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PHOTO- AND THERMOCHROMIC 2-AMINO-2H-CHROMENES*

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A number of N-aryl- and N-alkylimines of 2-hydroxy-5,6-benzocinnamaldehyde were synthesized. The cyclic 2-amino-2H-chromene structure in nonpolar solvents was established for them by IR, UV, and PMR spectroscopy. It is shown that the transition to polar solvents leads to the establishment of a tautomeric ring-chain equilibrium. The equilibrium thermal transformations and phototransformations of some N-aryl- and N-alkylimines were studied.

We have previously established that the N-arylimines of 2-hydroxy-5,6-benzocinnamaldehyde exist in the crystalline state and in solutions in nonpolar solvents in cyclic 2H-chromene form A [2]. In the present research we studied the equilibrium thermal transformations and phototransformations of N-aryl- and N-alkylimines of this aldehyde and also synthesized some new aldimines.

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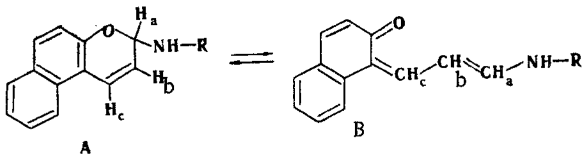


I $R=C_5H_4N$-α; II $R=C_6H_4OCH_3$ m; III $R=C_6H_4Br$ p, IV $R=C_6H_4CH_3$-p, V $R=C_6H_4OCH_3$ p;
VI $R=C_6H_4NMe_2$-p, VII $R=C_6H_2Me_3$-2,4,6; VIII $R=C_6H_5$; IX $R=CH_3$; X $R=CH_2C_6H_5$;
XI $R=C_4H_9$-n; XII $R=C(CH_3)_3$; XIII $R=CH(CH_3)_2$

Substantial differences between the N-aryl (I-VIII) and N-alkyl (IX-XIII) derivatives in the solid phase are observed. The former are colorless or light-yellow crystalline substances, while the crystals of IX-XIII have the deep-red coloration that is characteristic for conjugated quinoid structures of the B type [3]. The $\nu_{C=C}$ (1625-1650 cm^{-1}) and ν_{NH} (3250-3400 cm^{-1}) bands that are characteristic for 2H-chromene structure A [2] are observed in the IR spectra of solid I-VIII (mineral oil pastes). The latter band is absent in the IR spectra of IX-XIII (this is probably explained by the peculiarities of intermolecular association), while an intense structured band of a carbonyl group conjugated with a double bond is present at 1640-1675 cm^{-1}. This band is characteristic for the quinoid tautomers of imines of aromatic aldehydes [4] and constitutes evidence for a noncyclic structure of the B type for N-alkylimines IX-XIII.

N-Aryl- and N-alkylimines I-XIII exist in a nonpolar solvent (CCl_4) in the form of cyclic 2H-chromene structures of the A type. The IR spectra of solutions of these compounds in CCl_4 (at concentrations of 10^{-3} to 10^{-2} mole/liter) contain ν_{NH} bands (3285-3415 cm^{-1}) and $\nu_{C=C}$ bands of the 2H-pyran ring (1637-1650 cm^{-1}). The transition to polar solvents (methanol, DMSO, acetonitrile, and benzonitrile) leads to a shift of the tautomeric ring-chain equilibrium to favor noncyclic form B. The position of the equilibrium is determined by the type of substituent R. The electronic absorption and PMR spectra serve as suitable recording methods.

Whereas 2H-chromene form A does not absorb in the visible region of the spectrum [5], quinoid tautometers B are characterized by long-wave absorption bands at 400-500 nm. These bands are displayed with low intensities in the spectra of solutions of arylimine derivatives I-III with electron-acceptor groups in the ring. The intensities of the indicated bands increase markedly when electron-donor substituents are introduced in the aryl ring (IV-VII); this indicates a shift of the tautomeric ring-chain equilibrium to favor structures of the B type. Data on the electronic absorption spectra are presented in Table 1 and Fig. 1.

