Chiral photochromic 2-(*N*-acyl-*N*-arylaminomethylene)benzo[*b*]thiophen-3(2*H*)-ones

V. P. Rybalkin,[a]★ E. N. Shepelenko,[a] Ya. Yu. Vorob´eva,[a] G. S. Borodkin,[a] V. A. Bren´,[a] V. I. Minkin,[a] S. M. Aldoshin,[b] V. V. Tkachev,[b] and A. N. Utenyshev[b]

[a]*Institute of Physical and Organic Chemistry, Rostov State University, 194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation. E-mail: dubon@ipoc.rsu.ru*

[b]*Institute of Problems of Chemical Physics, Russian Academy of Sciences, 1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation. E-mail: sma@icp.ac.ru*

Photochromic 2-(*N*-acyl-*N*-arylaminomethylene)benzo[*b*]thiophen-3(2*H*)-ones containing *ortho*-substituents in the *N*-phenyl ring were studied by X-ray diffraction analysis and ^{1}H NMR spectroscopy. It was established that these compounds have stable chiral structures due to hindered rotation of the phenyl ring around the C—N bond. The energy barrier to racemization evaluated by dynamic NMR spectroscopy is $\Delta G^{\#}_{428\ K} = 98$ kJ mol^{-1}.

Key words: benzo[*b*]thiophenes, enaminoketones, photochromic compounds, chirality, hindered rotation, racemization.

At room temperature, the ^{1}H NMR spectra of 2-[*N*-(2-hydroxyphenyl)-*N*-(4-methyl-2-oxo-2*H*-benzopyran-7-yloxyacetyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (**1a**), which is a photochromic chemosensor for heavy metal cations,[1] are characterized by the presence of diastereotopic methylene protons. The latter are observed in the spectra as two doublets (AB system) at δ_1 4.52 (1 H, CH) and δ_2 4.82 (1 H, CH) with the spin-spin coupling constant of 16 Hz, which is indicative of chiral structure **1a** possessing a rather high barrier to racemization. The chirality of a receptor or the optical activity of a signal fragment can serve as useful characteristics in the construction of chemosensors. In addition, the fact that a molecule combines the photochromic properties with optical activity is of particular interest for the construction of optical switches and trigger elements performing non-destructive read-out of optically recorded information by monitoring optical rotation at wavelengths remote from those used for switching.[2—5]

The chirality of compound **1a** may be associated with either the hindered rotation about one of three single bonds at the nitrogen atom or the inversion of the nitrogen atom in the case of the pyramidal arrangement of the substituents at this atom. The aims of the present study were to investigate the molecular structures and structural features of photochromic ketoenamines of the benzo[*b*]thiophene series responsible for their chirality and high racemization barriers and to evaluate the energy barrier to racemization.

Results and Discussion

The principal results of X-ray diffraction study of the model compound, *viz.*, chiral photochromic 2-[*N*-(2-methylphenyl)-*N*-phenoxyacetylaminomethylene]benzo[*b*]thiophen-3(2*H*)-one (**2**), are presented in Fig. 1 and Table 1. Like acylated photochromic compounds of this series described earlier,[6] molecule **2** has the ketoenamine structure with the *Z* configuration relative to the C(2)=C(3) bond. The acyl group at the nitrogen atom is in the *s-trans* position and the phenyl group is in the *s-cis* position with respect to this bond. The bond length distribution in **2** is indicative of conjugation in the central moiety of the molecule (see Table 1). Thus, the C(2)=C(3) bond is elongated to 1.35(1) Å due, apparently, to conjugation with the lone electron pair of the nitrogen atom. This is evidenced by a shortening of the N—C(2) bond to 1.39(1) Å. The lone electron pair of the nitrogen atom is also actively involved in the amide conjugation resulting in a typical shortening of the N—C(1) bond to 1.35(1) Å and an elongation of the C(1)=O(2) bond to 1.23(1) Å.

