

for 4 h, after which the excess amine was removed with a rotary evaporator, the residue was treated with 100 ml of ether, and the precipitated amine hydrochloride was removed by filtration. The solvent was removed *in vacuo*, and the residue was chromatographed with a column packed with Al<sub>2</sub>O<sub>3</sub> in hexane. The characteristics of the compounds obtained are presented in Table 1.

#### LITERATURE CITED

1. G. V. Boyd and K. Heatherington, J. Chem. Soc., Perkin Trans. I, No. 21, 2523 (1973).
2. I. G. Tishchenko, O. G. Kulinkovich, and N. V. Masalov, Khim. Geterotsikl. Soedin., No. 6, 426 (1982).
3. I. G. Tishchenko, O. G. Kulinkovich, and N. V. Masalov, Zh. Org. Khim., 18, 991 (1982).
4. I. G. Tishchenko (Tischenko), O. G. Kulinkovich, and N. V. Masalov, Synthesis, No. 4, 268 (1982).
5. I. G. Tishchenko, O. G. Kulinkovich, and N. V. Masalov, Zh. Org. Khim., 16, 1203 (1980).

#### RING-CHAIN TAUTOMERISM AND THERMO- AND PHOTOCROMISM OF

#### 3-(1-HYDROXY-4-METHYL-2-NAPHTHYL)PROPENAL IMINES\*

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A series of previously undescribed 3-(1-hydroxy-4-methyl-2-naphthyl)propenal imines was synthesized. In the crystalline state all of the imines, except the N-(p-nitrophenyl)imine, have an open o-quinoid structure, whereas in solutions in nonpolar solvents they exist in the cyclic 2H-chromene form. In polar solvents the imines display ring-chain tautomeric equilibrium of the 2H-chromene and o-quinoid forms, the relative percentages of which are determined by the character of the substituent in the amino component of the molecule and by the polarity of the solvent. The N-(p-nitrophenyl)imine has the 2H-chromene structure in the solid phase and in solvents.

We have previously shown that 3-(2-hydroxy-1-naphthyl)propenal N-arylimines have the cyclic 2H-chromene structure in the crystalline state, whereas the N-alkylimines have an open quinoid structure [2]. In solutions in nonpolar solvents all of the imines exist in the form of cyclic structures, whereas in polar solvents one observes the establishment of a ring-chain tautomeric equilibrium between the 2H-chromene and quinoid forms, the relative percentages of which are determined by the polarity of the solvent and the character of the substituent in the amino component of the molecule, is established in polar solvents [2, 3]. The photo- and thermochromic properties of these compounds have been studied [3].

In the present paper we present the results of a study of the structure of the previously undescribed 3-(1-hydroxy-4-methyl-2-naphthyl)propenal imines; we also studied their equilibrium thermal and phototransformations. We described the preparation of 3-(1-hydroxy-4-methyl-2-naphthyl)propenal in [4] and the 3-(1-hydroxy-4-methyl-2-naphthyl)propenal imines by the reaction of the aldehyde and the corresponding amines in ethanol. Their crystals had the deep dark-violet or bright-red color that is characteristic for conjugated quinoid structures of the B type. Only V, the crystals of which are light yellow, constitutes an exception.

\*Communication 14 from the series "Photochromic and thermochromic spirans." See [1] for communication 13.

TABLE I. Electronic Absorption Spectra of 3-(1-Hydroxy-4-methyl-2-naphthyl)propenal Imines