A study of the PMR spectra of solutions of I-XIII gives data on the tautomeric equilibrium. The presence of quinoid forms of the B type in solutions is recorded from the appearance of a doublet of protons of the NH group (with a J_{HCNH} constant of ~10 Hz, which is typical [6] for structures of the B type [3]) at 8.5 ppm for the N-arylimines and at 6.4-6.8 ppm for the N-alkylimines, the position of which is extremely sensitive to the type of solvent. The signals of the protons of the NH group of 2H-chromene form A appear at 4.2-5.4 (CCl_4) and 6.0 ppm (DMSO), while the signals for the N-arylimines appear at 1.7-1.8 (CCl_4), as compared with 2.4 ppm (benzonitrile) for the N-alkylimines. Typical PMR spectra are presented in Fig. 2. The relative percentages of the tautomers can be estimated on the basis of an analysis of the intensities of the signals of the protons corresponding to the different tautomeric forms in the PMR spectra.

The results of an estimate of the positions of the tautomeric equilibria and the characteristics of the PMR spectra of the investigated compounds are presented in Table 2.

A study of the dependence of the electronic absorption spectra on the temperature of the solutions and the effect of UV irradiation showed that the observed interconversions of the tautomeric forms of the aminochromenes are more complex than simple paired equilibria. Thus, a sharp decrease in the intensity of the long-wave absorption band ($\lambda \approx 410$ nm), which is accompanied by the appearance of a longer-wave band ($\lambda \approx 500$ nm), is observed in the case of 2-phenylimino derivative VIII in benzonitrile when the temperature of the solution is raised from 20°C to 90°C. A return to low temperature does not restore the spectrum but rather leads to a further increase in the intensity of the band at $\lambda = 500$ nm, i.e., to a gradual accumulation of the new form that is responsible for it. These spectral changes are traced in Fig. 3.

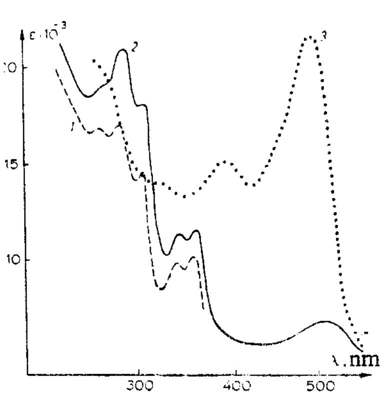


Fig. 1

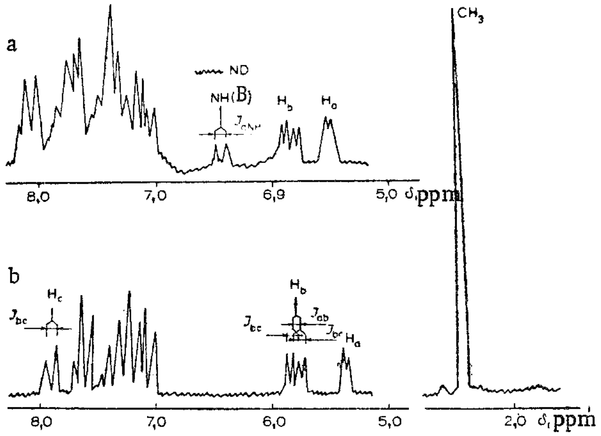


Fig. 2

Fig. 1. Electronic absorption spectra: 1) 2-(α-aminopyridine)-5,6-benzo-2H-chromene (I) in CCl_4; 2) I in DMSO; 3) 2-(p-dimethylaminophenylamino)-5,6-benzo-2H-chromene (VI) in DMSO.

Fig. 2. PMR spectra of 2-hydroxy-5,6-benzocinnamaldehyde N-methylimine (IX): a) in DMSO; b) in CCl_4.

TABLE 1. Electronic Absorption Spectra of Solutions of 2-Aryl(alkyl)amino-2H-5,6-benzochromenes in Various Solvents