In the crystal structure, there are no shortened intermolecular contacts. The central moiety of the molecule is nearly planar. The torsion angles about the bonds are at most 12° and are equal to 5.3° (C(2)—C(3)), 11.9° (C(2)—N), 4.3° (N—C(1)), and 6.9° (C(1)—C(11)). The *ortho*-tolyl fragment cannot be coplanar with the central moiety of the molecule due to steric repulsions between

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1706—1711, August, 2003.

1066-5285/03/5208-1800 $25.00

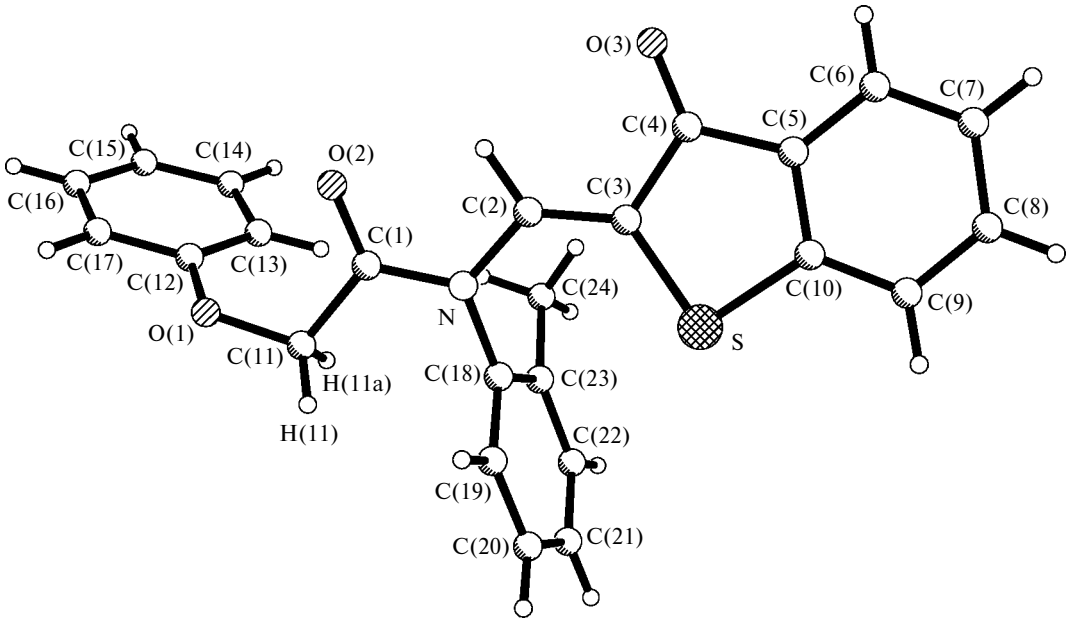


Fig. 1. Molecular structure of 2-[*N*-(2-methylphenyl)-*N*-phenoxyacetylaminomethylene]benzo[*b*]thiophen-3(2*H*)-one (**2**).