Com- pound	Solvent	$\lambda_{\text{max}}$ , nm ( $\epsilon \cdot 10^{-3}$ )
I	Benzene	315 (5,1)
	Dioxane	325 (4,9)
	CH <sub>3</sub> CN	330 (9,1)
	Acetone	327 (5,3)
	DMSO + MeONa	330 (10,7)
II	DMSO	335 (10,0)
	DMSO + MeONa	335 (10,4)
	Dioxane	338 (11,4)
	CH <sub>3</sub> CN	337 (6,3)
	Acetone	333 (7,1)
III	Ethanol	320 (12,1)
	DMSO	330 (7,7)
	DMSO + MeONa	310 (13,1)
	CCl <sub>4</sub>	313 (6,3)
	Dioxane	290 (10,8)
IV	CH <sub>3</sub> CN	325 (6,0)
	Acetone	333 (5,8)
	DMSO	335 (8,4)
	DMSO + MeONa	313 (6,3)
	Dioxane	292 (7,6)
V	Acetone	338 (6,3)
	CH <sub>3</sub> CN	335 (6,4)
	DMSO	330 (5,2)
	DMSO + MeONa	290 (4,5)
	Dioxane	313 (5,6)
		358 (4,0)
		358 (7,0)
		357 (4,3)
		357 (8,2)
		355 (7,5)
		357 (10,9)
		357 (6,3)
		357 (6,5)
		355 (10,4)
		357 (6,3)
		357 (4,1)
		358 (5,8)
		357 (4,5)
		358 (4,5)
		357 (6,6)
	357 (3,8)	
	355 (5,3)	
	355 (5,6)	
	350 (4,0)	
	353 (7,2)	
	358 (16,6)	
	357 (13,0)	
	355 (17,4)	
	370 (14,2)	
	373 (1,6)	
	490 (4,3)	
	373 (8,1)	
	373 (3,8)	
	370 (5,0)	
	390 (8,9)	
	388 (5,9)	
	373 (1,7)	
	375 (1,4)	
	385 (1,2)	
	387 (5,1)	
	500 (0,5)	
	500 (1,2)	
	505 (1,1)	
	530 (2,4)	
	515 (27,2)	
	510 (1,5)	
	510 (5,3)	
	510 (5,2)	
	520 (6,3)	
	480 (5,8)	
	540 (4,0)	
	540 (4,0)	
	560 (5,7)	
	530 (0,7)	
	540 (2,7)	
	535 (2,5)	
	530 (13,5)	
	520 (19,0)	
	530 (1,5)	
	550 (3,6)	
	545 (2,4)	
	555 (7,6)	
	515 (3,4)	
	520 (9,7)	
	518 (19,0)	
	590 (7,3)	
	585 (4,0)	
	530 (14,0)	
	550 (15,0)	
	380 (13,3)	

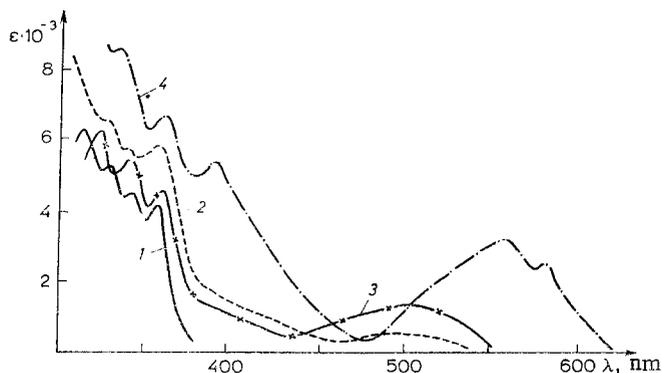
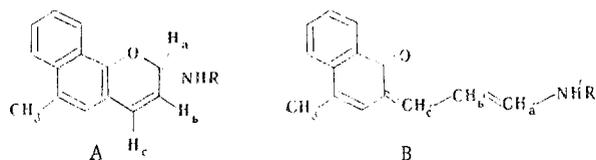


Fig. 1. Electronic absorption spectra of 3-(1-hydroxy-4-methyl-2-naphthyl)propenal N-(p-bromophenyl)imine (III): 1) in  $\text{CCl}_4$ ; 2) in dioxane; 3) in acetonitrile; 4) in DMSO.