Compound	R	Solvent	λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)			
I	C_5H_4N-α	CCl_4	315 (10,3)*	350 (5,3)*		
		MeOH	313 (1,3)	350 (5,3)		
		C_6H_5CN	315 (9,4)	354 (4,9)		
		DMSO	315 (12,4)	353 (6,0)		530 (1,3)
		DMSO + MeONa				510 (11,8)
II	$C_6H_4OCH_3$-*m*	CCl_4	300 (12,7)	354 (5,4)		
		MeOH	310 (9,0)	345 (5,3)		
		C_6H_5CN	310 (5,8)	350 (4,1)	495 (8,3)	
		DMSO	295 (11,4)	350 (5,4)		480 (1,6)
IV	$C_6H_4CH_3$-*p*	MeOH	310 (8,8)	348 (6,0)	380 (3,8)	547 (0,7)
		DMSO		355 (5,8)	380 (3,8)	506 (0,2)
		CH_3CN	337 (11,6)	355 (10,6)	385 (7,4)	
		C_6H_5CN	315 (8,4)	353 (7,1)		490 (10,0)
V	$C_6H_4OCH_3$-*p*	MeOH	310 (9,4)	346 (5,4)	386 (1,6)	
		DMSO	310 (11,2)	357 (8,9)	384 (8,2)	498 (7,8)
VI	$C_6H_5NMe_2$-*p*	CCl_4	318 (10,2)	355 (9,0)		
		MeOH	310 (8,6)	347 (6,0)	410 (6,3)	547 (1,1)
		CH_3CN	312 (9,3)	340 (7,3)	400 (2,0)	
		C_6H_5CN	313 (8,5)	350 (6,1)		540 (5,0)
		DMSO		330 (11,9)	385 (13,7)	498 (22,7)
		DMSO + MeONa		370 (13,9)		495 (31,2)
VII	$C_6H_2Me_3$-2,4,6	$C_6H_5Cl_2$-*o*	315 (8,4)	355 (5,5)		
		C_6H_5CN	317 (10,4)	350 (6,9)		
		DMSO	317 (7,7)	370 (10,2)		535 (0,8)
IX	CH_3	CCl_4	315 (6,5)	355 (4,6)		
		MeOH	310 (9,6)	350 (9,7)	420 (7,7)	510 (8,3)
		C_6H_5CN	315 (12,7)	355 (9,1)		520 (1,0)
		DMSO	318 (5,7)	358 (5,2)		520 (5,8)
		CH_3CN	312 (4,6)	350 (3,2)		520 (0,3)
X	$CH_2C_6H_5$	C_6H_5CN	315 (5,6)	353 (3,8)		
XI	C_4H_9-*n*	CCl_4	318 (7,0)	360 (4,8)		
		C_6H_5CN	315 (8,6)	352 (6,6)		
		MeOH	315 (9,3)	330 (9,3)		510 (15,0)
		DMSO	320 (10,0)	362 (10,7)		520 (12,2)
		CH_3CN	314 (11,7)	353 (8,0)		520 (0,3)
XII	$C(CH_3)_3$	DMSO	313 (8,0)	344 (9,1)		520 (12,7)
		CH_3CN	310 (4,9)	350 (3,3)	420 (1,4)	520 (0,7)
		C_6H_5CN	317 (16,5)	357 (9,9)	430 (3,2)	540 (1,1)
XIII	$CH(CH_3)_2$	CCl_4	315 (6,3)	355 (4,6)		
		MeOH	315 (8,7)	360 (8,3)		510 (12,6)
		C_6H_5CN	317 (16,0)	357 (9,4)		520 (0,7)
		DMSO	320 (9,9)	358 (9,3)	502 (6,5)	520 (8,4)
		DMSO + MeONa	310 (9,0)	363 (5,9)	450 (14,4)	

*The band has a vibrational structure. The long-wave maximum is presented in the table.