Table 1. Selected bond lengths (*d*) and bond angles (ω) in compound **2**

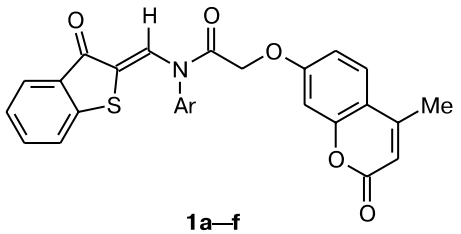
Bond	*d*/Å	Angle	ω/deg
S—C(3)	1.755(8)	C(3)—S—C(10)	90.9(4)
S—C(10)	1.759(9)	O(2)—C(1)—N	122.9(8)
C(1)—O(2)	1.233(11)	O(2)—C(1)—C(11)	120.9(8)
C(1)—N	1.355(10)	N—C(1)—C(11)	116.2(8)
C(1)—C(11)	1.534(12)	C(1)—N—C(2)	118.2(7)
N—C(2)	1.385(11)	C(1)—N—C(18)	121.4(7)
N—C(18)	1.444(10)	C(2)—N—C(18)	120.2(6)
O(3)—C(4)	1.220(10)	C(10)—C(5)—C(4)	112.8(7)
C(5)—C(4)	1.453(11)	C(5)—C(10)—C(9)	120.8(8)
C(2)—C(3)	1.349(11)	C(5)—C(10)—S	114.5(6)
C(3)—C(4)	1.493(11)	C(3)—C(2)—N	127.9(7)
O(1)—C(12)	1.394(11)	C(2)—C(3)—C(4)	119.1(7)
O(1)—C(11)	1.419(11)	C(2)—C(3)—S	129.2(7)
C(23)—C(24)	1.513(13)	C(4)—C(3)—S	111.7(6)
		O(3)—C(4)—C(5)	126.2(8)
		O(3)—C(4)—C(3)	123.7(8)
		C(5)—C(4)—C(3)	110.0(7)
		C(12)—O(1)—C(11)	117.8(8)
		O(1)—C(11)—C(1)	111.0(7)

the C(24), C(23), and C(19) atoms of this fragment and the S and C(11) atoms of the central moiety. As a result, this fragment is rotated about the N—C(18) bond by 71°, the S and C(24) atoms approaching each other. This turn of the *ortho*-tolyl fragment about the N—C(18) bond in the case of the planar coordination of the N atom and small angles of rotation about the bonds in the central moiety (the maximum angle of rotation of 19.9° is observed for the N—C(2) bond) are responsible for an increase in the nonbonded S...C(24), S...C(23), S...C(19), C(11)...C(23), and C(11)...C(24) distances to >3.5, 3.348, 2.434, >3.5, and >3.5 Å, respectively, and an increase in the C(3)—C(2)—N bond angle to 127.9°. The dihedral angle between the average plane of the central fragment and the N—Ph ring is 71°.

The phenyl ring of the phenoxyacetyl substituent is also acoplanar with the central moiety of the molecule. This ring is rotated about the C(11)—O(1) bond by 78.9° and located on the same side of the central moiety as the methyl C(24) group of the *ortho*-tolyl substituent.

Hence, the chirality of the compounds under consideration is associated with a distortion of the planar structure of the conjugated fragment of the molecule and, primarily, with the almost perpendicular arrangement of the plane of the phenyl ring of amine with respect to the plane of the major moiety of the molecule. Consequently, the problem is reduced to the problem of revealing the bond characterized by the highest rotation barrier.

To solve this problem, we synthesized a series of photochromic 2-(*N*-acyl-*N*-arylaminomethylene)benzo[*b*]thiophen-3(2*H*)-ones (**1b—f**) containing the methylene group of the (4-methyl-2-oxo-2*H*-benzopyran-7-yloxy)acetic acid residue as a diastereotopic label:



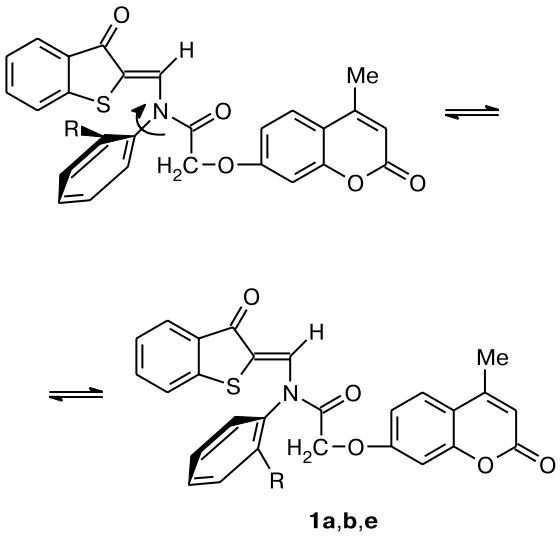
1a—f

Ar = C_6H_4OH-2 (**a**), C_6H_4OMe-2 (**b**), C_6H_4OMe-3 (**c**), C_6H_4OMe-4 (**d**), C_6H_4Me-2 (**e**), $C_6H_2(Me)_3$-2,4,6 (**f**)