I R =  $\text{C}_6\text{H}_5$ ; II R =  $p\text{-C}_6\text{H}_4\text{OCH}_3$ ; III R =  $p\text{-C}_6\text{H}_4\text{Br}$ ; IV R =  $\text{CH}_2\text{C}_6\text{H}_5$ ; V R =  $p\text{-C}_6\text{H}_4\text{NO}_2$

An intense absorption band of a carbonyl group conjugated with a double bond is observed in the IR spectra of I-IV in mineral oil at  $1645\text{--}1650\text{ cm}^{-1}$ . This band is characteristic for quinoid tautomers of hydroxynaphthaldehyde imines [5] and constitutes evidence for a noncyclic structure of the B type of N-arylimines I-IV. As in the case of 3-(2-hydroxy-1-naphthyl)propenal N-alkylimines, which have a quinoid structure [3], the absorption bands of the NH group in the IR spectra of I-IV are markedly diffuse and destructured; this can be explained by intermolecular association of compounds of the B type. Bands of C=C bonds of the dihydropyran ring at  $1605\text{ cm}^{-1}$  and of the NH bond at  $3395\text{ cm}^{-1}$ , which are characteristic for cyclic 2H-chromene structure A [2], are present in the IR spectrum of imine V in the solid phase.

In nonpolar solvents ( $\text{CCl}_4$  and benzene) all imines I-V exist in the form of cyclic 2H-chromene structures of the A type. Bands of the NH ( $3440\text{ cm}^{-1}$ ) and C=C ( $1625\text{ cm}^{-1}$ ) bonds of the 2H-pyran ring appear in the IR spectrum of a solution of N-phenylimine I in  $\text{CCl}_4$ . The electronic absorption spectra of I-V, like the spectra of 3-(2-hydroxy-1-naphthyl)propenal imines [2, 3], in nonpolar solvents are characterized by the typical (for 2H-chromenes) clearly expressed vibrational structure of the long-wave absorption bands at  $320\text{--}360\text{ nm}$  (Fig. 1 and Table 1).

A ring-chain tautomeric equilibrium of the  $A \rightleftharpoons B$  type, which is recorded from the appearance in the electronic spectra of long-wave bands at  $500\text{--}580\text{ nm}$ , which correspond to the absorption of quinoid tautomer B (compare with the data in [2, 3]), is established in polar solvents (ethanol, acetone, acetonitrile, and DMSO) for imines I-III. The intensities of the indicated bands increase as the polarity of the solvent increases and when an electron-donor substituent is introduced into the N-aryl ring (Fig. 1 and Table 1) and particularly on passing to the N-benzylimine (IV), where it becomes the same as that of the anion of IV (Table 1). This indicates a shift of the tautomeric equilibrium to favor open form B up to complete disappearance of the cyclic structure in the case of the N-benzylimine, which has primarily a quinoid structure in polar solvents. In the case of imine V the presence of an electron-acceptor substituent in the N-aryl fragment shifts the  $A \rightleftharpoons B$  equilibrium, even in polar solvents, to favor cyclic form A. A long-wave band of low intensity, which indicates the presence of small amounts of the VB form in the equilibrium, appears only in the spectrum of a solution in DMSO.

A study of the fluorescence spectra of tautomeric 3-(1-hydroxy-4-methyl-2-naphthyl)propenal imines indicates the presence in solutions of two conformers with a quinoid structure of the B type ( $B_1$  and  $B_2$ ) in equilibrium with chromene form A. This follows from the presence of three different fluorescence bands, the excitation spectra of which correspond to certain absorption bands (Table 2).