TABLE 2. Characteristics of the PMR Spectra of I, II, IV-VII, and IX-XIII

Compound	R	Form	Solvent	δ, ppm					J, Hz
I	C_5H_4N-α	A	CCl_4	δ_a, q, 6,46,	δ_b, q, 5,90,	δ_c, d, 8,00,	δ_{NH}, d, 5,45		J_{ab} [4], J_{bc} [10], J_{aNH} [10]
II	$C_6H_4OCH_3$-*m*	A	CCl_4	δ_a, q, 6,07,	δ_b, q, 5,94,	δ_c, d, 7,94,	δ_{NH}, d, 4,90,	δ_{CH_3}, s, 3,67	J_{ab} [4], J_{bc} [10], J_{aNH} [10]
		A	DMSO	δ_{a+b+NH}, m 6,12		δ_c, d 8,15,			J_{bc} [10],
		A	C_6H_5CN	δ_a, q, 6,20,	δ_b, q, 6,00,		δ_{NH}, d, 5,27,	δ_{CH_3}, s, 3,57	J_{ab} [4], J_{bc} [10], J_{aNH} [10]
IV	$C_6H_4CH_3$-*p*	A	DMSO	δ_{a+b+NH}, m 6,15		δ_c, d, 8,15,			J_{bc} [10],
		A : B (65 : 35)	C_6H_5CN	δ_a, q, 6,20,	δ_b, q, 6,00,		δ_{NH}, d, 5,15,	δ_{CH_3}, s, 2,15	J_{ab} [4], J_{bc} [10], J_{aNH} [10]
V	$C_6H_4OCH_3$-*p*	A : B (60 : 40)	DMSO	δ_a, q, 6,14,	δ_b, q, 5,92,	δ_c, d, 8,20,	δ_{NH} (A), d 6,35		J_{ab} [5], J_{bc} [10], $J_{aNH(A)}$ [10]
		A : B (60 : 40)	C_6H_5CN				δ_{NH} (B), d 8,51 δ_{NH} (A), s 5,05,	δ_{CH_3}, s, 3,55	$J_{aNH(B)}$ [10]
VI	$C_6H_4NMe_2$-*p*	A : B (30 : 70)	DMSO	$\delta_{a+b+NH(A)}$, m 5,95,		δ_c, d, 8,15,	δ_{NH} (B), d, 8,50		$J_{aNH(B)}$ [10]
		B	C_6H_5CN					δ_{CH_3}, s 2,70	
VII	$C_6H_2Me_3$-2,4,6	A : B (40 : 60)	C_6H_5Cl				δ_{NH} (A), d, 3,65,	δ_{CH_3}, d, 1,94	
		B	$C_6H_4Cl_2$-*o*					δ_{CH_3}, d, 2,00	
		A	C_6H_5CN				δ_{NH}, c, 3,75,	δ_{CH_3}, s, 2,00	
		B	DMSO			δ_c, d, 8,40,			
IX	CH_3	A	CCl_4 $CHCl_3$ (−50°)	δ_a, d, 5,35,	δ_b, q, 5,80,	δ_c, d, 7,93,	δ_{NH}, d, 1,70,	δ_{CH_3}, s, 2,45 δ_{CH_3}, d, 2,45	J_{CH_3NH} [5]
IX	CH_3	A : B (75 : 25)	DMSO	δ_a, d, 5,50,	δ_b, q, 5,85,	δ_c, d, 8,15,	δ_{NH} (B), d, 6,43		J_{ab} [4], J_{bc} [10], $J_{aNH(B)}$ [10]
		A : B_2 (50 : 50)	C_6H_5CN	δ_a, d, 5,50,	δ_b, q, 5,90,		$\delta_{NH(A)+CH_3}$ (A), s, 2,45 δ_{CH_3} (B_2), s 2,75		J_{ab} [4], J_{bc} [10],
		A : B : B_2*	CCl_4				δ_{CH_3} (A), s 2,45 δ_{CH_3} (B_2), s, 2,80 δ_{CH_3} (B_1), s, 3,43		
X	$CH_2C_6H_5$	A	C_6H_5CN	δ_a, d, 5,55,	δ_b, q, 5,90,		δ_{NH}, s, 2,60,	δ_{CH_2}, s, 4,00	J_{ab} [4], J_{bc} [10]
XI	C_4H_9-*n*	A	CCl_4	δ_a, d, 5,43,	δ_b, q, 5,80,	δ_c, d, 7,90,	δ_{NH}, s 1,8, δ_{NCH_2}, t, 2,78,	δ_{CH_3}, d, 0,8 $\delta_{(CH_2)_2}$, m, 1,3	J_{ab} [4], J_{bc} [10],
		A : B (40 : 60)	DMSO	δ_a, d, 5,65,	δ_b, q, 5,95,	δ_c, d, 8,20,		$\delta_{NH(B)}$, d 6,50	J_{ab} [4], J_{bc} [10], $J_{aNH(B)}$ [10]
		A	C_6H_5CN	δ_a, d, 5,55,	δ_b, q, 6,00,	δ_{NH+NCH_2}, m, 2,78,		δ_{CH_3}, d, 0,8 $\delta_{(CH_2)_2}$ m 1,25	
XII	$C(CH_3)_3$	A : B (35 : 65)	DMSO	δ_a, d, 5,83,	δ_b, q, 6,02,	δ_c, d, 8,15,	δ_{NH} (B), d, 6,82		$J_{aNH(B)}$ [10]
		A : B (35 : 65)	C_6H_5CN				δ_{NH} (A), s, 3,75,	δ_{CH_3}, s, 1,0	
XIII	$CH(CH_3)_2$	A	CCl_4	δ_a, d, 5,50,	δ_b, q, 5,80,	δ_c, d, 7,90,	δ_{NH}, s, 1,75, δ_{CH}, m, 3,25	δ_{CH_3}, d, 1,0	J_{ab} [4], J_{bc} [10],
		A : B (25 : 75)	DMSO	δ_a, d, 5,70,	δ_b, q, 5,87,	δ_c, d, 8,20,	δ_{NH} (B), d, 6,40		J_{ab} [4], J_{bc} [10], $J_{aNH(B)}$ [10]
		A	C_6H_5CN	δ_a, d, 5,62,	δ_b, q, 5,87,		δ_{NH+CH}, m, 3,20,	δ_{CH_3}, d, 0,87	J_{ab} [5], J_{bc} [10],