All the compounds synthesized have ketoenamine structures as evidenced by the presence of absorption bands of the amide (1700—1730 cm^{-1}) and cyclic (1660—1680 cm^{-1}) carbonyl groups in their IR spectra as well as by the characteristic absorption at λ_{max} 427 nm in the electronic absorption spectra of their solutions. The ^1H NMR spectra of these compounds in $CDCl_3$ at room temperature have a signal for the methine proton at low field (δ 8.9), which is indicative[7] of the *Z*-ketoenamine configuration. In solutions, all the compounds synthesized exhibit an ability to undergo the photoinitiated thermally reversible N→O acylotropic rearrangement described by us earlier.

At room temperature, diastereotopic methylene protons are observed only in ketoenamines **1a**,**b**,**e** containing the 2-substituted *N*-phenyl ring (Fig. 2). The presence of one substituent in the *ortho* position of the phenyl ring of amine is of fundamental importance only in the presence of the chiral C_{Ar}—N axis due to the orthogonal arrangement of the *N*-phenyl ring with respect to the plane of the ketoenamine fragment (Scheme 1), because bulky substituents R in the *ortho* position of the phenyl ring can give rise to a high energy barrier to rotation about the C_{Ar}—N bond (racemization barrier), and the unsymmetrical substitution in the phenyl ring with respect to the chiral axis leads to a loss of the molecular symmetry plane.

Scheme 1



1a,**b**,**e**

This axial chirality accounts for the presence of diastereotopic methylene protons in compounds **1a**,**b**,**e**