TABLE 3. PMR Spectra of I-V\*

Compound	Solvent	Form (%)	$\delta$ , ppm	$J$ , Hz
I	CCl <sub>4</sub>	A	6,24 (1H, q, H <sub>a</sub> ); 5,82 (1H, q, H <sub>b</sub> ); 4,34 (1H, d, NH); 2,56 (3H, s, CH <sub>3</sub> ); 6,52—6,92 (4H, m, <i>o,p</i> -H <sub>3</sub> , H <sub>c</sub> ); 6,96—7,17 (3H, m, <i>m</i> -, 5-H <sub>3</sub> ); 7,17—7,47 (2H, m, 8,9-H <sub>2</sub> ); 7,74 (1H, q, 7-H), 8,07 (1H, q, 10-H)	$J_{ab}=4$ , $J_{bc}=10$ , $J_{aNH}=10$ , $J_{10,9}=J_{7,8}=7$ , $J_{10,8}=J_{7,9}=4$
	DMSO	A (70)	6,32 (0,7H, q, H <sub>a</sub> ); 5,94 (0,7H, q, H <sub>b</sub> ); 6,88 (0,7H, d, H <sub>c</sub> )	$J_{ab}=4$ , $J_{bc}=10$ , $J_{aNH}=8$ , $J_{a'b'}=9$ , $J_{10',9'}=7$
		B (30) A+B	8,30 (0,3H, d, H <sub>a'</sub> ); 8,20 (0,3H, d, 10'-H) 7,08 (1,7H, d, <i>p,p'</i> -H, NH); 7,12—7,54 (5,3H, m, Ar, H <sub>b'</sub> ); 7,54—8,10 [2,3H, m, H <sub>c'</sub> , (NH)', 7,7',10-H]; 6,70 (2H, d, <i>o,o'</i> -H)	
II	Dioxane	A	6,28 (1H, q, H <sub>a</sub> ); 5,88 (1H, q, H <sub>b</sub> ); 5,33 (1H, d, NH); 6,64—6,96 (3H, m, <i>o</i> -H <sub>2</sub> , H <sub>c</sub> ); 6,96—7,63 (5H, m, <i>m</i> , 5,8,9-H <sub>5</sub> ); 7,86 (1H, m, 7-H); 8,10 (1H, m, 10-H)	$J_{ab}=4$ , $J_{bc}=10$ , $J_{aNH}=10$
	Dioxane + D <sub>2</sub> O	A	6,28 (1H, d, H <sub>a</sub> ); 5,88 (1H, q, H <sub>b</sub> ); 6,64—6,96 (3H, m, <i>o</i> -H <sub>2</sub> , H <sub>c</sub> ); 6,96—7,63 (5H, m, <i>m</i> , 5,8,9-H <sub>5</sub> ); 7,86 (1H, m, 7-H); 8,10 (1H, m, 10-H)	$J_{ab}=4$
	DMSO	A (35)	6,35 (0,35H, q, H <sub>a</sub> ); 5,95 (0,35H, q, H <sub>b</sub> )	$J_{ab}=4$ , $J_{bc}=10$ , $J_{a'b'}=9$ , $J_{10',9'}=7$
		B (65) A+B	8,30 (0,65H, d, H <sub>a'</sub> ); 8,20 (0,65H, d, 10'-H) 6,64—7,12 (2,70H, m, NH, H <sub>c</sub> , <i>o,o'</i> -H); 7,14—7,68 (5,65H, m, <i>m,m'</i> , 5,5',8,8',9,9'-H <sub>5</sub> , H <sub>b'</sub> ); 7,68—8,10 [2,65H, m, H <sub>c'</sub> , (NH)', 7,7',10-H]	
	III	Dioxane	A	6,30 (1H, q, H <sub>a</sub> ); 5,88 (1H, q, H <sub>b</sub> ); 5,77 (1H, d, NH); 6,65—6,95 (3H, m, H <sub>c</sub> , <i>o</i> -H <sub>2</sub> ); 7,00—7,60 (5H, m, <i>m</i> , 5,8,9-H <sub>5</sub> ); 7,92 (1H, m, 7-H); 8,05 (1H, m, 10-H)
DMSO		A (80)	6,30 (0,8H, q, H <sub>a</sub> ); 5,92 (0,8H, q, H <sub>b</sub> )	$J_{ab}=4$ , $J_{bc}=10$
		B (20) A+B	8,25 (0,4H, m, H <sub>a'</sub> , 10'-H) 6,60—7,00 (3,6H, m, H <sub>c</sub> , NH, <i>o,o'</i> -H), 7,10—7,60 (5,2H, m, <i>m,m'</i> , 5,5',8,8',9,9'-H <sub>5</sub> , H <sub>b'</sub> ); 7,60—8,10 [2,2H, m, 7,7',10-H, H <sub>c'</sub> , (NH)']	
IV	Dioxane	A	5,63 (1H, q, H <sub>a</sub> ), 5,80 (1H, q, H <sub>b</sub> ); 6,68 (1H, d, H <sub>c</sub> ); 6,94—7,60 (8H, m, Ar); 7,84 (1H, q, 7-H); 8,30 (1H, q, 10-H)	$J_{ab}=4$ , $J_{bc}=10$ , $J_{10,9}=J_{7,8}=7$ , $J_{10,8}=J_{7,9}=3$
	DMSO	B	8,42 (1H, d, H <sub>a'</sub> ), 8,34 (1H, d, 10'-H); 4,74 (2H, s, CH <sub>2</sub> ); 7,16—8,30 [12H, m, H <sub>c'</sub> , H <sub>b'</sub> , (NH)', Ar]	$J_{10',9'}=7$ , $J_{a'b'}=8$
V	Acetone	A	6,50 (1H, q, H <sub>a</sub> ), 6,04 (1H, q, H <sub>b</sub> ); 6,86 (1H, d, H <sub>c</sub> ), 6,70 (1H, d, NH); 7,10—7,25 (3H, m, <i>o</i> -, 5-H <sub>3</sub> ); 7,32—7,60 (2H, m, 8,9-H <sub>2</sub> ); 7,70—8,20 (4H, m, <i>m</i> , 7,10-H <sub>4</sub> )	$J_{ab}=4$ , $J_{bc}=10$ , $J_{aNH}=10$
	DMSO	A	6,45 (1H, q, H <sub>a</sub> ); 6,01 (1H, q, H <sub>b</sub> ); 6,87 (1H, d, H <sub>c</sub> ); 6,55 (1H, d, NH); 7,00—7,26 (3H, m, <i>o</i> -, 5-H <sub>3</sub> ); 7,26—7,60 (2H, m, 8,9-H <sub>2</sub> ); 7,70—8,15 (4H, m, <i>m</i> , 7,10-H <sub>4</sub> )	$J_{ab}=4$ , $J_{bc}=10$ , $J_{aNH}=10$