*Prolonged refluxing in o-dichlorobenzene.

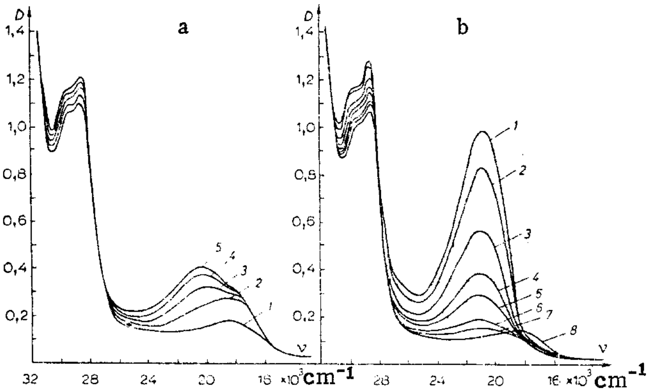


Fig. 3

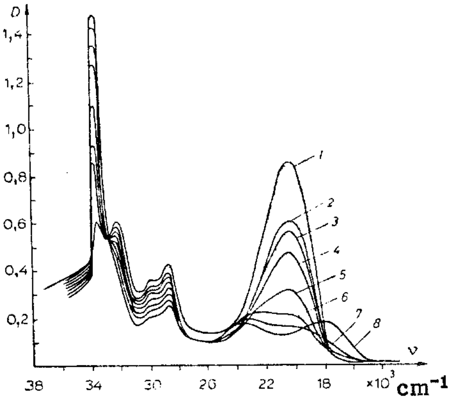


Fig. 4

Fig. 3. Electronic absorption spectra of 2-phenylamino-5,6-benzo-2H-chromene (VIII) in benzonitrile (c 10^{-4} mole/liter): a) as the temperature is raised from 20°C to 90°C: 1) 20; 2) 30; 3) 40; 4) 50; 5) 60; 6) 70; 7) 80; 8) 90°C; b) as the temperature is lowered from 90°C to 20°C: 1) 90; 2) 70; 3) 50; 4) 30; 5) 20°C.

Fig. 4. Electronic absorption spectra of 2-(m-methoxyphenylamino)-5,6-benzo-2H-chromene (II) in benzonitrile (c 10^{-4} mole/liter) as the temperature is raised from 15°C to 90°C: 1) 15; 2) 30; 3) 40; 4) 50; 5) 60; 6) 70; 7) 80; 8) 90°C.

Similar transformations are also characteristic for other N-arylaminochromenes (III, VI) in solution in benzonitrile. In the case of II cyclic chromene form A is also included in the relaxation process, as one can see from the data in Fig. 4.

Irradiation of solutions of the aminochromenes in isopentane—isopropyl alcohol (4:1) at —85°C at the wavelength of the absorption band of the closed form (λ = 313 nm) leads to a further increase in the absorption intensity of one of the long-wave bands (λ = 410 nm) (Fig. 5a). At the same time, the absorption intensity decreases in the case of excitation of the colored form at the wavelength of the band at 405 nm, during which the shortwave absorption band increases (Fig. 5b). A longer-wave absorption band at 500 nm additionally appears in the case of VI.