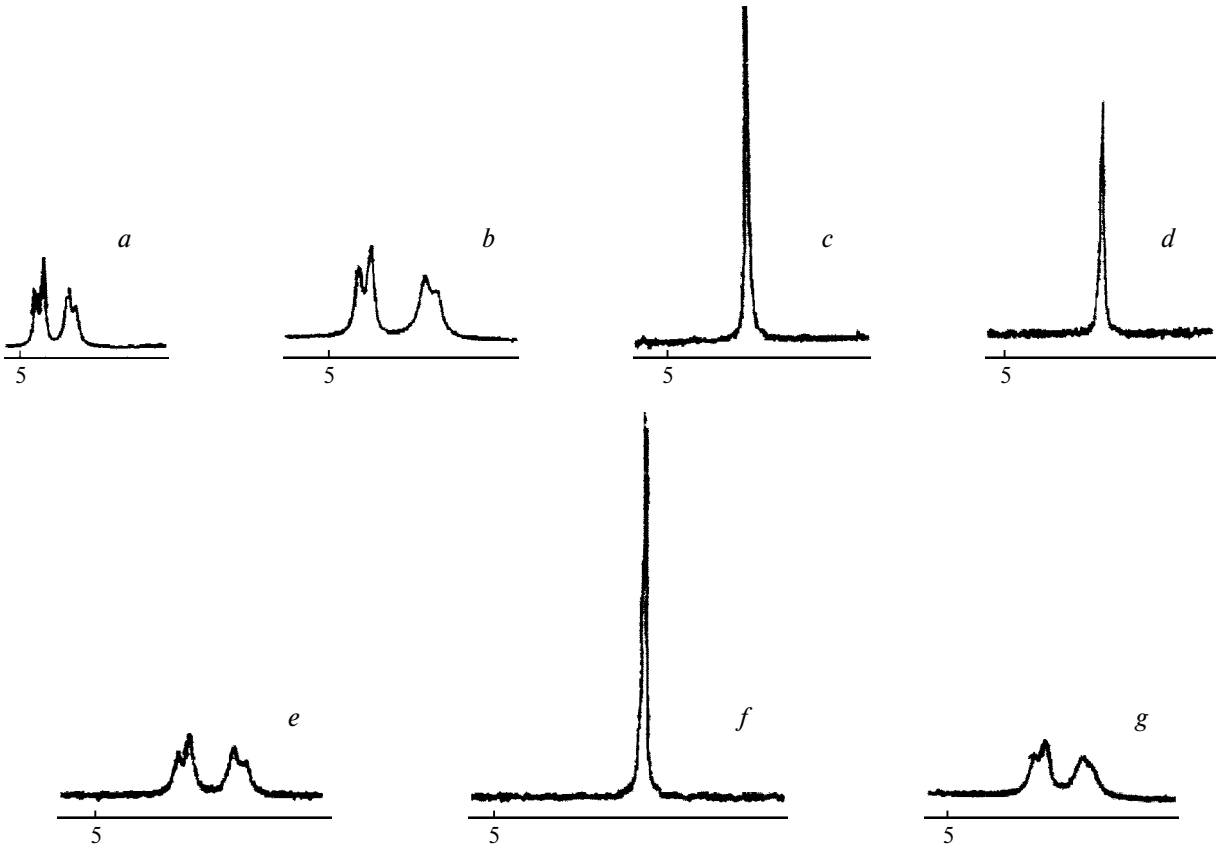


Fig. 2. Signals for the methylene protons in the ^1H NMR spectra of compound **1a** in DMSO-d_6 (*a*) and compounds **1b**—**f** (*b*—*f*) and **2** (*g*) in $CDCl_3$ at room temperature.

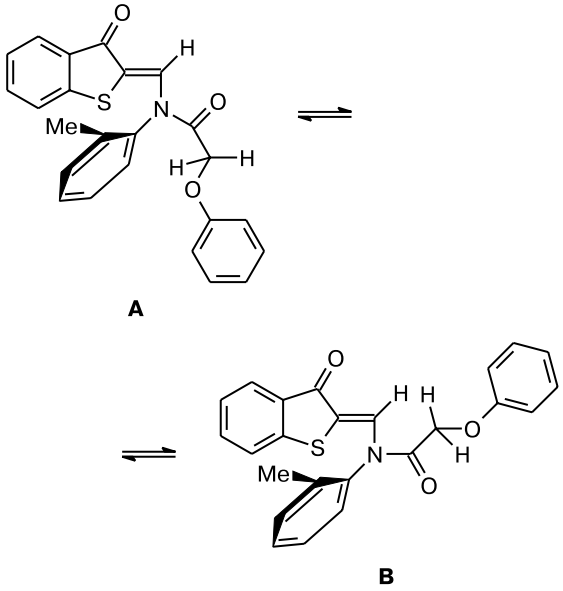
and thier absence in compounds **1d**,**f**. The absence of diastereotopic methylene protons in *meta*-substituted compound **1c** at room temperature is associated with either a substantial decrease in the energy barrier to rotation about the C_{Ar}—N bond or a remote location of the diastereotopic group relative to the *meta*-substituent in the phenyl ring (difference in the chemical shifts of the protons is equal to zero). In spite of the fact that the first assumption seems to be more reasonable, the available experimental data do not allow us to unambiguously decide between these two explanations.