\*The hydrogen atoms of the phenyl ring of substituent R are designated as *o*-, *m*-, and *p*-H. For the B tautomers the positions of the hydrogen atoms are designated by the primed numbers of the corresponding positions of tautomers A.

the solvent and for N-arylimines ranges from 4.33 ppm in CCl<sub>4</sub> to 5.80 ppm in dioxane and 6.55–7.10 ppm in acetone and DMSO. The signal of the NH proton in the spectrum of the N-benzylimine (IV) is covered by the signals of the protons of the solvent and the aromatic protons. The doublet of the H<sub>c</sub> proton appears at 6.87 ppm, which is in agreement with the data on the chemical shifts of the protons of substituted ethylenes [7]. The signal of this proton is shifted 1 ppm to strong field as compared with 3-(2-hydroxy-1-naphthyl)propenal

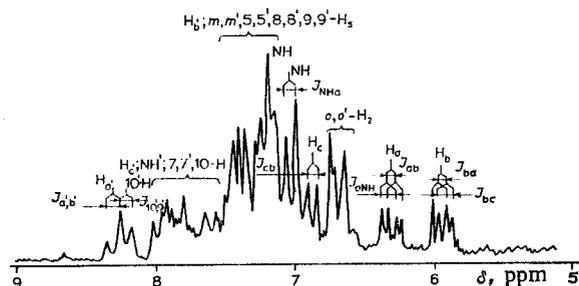


Fig. 4. PMR spectrum of 3-(1-hydroxy-4-methyl-2-naphthyl)propenal N-phenylimine (I) in DMSO.