Two absorption bands at 390-430 and 460-520 nm, which differ substantially with respect to their relaxation times (100-400 and 800-2100 msec, respectively, which indicates that they are determined by different structural forms), appear in the case of pulse excitation of solutions of the arylaminochromenes in acetonitrile with the light of a photolytic lamp.

Compound III displays the greatest photochemical activity. The kinetics of the dark relaxation processes at the individual absorption bands obey an exponential extinction law in the case of III, VI, and VIII, and this constitutes evidence for a parallel mechanism of the dark reactions $B_1 \rightleftarrows A \rightleftarrows B_2$ [where B_1 and B_2 are two different quinoid structures ($\lambda_{max} \simeq$ 410 and 500 nm)] after photoirradiation.

A different form of kinetic curves, which is characteristic for a consecutive reaction mechanism ($A \rightleftarrows B_1 \rightleftarrows B_2$) and is shown in Fig. 6, is observed for II and VII.

The set of results obtained in this research constitutes evidence that equilibria that include at least three forms, viz., ring chromene form A and chain forms B_1 ($\lambda_{max} \simeq$ 410 nm) and B_2 ($\lambda_{max} \simeq$ 500 nm), are established in solutions of N-arlyaminochromenes in polar solvents under the influence of temperature effects or photoirradiation. The B_2 form, which absorbs in the long-wave region of the visible spectrum and is separated from B_1 and A by considerable potential barriers, the heights of which depend on the nature of the substituent in the aryl ring, is the most stable form in the ground state. Depending on the relative sizes of these barriers, the realization of parallel or consecutive processes for the formation of the A form from B_1 and B_2 becomes possible. Product B_2 is photochemically active and, depending on the nature of the substituent, can be converted by excitation either to only A or to A and B_1 simultaneously.

The problem of the structures of the spectrally observed B_1 and B_2 forms is a fundamental one. Considering the rather high kinetic barriers to the transition between them, as well as between each of them and the A form, one might have assumed that structures B_1 and B_2 are cis-trans isomers relative to the C=C bonds in the B structure. It is known [7] that the presence of a conjugated chain in such structures actually lowers the barriers to isomerization relative to the double bond to thermally attainable values. We calculated the relative stabilities and absorption spectra of all four possible geometrical isomers with chain quinoid structure B by the Pariser–Parr–Pople (PPP) method with the corresponding parametrizations (the Dewar σ, π method [8]) of the ground and excited states. The results of the calculations are presented in Table 3.

It follows from the data in Table 3 that the four geometrical isomers of quinoid tautomer B are not energetically and spectrally distinguishable. Their expected spectral characteristics agree quite well with the spectrum of the B_1 form (the difference in the calculated and experimental energies of the spectral transitions is less than 0.2 eV).

Relative to the structure of the B_2 form, one may draw a conclusion on the basis of an analogy with the characteristics of one of the photoisomers of salicylalaniline, which has long-wave absorption at 480-500 nm. A quinoid structure that is twisted about the Ar=C double bond is proposed for it [9, 10]. Our calculations actually show that this sort of deformation leads to a pronounced bathochromic shift of the spectrum to $\lambda_{max} \approx 500$ nm both in the quinoid form of salicylalaniline and for quinoids B, which are its vinylogs.

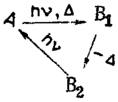
For N-methylamine derivative IX we were able to observe interconversions of three isomeric forms under the conditions of their preparative isolation. As established in [2], bubbling of methylamine into an alcohol or benzene solution of 2-hydroxy-5,6-benzocinnamaldehyde leads to a bright-red precipitate, which, after prolonged refluxing in hexane with subsequent cooling of the extract, gives a yellow substance with mp 105°C. The signal of the NCH_3 protons of this compound is observed in the PMR spectrum at weak field at 3.48 ppm (in CCl_4), which is close to the position of the CH_3 signal for the quinoid form of salicylalmethylimine [11]. The long-wave absorption band of the isomer with mp 105°C is found at 400 nm, which is in extremely precise agreement with the calculated value for the geometrical isomers of cis- and trans-quinoids of the B type (the B_1 structure).