The absence of diastereotopic methylene protons in mesidine derivative **1f** in contrast to *ortho*-methyl derivative **1e** is particularly important evidence in favor of axial chirality. If the signals of the diastereotopic methylene groups of compounds **1** observed at usual temperatures had been determined only by rigidity of the noncoplanar skeleton of the bonds in the C(11)—C(1)—N—C(2)—C(3) fragment, the passage from the *N*-*ortho*-tolyl derivative to the *N*-mesidine derivative would lead to an additional increase in the racemization barrier. Consequently, the absence of diastereotopic methylene protons in mesidine derivative **1f** is not associated with rapid racemization. At the same time, as a result of the symmetrical arrangement of the substituents with respect to the chiral axis in the mesidine ring, the molecule as a whole has a symmetry plane and, consequently, loses chirality and the related diastereotopism. Therefore, it can be concluded that chirality of photochromic ketoenamines of the benzo[*b*]thiophene series is a consequence of hindered rotation about the C_{Ar}—N bond. Hence, stable optically active compounds of this type should be searched for among heterocyclic ketoenamines containing *ortho*-substituents in the phenyl ring as well as among their structural analogs.

The energy barrier to racemization was determined by dynamic NMR using compound **2** as an example. Analysis of the temperature dependence of the line shapes in the ^{1}H NMR spectra of solutions of compound **2** in deuteriochloroform and deuterionitrobenzene revealed the following two processes.

1. The conformational equilibrium in $CDCl_3$ (**A** $\rightleftharpoons$ **B**) (Scheme 2) was observed at low temperatures, the percentage of the minor conformer (**B**) being ~7%. Coalescence of the signals for the methylene protons is observed in a solution of compound **2** at ~283 K, the diastereotopic methylene protons persisting after coalescence (Fig. 3). Apparently, this is the amide rotation because the exchange process occurs with the active involvement of the methine proton, the latter in the major conformation (**A**) being deshielded by the magnetic field of the lone electron pair of the oxygen atom. The absence of an AB system in the spectrum of the minor conformer is attributed to the fact that the diastereotopic label is remote from the chiral axis, whereas the appearance of an AB system in the spectrum of the major conformer is associated with the fact that the diastereotopic label is shielded by the magnetic field of the phenyl ring.

Scheme 2



2. Upon heating of a solution of compound **2** in deuterionitrobenzene, coalescence of the AB system of the diastereotopic protons was observed at 428 K (Fig. 4). At this temperature, the calculated free activation energy[9] of the interconversion of the enantiomers is $\Delta G^{\#}_{428\ K}$ = 98 kJ mol^{-1}, which makes possible the preparative resolution of the enantiomers at usual temperatures. Actually, compound **2** crystallizes as a conglomerate, because the X-ray diffraction study revealed that single crystals of **2** contained only one of the enantiomers. Apparently, the racemization barrier for derivatives of **2** can be additionally increased by introducing bulkier substituents into the *N*-phenyl fragment.

To summarize, the introduction of a bulky substituent at the *ortho* position of the phenyl ring of the amine fragment in 2-(*N*-acyl-*N*-arylaminomethylene)benzo[*b*]thiophen-3(2*H*)-ones gives rise to stable chiral structures with the chiral C_{Ar}—N axis. The energy barrier to racemization is sufficiently high for the preparative resolution of enantiomers at usual temperatures and permits the use of these compounds as photoswitches of optical activity and optical rotation.

Experimental

The electronic absorption spectra of compounds **1a**—**f** and **2** in toluene were recorded on a Specord M-40 spectrophotometer. The solutions were irradiated using a DRSh-250 mercury lamp equipped with a set of interchangeable light filters. The IR