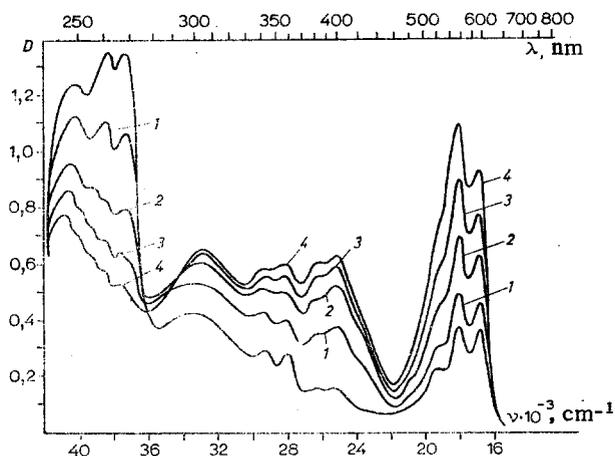


Fig. 5. Electronic absorption spectra of 3-(1-hydroxy-4-methyl-2-naphthyl)propenal N-(p-bromophenyl)imine (III) in isopentane-isopropyl alcohol (4:1,  $c 10^{-4}$  mole/liter) at  $-90^{\circ}\text{C}$  before and after irradiation ( $\lambda 313$  nm) for 60 (1), 150 (2), 270 (3), and 510 sec (4).

imines, where it experiences the pronounced deshielding effect of the peri hydrogen atom of the naphthalene ring [2].

It is apparent from the PMR spectrum of 2-phenylamino-5-methyl-7,8-benzo-2H-chromene (IA) in  $\text{CCl}_4$  (Fig. 3 and Table 3) that the position of the signals of the aromatic protons of the ring annelated with the pyran ring is extremely characteristic. In conformity with the handbook values of the chemical shifts of  $\alpha$ - and  $\beta$ -naphthalene protons [7], the multiplet at 7.17-7.47 ppm may be related to the resonance of the 8-H and 9-H protons, while the quartet at 7.74 ppm is related to the signal of the 7-H proton. As a consequence of the deshielding effect of the peri oxygen atom of the pyran ring the signal of the 10-H proton appears at weaker field in the form of a quartet with characteristic spin-spin coupling constants (SSCC) ( $J_{10,9} = J_{7,8} = 7$  Hz, and  $J_{10,8} = J_{7,9} = 4$  Hz), which is in agreement with the data in [5]. The signal of the 5-H proton is shifted to stronger field as a consequence of the shielding effect of the protons of the methyl group and the  $H_c$  proton of the pyran ring and shows up in the region of the signals of the N-phenyl system.

Changes that constitute evidence for the presence of signals of the protons of both tautomers occur in the PMR spectra of I-IV in DMSO (Table 3 and Fig. 4). A two-proton triplet at 8.10-8.40 ppm, which is absent in the spectra of imines I-IV in dioxane and  $\text{CCl}_4$ , is related to the signals of the protons of quinoid form B (Table 3 and Fig. 3). A similar signal is present in the spectrum of the N-benzylimine (IV, Table 3), which in solution in DMSO exists exclusively in the quinoid form. A comparison of the data in Table 3 with the previously investigated PMR spectra of 3-(1-hydroxy-4-bromo-2-naphthyl)propenal [8] and 3-(2-hydroxyphenyl)propenal imines [9] and 1-hydroxy-2-naphthaldehyde imines [5] makes it possible to regard this signal as being the result and superimposition of the doublets of the  $H_{a'}$ , and

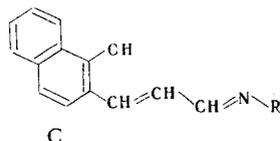
TABLE 4. Relative Stabilities of the Tautomeric Forms of 3-(1-Hydroxy-4-methyl-2-naphthyl)propenal N-R Imines

R	Tautomer	Relative energies, kcal/mole		
		gas	$\epsilon=2$	$\epsilon=20$
C <sub>6</sub> H <sub>5</sub>	A	0	0	0
	B	28	13	0,01
	C	25	21	17
<i>p</i> -C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>	A	0	0	0
	B	28	14	0,03
	C	25	21	17
<i>p</i> -C <sub>6</sub> H <sub>4</sub> CHO	A	0	0	0
	B	29	13	0,46
	C	24	19	15