After recrystallization from chlorobenzene or chloroform, the hexane-insoluble residue gives bright-red crystals with mp 172°C (mp 165°C [2]). The presence of a long-wave band with $\nu_{max} \approx 500$ nm in its absorption spectrum makes it possible to assign this isomer to the B_2 form with the hypothetical twisted (about the double bond) structure. The signal of the protons of the NCH_3 group is observed at 2.80 ppm.

Cyclic tautomer A, with mp 130°C, was also isolated when the compound with mp 172°C was refluxed in benzene for 30 min with subsequent removal of the solvent and extraction with hexane. The IR spectrum of a mineral oil suspension of this compound contained a ν_{NH} band at 3320 cm^{-1} and a $\nu_{C=C}$ band at 1650 cm^{-1}; λ_{max} 330 nm (CCl_4), and $\delta_{NCH_3} = 2.45$ ppm (CCl_4).

Equilibrium between the A and B_2 forms (1:1), which was established from the presence in the PMR spectrum of signals of protons of methyl groups at 2.45 and 2.80 ppm, is established rapidly when red substance IX, with mp 172°C, is dissolved in benzonitrile. When the temperature of a solution in $CHCl_3$ is lowered to −50°C, the signal at 2.45 ppm is split into a doublet as a result of coupling with the protons of the NH group ($^3J = 5$ Hz). Equilibrium involving all three forms (A, B_1, and B_2) can be observed when the red substance with mp 172°C is refluxed in chlorobenzene for a long time. In addition to the indicated two types of peaks, a peak of a signal the NCH_3 group appears in the PMR spectrum at 3.43 ppm (the B_1 form). It is interesting that thermal conversion to equilibrium mixtures is possible only on the basis of the A and B_2 forms. Prolonged heating (in o-dichlorobenzene at 170°C) of the compound with mp 105°C (B_1) does not lead to the development of isomeric products in solution.

The complex phototransformations and thermal transformations of 2-amino-2H-5,6-benzochromenes found in this research may qualify as a new previously unknown (see previous reviews [12, 13]) scheme for the accumulation of light energy. Thus, the relative stabilities and photoactivities of the B_2 isomers in series of arylamine derivatives ensure a reversible cycle in which heat energy is released in the B_1 → B_2 step:



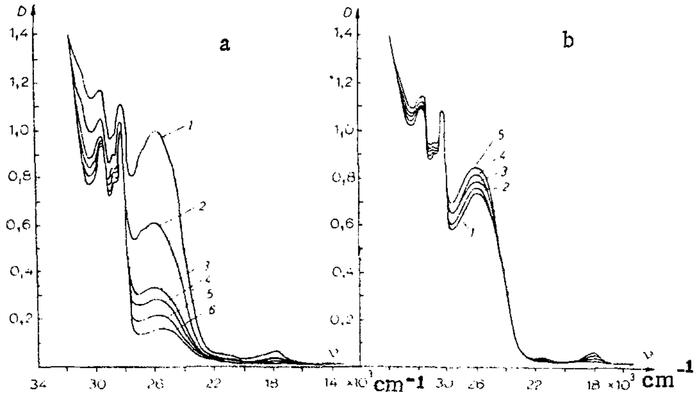


Fig. 5

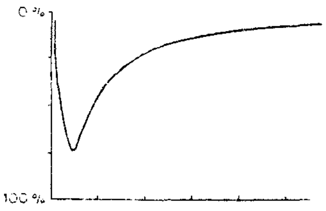
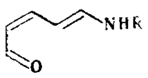
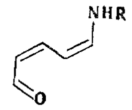
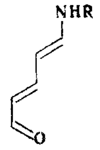
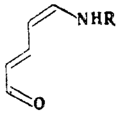


Fig. 6

Fig. 5. Electronic absorption spectra of 2-phenylamino-5,6-benzo-2H-chromene (VIII) in isopentane–isopropyl alcohol (4:1) when t = –85°C and c = 10^{-4} mole/liter: a) irradiation at the wavelength of the band at 313 nm: 1) 2340; 2) 1140; 3) 540; 4) 240; 5) 60; 6) 0 sec; b) irradiation at the wavelength of the band at 405 nm: 1) 2340; 2) 1140; 3) 540; 4) 240; 5) 0 sec.

