 35-min irradiation (153 K, $c = 4 \cdot 10^{-5}$ mole/liter).

Fig. 2. Photoinduced change in the absorption spectrum of aminochromene IX in 4:1 isopentane-isopropanol. $\lambda_{\text{irr}} = 313 \text{ nm}$: 1, 2) 0 and 10-min irradiation, respectively (188 K, $c = 5 \cdot 10^{-5}$ mole/liter); 3) 4-min irradiation (143 K, $c = 3 \cdot 10^{-5}$ mole/liter).

Fig. 3. Photoinduced absorption spectra (293 K, CH_3CN , $c = 10^{-6}$ mole/liter) of aminochromene X recorded 1 (1) and 15 msec (2) after impulse from photolytic lamp.

TABLE 3. Lifetimes τ_1 and τ_2 of Photoproducts B_1 and B_2 Respectively, Formed after Pulse Excitation of Solutions of Aminochromenes in Acetonitrile at 295 K

Com- pound	$\tau_1, 10^{-3} \text{ s}$ (λ^* , nm)	$\tau_2, 10^{-3} \text{ s}$ (λ^* , nm)	Com- pound	$\tau_1, 10^{-3} \text{ s}$ (λ^* , nm)	$\tau_2, 10^{-3} \text{ s}$ (λ^* , nm)
I	330 (390)	70 (510)	VII	600 (430)	2000 (510)
II	350 (390)	200 (510)	VIII	290 (420)	580 (510)
III	120 (390)	80 (510)	IX	460 (420)	900 (520)
IV	960 (380)	1800 (500)	X	60 (390)	30 (500)
VI	660 (400)	510 (510)			

* λ , Wavelength at which lifetime of photoproduct was determined.

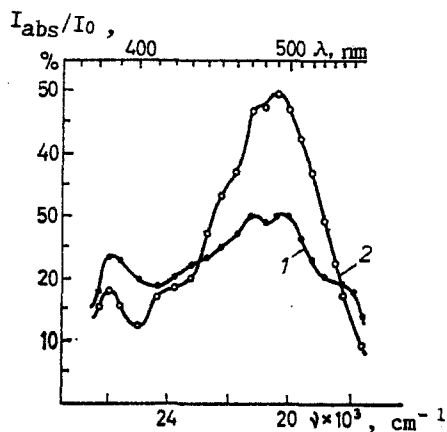


Fig. 4

Fig. 4. Photoinduced absorption spectra (293 K, CH_3CN , $c = 10^{-6}$ mole/liter) of aminochromene IV recorded 1 (1) and 70 msec (2) after impulse from photolytic lamp.

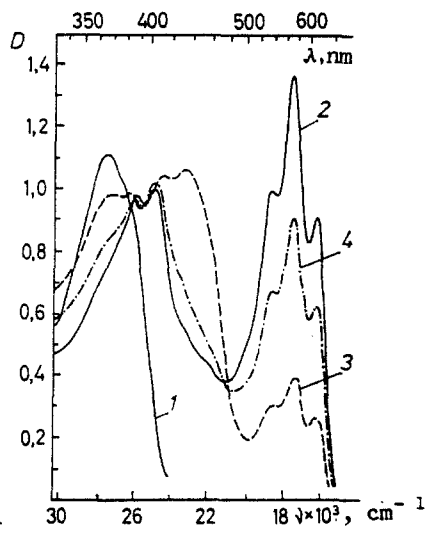


Fig. 5

Fig. 5. Photoinduced changes in the absorption spectrum of a solution of aminochromene XI in 4:1 isopentane-isopropanol, 128 K, $c = 4 \cdot 10^{-5}$ mole/liter: 1, 2) 0 and 20-min irradiation, respectively ($\lambda_{\text{irr}} = 365$ nm); 3) 20 min after 2nd irradiation ($\lambda_{\text{irr}} = 546$ nm); 4) 0.5 min after 3rd irradiation ($\lambda_{\text{irr}} = 436$ nm).

aryl to alkyl substituents (Table 1). In addition, reducing the temperature creates conditions for the stabilization of the photolytically formed B_2^i form which absorbs at a considerably longer wavelength (Fig. 1, curve 3).

The dependence of the relative amounts of forms B_1 and B_2^i in the photostationary state on the wavelength of excitation points to the photoactivity of the structures B_1 and B_2 . This is determined by the effectiveness of the photoprocesses $B_1 = A$, $B_1 = B_2^i$, and $B_2^i = B_2^j$ ($i, j = 1, 2, 3, 4; i \neq j$) and also by the overlapping of absorption bands corresponding to $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions in the A, B_1 , and B_2 structures.