10'-H protons of the quinoid form B with characteristic SSCC  $J_{a'b'}$  = 9 Hz and  $J_{10',9'}$  = 7 Hz. The assignment of the remaining signals is indicated in Fig. 4. Imine V is stable in the cyclic form, regardless of the polarity of the solvent; this is associated with the presence of a strong electron-acceptor substituent in the N-aryl fragment, which significantly increases the electrophilicity of the carbon atom of the C=N bond. The percentages of the tautomers indicated in Table 3 were calculated from the relative intensities of the signals of the protons belonging to the tautomeric A and B forms. The percentage of the quinoid form in solution in DMSO increases from 20% for imine III to 65% for II.

When one compares the results obtained in this research with the previously published data [2, 3], it becomes evident that the conversion of 3-(2-hydroxy-1-naphthyl)propenal imines to the investigated I-V is accompanied by a shift of the tautomeric equilibrium of the A  $\rightleftharpoons$  B type to favor quinoid form B. Thus for 3-(1-hydroxy-4-methyl-2-naphthyl)propenal imines that have a quinoid structure in the crystalline state tautomeric equilibrium in polar solvents is observed even for imine III, which contains a weak electron-acceptor substituent, whereas in the case of 3-(2-hydroxy-1-naphthyl)propenal imines a tautomeric equilibrium is recorded only for N-alkylimines and compounds with strong electron donors in the N-aryl fragment, while all of the N-arylimines have a cyclic structure in the solid state.

The cyclic 2H-chromene structure turns out to be preferable for the investigated imines, just as for 3-(2-hydroxy-1-naphthyl)propenal imines, as evidenced by the results of quantum-mechanical calculations of the relative stabilities of the tautomers of I-V. The calculations were made by the self-consistent-field (SCF) MO Pariser-Parr-Pople (PPP) method in the Dewar  $\sigma, \pi$  parametrization via a previously described scheme [2, 9], which makes it possible to take into account the effect of the solvent. The specific characteristics of the solvent are reflected by the dielectric permeability constant  $\epsilon$ . The results of the calculations are given in Table 4. Estimates for benzenoid form C, the presence of which was not established experimentally, are also presented in Table 4.



Like the data for other o-hydroxy aldehydes [2], the calculations correctly reflect the tendency of the tautomeric equilibrium to undergo a shift to favor the quinoid form on passing to a polar solvent. The effect of the substituent in the amine ring is not revealed in the calculations. This is explained by inadequate transmission of the interaction of the substituents with the  $\pi$  system of the benzene ring in the scheme of calculations by the PPP method and other methods in the zero-differential-overlap approximation [10].

Compounds I-V have photochromic properties. Photoexcitation leads to a substantial shift of the A  $\rightleftharpoons$  B tautomeric equilibrium. In the photoelectric steady state the position of the equilibrium depends significantly on the wavelength of the photoexcitation and the temperature of the solution. Thus the equilibrium is shifted substantially to favor the B<sub>1</sub> and B<sub>2</sub> structures in the case of primary excitation in the absorption band of the A form ( $\lambda$  313, 360 nm) at -110°C (Fig. 5). On the other hand, excitation under these conditions in the re-

TABLE 5. 3-(1-Hydroxy-4-methyl-2-naphthyl)propenal Imines

Compound	mp, °C	Found, %			Empirical formula	Calc., %		
		C	H	N		C	H	N
I	146	83,4	5,8	4,6	C <sub>20</sub> H <sub>17</sub> NO	83,6	6,0	4,9
II	158	79,5	5,8	4,1	C <sub>21</sub> H <sub>19</sub> NO <sub>2</sub>	79,5	6,0	4,4
III	160	65,4	4,2	3,6	C <sub>20</sub> H <sub>16</sub> BrNO*	65,6	4,4	3,8
IV	176	83,4	6,5	4,4	C <sub>21</sub> H <sub>19</sub> NO	83,7	6,4	4,6
V	174	72,5	4,7	8,1	C <sub>20</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	72,3	4,8	8,4