Fig. 6. Form of the kinetic curve obtained by pulse excitation of a solution of II in acetonitrile (c 10^{-4} mole/liter, λ_{obs} = 390 nm).

TABLE 3. Relative Energies and Long-Wave Absorption Bands of the Geometrical Isomers with the B Structure (R = Ph)

Structure	Designation	Relative energy, kcal/mole	λ_{max}, nm
	*ct*	0*	330, 440
	*cc*	0,3	331, 442
	*tt*	0,2	329, 425
	*tc*	0,3	333, 435

*E_{at} = –4137 kcal/mole.

EXPERIMENTAL

The absorption spectra of the investigated compounds were recorded with a Specord UV-vis recording spectrophotometer with a device for effecting a smooth change in the temperature of

TABLE 4. 2-Hydroxy-5,6-benzocinnamaldehyde Imines

Compound	R	mp, °C	Found, %			Empirical formula	Calc., %		
			C	H	N		C	H	N
I	C_5H_4N-α	123[a]	78,7	5,2	10,4	$C_{18}H_{14}N_2O$	78,8	5,1	10,2
II	$C_6H_4OCH_3$-*m*	120[b]	79,3	5,5	4,5	$C_{20}H_{17}NO_2$	79,2	5,7	4,6
VI	$C_6H_4NMe_2$-*p*	160[c]	79,6	6,5	8,7	$C_{21}H_{20}N_2O$	79,7	6,4	8,9
VII	$C_6H_2Me_3$-2,4,6	170[d]	83,4	6,9	4,6	$C_{22}H_{21}NO$	83,8	6,7	4,4
XI	C_4H_9-*n*	125[d]	80,5	7,9	5,2	$C_{17}H_{19}NO$	80,6	7,6	5,5
XIII	$CH(CH_3)_2$	140[d]	80,3	7,3	5,6	$C_{16}H_{17}NO$	80,3	7,2	5,9

[a] From benzene—hexane. [b] From isobutanol. [c] From dioxane—water. [d] From hexane.

the samples. Acetonitrile, benzonitrile, and isopentane—isopropyl alcohol (4:1) were used as the solvents. The flash photolysis spectra were recorded with a device for lamp pulse photolysis with a resolution time of 10^{-6} sec. This resolution was achieved by means of a noninductive discharge circuit. The overalll power in the pulse of the photolytic lamp was ~18 MW. The spectra were scanned with respect to points. A halogen lamp (KGM 30 V × 300 W) was used as the probe source. Recording was accomplished with an SPM-2 monochromator with FEU-18 A and FEU-22 photomultipliers and an S8-7A high-speed storage oscillograph with an FP-722 photoadapter. The IR spectra of mineral oil suspensions and solutions of the compounds in carbon tetrachloride were obtained with a UR-20 spectrometer. The PMR spectra of 10-15% solutions of the compounds were recorded with a Varian XL-100/15 radiospectrometer with hexamethyldisiloxane as the internal standard. The percentages of the tautomeric forms in DMSO were calculated by comparison of the intensities of the H_a and H_b protons of the chromene (the A form) or the intensity of the quinoid NH proton (the B form) and the overall intensities of all of the remaining protons of the cyclic (A) and quinoid (B) forms, except for the NH proton of chromene and the NR protons (for the N-alkylimines) that are shielded by the solvent. The intensities of the NH proton (or the H_a and H_b protons) of chromene (the A form) and the overall intensities of the protons of both forms in the N—R groups were compared.

Synthesis of 2-Hydroxy-5,6-benzocinnamaldehyde Aldimines. The N-aryl- and N-alkylimines were obtained by mixing ethanol solutions of the aldehyde and the corresponding amines in equimolar amounts and subsequent recrystallization of the precipitates from a suitable solvent. The characteristics of the compounds obtained are given in Table 4.

Computational Method. The calculations of the relative stabilities and the spectral characteristics of the open forms were accomplished by means of the program of V. A. Kosobutskii [14]. We have previously set forth the parameters and details of the calculations [10]. Twenty of the singly excited configurations that are closest to the ground state were taken into account for the calculation of the energies of the spectral transitions.

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