In flash photolysis of solutions of aminochromenes I-X both B_1 and B_2 types of isomer are formed during the impulse. The photoinitiated dark evolution of the B structures is connected with their interconversions and transitions to form A. Thus, it follows from the experimental results (Table 3) that for all the compounds whose noncyclic B isomers are less stable thermodynamically (compounds I-III, X), such isomers are also less stable kinetically. The relationship $\tau_{B_2} < \tau_{B_1}$ is characteristic and in the dark-conversions of B structures the process $B_2 \rightarrow B_1$ predominates (Fig 3).

For compounds IV and VI-IX for which a higher thermodynamic stability of the B structures is characteristic, their kinetic stability (especially B_2) increases considerably (Table 3) so that $\tau_{B_2} > \tau_{B_1}$ and in the initial stages of the relaxation the process $B_1 \rightarrow B_2$ predominates (Fig. 4).

In both processes, the concluding stage of the relaxation is the $B_1 \rightarrow A$ process. Thus the kinetic stability of the photoisomers is determined by the same structural factors which also determine the thermodynamic stability, which results from the position of the tautomeric equilibrium of these structures in the ground state.

In contrast to the behavior of compounds I-X, photolysis of solutions of the 2-amino-6-methyl-7,8-benzo-2H-chromenes XI-XV leads to the preferential formation of B_2^i and not B_1 forms. In this case, the effectiveness of the photoreaction increases as the structure of the substituent R is changed in the succession $R = \text{Alk}, \text{Ar}$, and in the series of aryl substituents in the order $\text{Ph}-\text{D}, \text{Ph}-\text{A}$ (D, donor; A, acceptor) (Table 2). This succession is in reverse order to that which determines the increase in effectiveness of the photoreaction for compounds I-X and the shift in tautomeric equilibrium in the direction of type B quinoid structures in the ground state of both types of molecules — 5,6- and 7,8-benzannelated aminochromenes.

This variation in properties along the series of compounds XI-XV leads to the conclusion that only molecule XI, existing as it does in the A form prior to irradiation and having, in addition, a high photoconversion efficiency, is a suitable subject for a detailed study of photoinitiated processes.

Irradiation of compound XI in the absorption band of A-form chromenes at $T \approx 200$ K leads to a shift, characteristic for aminochromenes XI-XV, in the equilibrium in the photostationary state in the direction of

photoisomer B_2 exclusively ($\lambda_{\max} = 560$ nm). On reducing the temperature of the solution to $T < 130$ K, conditions become favorable for the photoinitiated accumulation of B_1 isomers ($\lambda_{\max} = 430$ nm) (Fig. 5, curve 2).

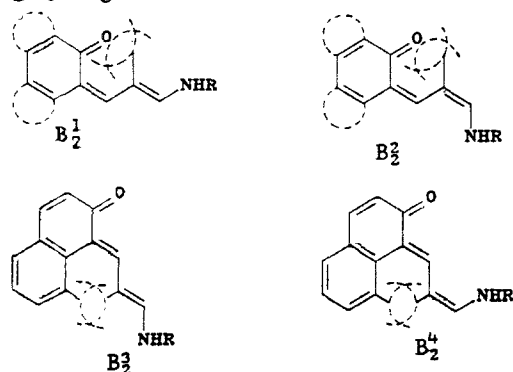
The photoactivity of quinoid structures B_1 and B_2 is displayed spectroscopically in the recording of the processes $B_2 \xrightarrow{h\nu} B_1 \rightarrow A$ and $B_1 \xrightarrow{h\nu} B_2$ on irradiation in the absorption band of the corresponding B form (Fig. 5, curves 3 and 4). Because of the fact that the accumulation of isomer B_1 is observed only at $T < 130$ K, at higher temperatures the first process is recorded spectroscopically as $B_2 \xrightarrow{h\nu} A$, and the second does not appear at all. Thus, the characteristic, structurally dependent feature which determines the photochromic properties of compounds XI-XV is the inherently lower stability of form B_1 relative to B_2 in comparison with compounds I-X.

From the above results it follows that the overall scheme of photoinduced processes in the excitation of compounds I-XV with chromene structure A must include as a first stage the photolytic formation of the acoplanar cis-S-cis-trans isomer B_1 .

A detailed study of the way in which the fluorescence excitation spectra vary with the structure of the molecule and the nature of the solvent shows that fluorescence excitation of form B_1 is absent in the absorption bands of structure A which is evidence for a diabatic mechanism in the photoprocess.