\*Found: Br 21.4%. Calculated: Br 21.8%.

gion of the long-wave bands of the B form ( $\lambda$  436, 546 nm) shifts the equilibrium to favor chromene form A. Elimination of the photoexcitation leads to the establishment of the A  $\rightleftharpoons$  B equilibrium corresponding to the given temperature at a rate that increases markedly as the temperature is raised. Steady state photoexcitation therefore does not lead to visible shifts of the equilibrium at room temperature as a consequence of the extremely high rates of the dark processes.

#### EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil and of solutions in CCl<sub>4</sub> (10<sup>-3</sup> mole/liter) were obtained with a UR-20 spectrometer. The electronic absorption spectra were recorded with a Specord UV-vis spectrophotometer with an apparatus for smooth changing of the temperature of the samples. The luminescence and luminescence excitation spectra were recorded with a Fotolyum multipurpose apparatus manufactured by the control design office of the Academy of Medical Sciences of the USSR with a device for regulating the temperature of the samples from 80 to -110°C. The PMR spectra of 10-15% solutions were measured with a Varian XL-100/15 radiospectrometer (100 MHz) with hexamethyldisiloxane as the internal standard. The percentages of the tautomeric forms were calculated by comparison of the intensities of the signals of the H<sub>a</sub> and H<sub>b</sub> protons of 2H-chrome form A and the H<sub>a</sub>' and 10'-H protons of quinoid form B, as well as by comparison of the overall intensities of the signals of all of the remaining protons of both tautomeric forms, except for the protons of the CH<sub>3</sub> and OCH<sub>3</sub> groups, which are covered by the signals of the solvent.

3-(1-Hydroxy-4-methyl-2-naphthyl)propenal Imines (I-V, Table 5). These compounds were obtained by mixing ethanol solutions of equimolar amounts of the aldehyde and the corresponding amines with subsequent recrystallization of the resulting precipitate from a suitable solvent.

#### LITERATURE CITED

1. B. Ya. Simkin, S. P. Makarov, and V. I. Minkin, *Khim. Geterotsikl. Soedin.*, No. 8, 1028 (1982).
2. I. M. Andreeva, O. M. Babeshko, E. A. Medyantseva, and V. I. Minkin, *Zh. Org. Khim.*, 15, 1899 (1979).
3. I. M. Andreeva, E. M. Bondarenko, N. V. Volbushko, M. I. Knyazhanskii, E. A. Medyantseva, A. V. Metelitsa, V. I. Minkin, and B. Ya. Simkin, *Khim. Geterotsikl. Soedin.*, No. 8, 1035 (1980).
4. I. M. Andreeva, E. M. Bondarenko, E. A. Medyantseva, R. G. Pudeyan, and V. I. Minkin, *Khim. Geterotsikl. Soedin.*, No. 5, 610 (1982).
5. V. I. Minkin, O. A. Osipov, and V. N. Sheinker, *Zh. Fiz. Khim.*, 44, 23, 2438 (1970).
6. M. I. Knyazhanskii, B. Ya. Simkin, and B. V. Golyanskii, *Teor. Eksp. Khim.*, 18, 108 (1982).
7. A. Gordon and R. Ford, *A Chemist's Companion*, Wiley (1973).
8. I. M. Andreeva, E. M. Bondarenko, E. A. Medyantseva, and V. I. Minkin, *Khim. Geterotsikl. Soedin.*, No. 2, 181 (1983).
9. E. A. Medyantseva, O. M. Babeshko, and V. I. Minkin, *Zh. Org. Khim.*, 12, 837 (1972).
10. B. Ya. Simkin, V. A. Bren', and V. I. Minkin, *Zh. Org. Khim.*, 13, 1910 (1977).
11. J. A. Pople and D. H. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York (1970).