In subsequent stages the population of each of the structures A, B_1 , and B_2 is determined by the relative rates of the thermal processes in the ground state, and in the photostationary state also by the effectiveness of the excitation processes and the diabatic processes of mutual interconversion of these structures. The nature of the thermal processes depends on the relative thermodynamic stability and the relative kinetic stabilities of the A, B_1 , and B_2 forms. The general characteristic feature of the 5,6- and 7,8-benzannelated aminochromenes I-XV which distinguishes them from other chromene structures studied previously is the unusually high stability of the acoplanar cis-S-cis-trans B_1 isomer and also the planar S-trans B_2^1 isomers relative to the cyclic A structure. This is, in all probability, associated with the stabilizing effect which results from the delocalization of the unshared electron pair on the amino nitrogen along the conjugated bond system of the noncyclic structures. In fact, such an interpretation is in accord with the observed increase in stability of the B isomers in the order $R = \text{Ph}-A, \text{Ph}-D, \text{Alk}$.

The experimental results provide evidence of the considerable destabilization of the B_2 trans structures relative to the B_1 isomers in the electronic ground state of compounds I-X. According to calculations which we carried out, electronic factors prove to have no effect on the relative stability of the B_1 and B_2 isomers in benzannelation at the 5,6- and 7,8-positions of 2H-aminochromene. The difference in the heats of atomization of the acoplanar and planar S-trans isomers is independent of the position of annelation and amounts to approximately 74.5 kJ/mole. Hence, the differences in the relative stability which are observed in the spectra of the B_1 and B_2 isomers in 2-amino-5,6-benzo-2H-chromenes and 2-amino-6-methyl-7,8-benzo-2H-chromenes are explained by steric factors: benzannelation in position 5,6 lowers the stability of the more stable nonannelated chromene isomers B_2^3 and B_2^4 because of the steric hindrance which arises and thereby gives preference to the formation of the B_1 form (one could assume that steric interactions of the oxygen atom with a neighboring hydrogen leads to destabilization of the B_2^1 and B_2^2 isomers).



On the other hand, on annelation in position 7,8 steric factors do not hinder the formation of type B_2 isomers.

The influence of electronic factors is apparent on the introduction of substituents R of different electronic activity into the amino component. Substituents with π -acceptor properties stabilize the acoplanar B_1 isomer. Reduction in the electron acceptor properties, and the introduction of electron-donor substituents promotes the relative stability of the flat B_2^1 structures.

The increase in the efficiency of the buildup of B_1 photoproducts for molecules of I-XV, together with B_2^1 absorbing in the longwave region of the spectrum, at low temperatures is evidence of the thermodynamic instability of these structures and of their kinetic stabilization by the viscosity barriers of the solvent.

The authors express their gratitude to E. A. Medyantseva for placing at their disposal the compounds for the study, to S. P. Makarov for carrying out the calculations, and to V. I. Minkin for participating in the discussion of the results.

EXPERIMENTAL

Electronic absorption spectra were obtained from Specord UV-Vis and M-40 spectrophotometers provided with a device for smooth temperature changes in the sample and irradiation by a DRSh-250 mercury lamp (with a set of light filters). Flash photolysis spectra were run on apparatus with a time resolution of 10^{-6} sec as described in [3].

For determining the relative quantum yields of the photoreaction products B_1 of compounds I-IX, the quantum yield for compound IX was taken as equal to 1. Determination of the relative quantum yields at 128 K was carried out on the assumption that the molar extinction coefficients at the maximum of the absorption band of the B_1 forms of these compounds were the same. Similarly, the quantum yields of the photoreaction products B_2 of the aminochromenes XI-XV were calculated relative to compound XI at 163 K. The heats of atomization of the twisted structures were calculated by an additive approach from the heat of atomization of the 1,2-naphthaquinone-1-methane and the corresponding aminoethylene forms. In this approach the heats of atomization of the twisted structures were determined with a systematic error resulting from the imprecision of the experimental values for the rupture energy of the chemical bonds. Hence, to determine the preferred form at different positions of annelation, a comparison was made of the difference in the heats of atomization of twisted (B_1) and planar (B_2) isomers.

LITERATURE CITED

1. S. M. Aldoshin, V. A. Lokshin, A. N. Rezonov, N. V. Volbushko, N. E. Shelepin, M. I. Knyazhanskii, L. O. Atovmyan, and V. I. Minkin, *Khim. Geterotsykl. Soedin.*, No. 6, 744 (1987).
2. B. Ya. Simkin, S. P. Makarov, and V. I. Minkin, *Khim. Geterotsykl. Soedin.*, No. 8, 1028 (1982).
3. I. M. Andreeva, E. A. Bondarenko, N. V. Volbushko, M. I. Knyazhanskii, E. A. Medyantseva, A. V. Metelitsa, V. I. Minkin, and B. Ya. Simkin, *Khim. Geterotsykl. Soedin.*, No. 8, 1035 (1980).
4. I. M. Andreeva, O. M. Babeshko, E. M. Bondarenko, N. V. Volbushko, M. I. Knyazhanskii, E. A. Medyantseva, A. V. Metelitsa, and V. I. Minkin, *Khim. Geterotsykl. Soedin.*, No. 8, 1031 (1983).