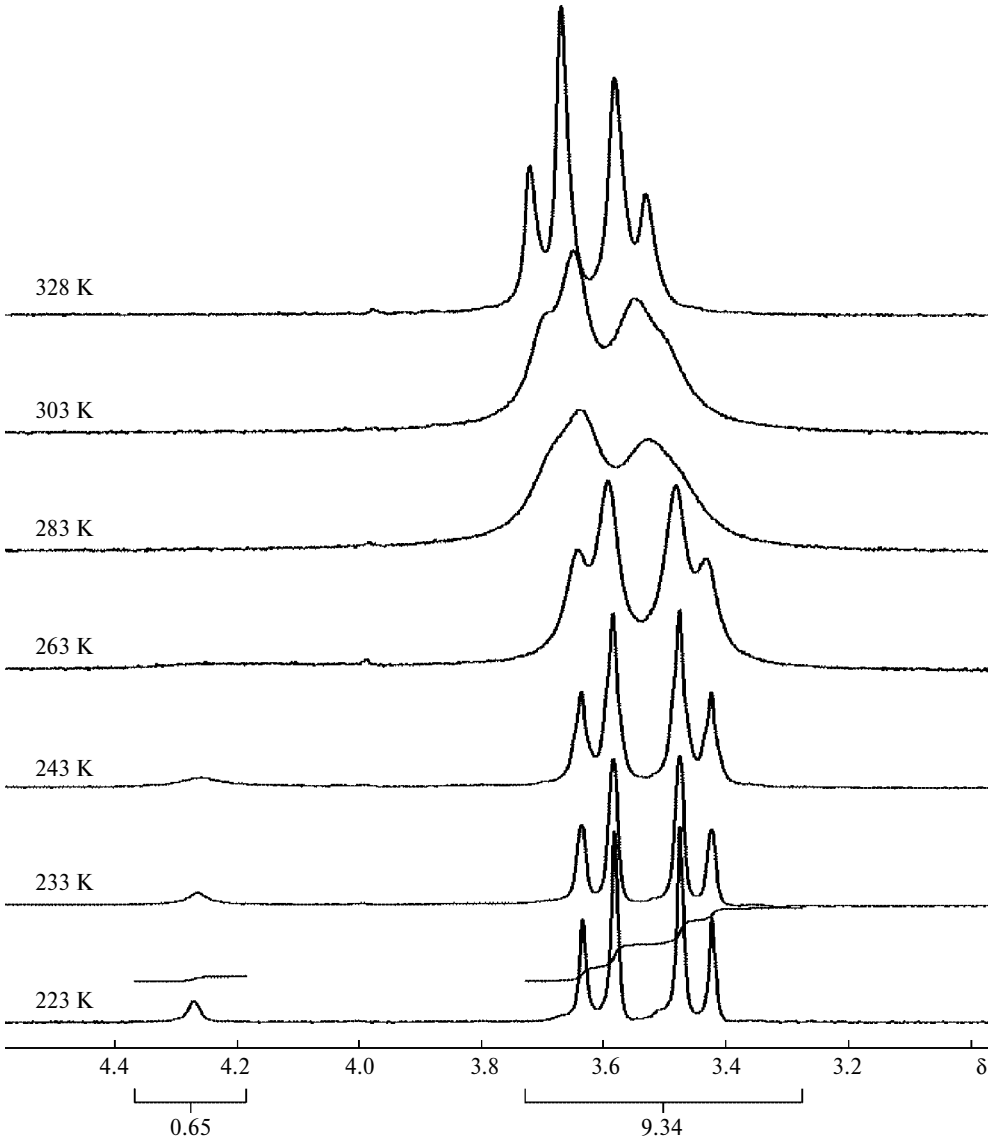


Fig. 3. Temperature dependence of the line shapes in the ^{1}H NMR spectra of solutions of compound **2** in $CDCl_3$.

spectra were recorded on a Specord IR-75 instrument in Nujol mulls. The ^{1}H NMR spectra were measured on a Varian Unity-300 instrument (300 MHz) in $CDCl_3$, with $SiMe_4$ as the standard. The rate constant at the coalescence temperature was calculated according to an approximate equation for the exchange between AB and A_2 systems.[9]

2-[*N*-2-Methoxyphenyl-*N*-(4-methyl-2-oxo-2*H*-benzopyran-7-yloxyacetyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (1b) has been synthesized earlier.[1] IR, ν/cm^{-1}: 1730, 1710, 1660. UV, λ_{max}/nm (ε): 309 (31500), 426 (11500). ^{1}H NMR, δ: 8.63 (s, 1 H, CH); 7.76—7.44 (m, 5 H, Ar); 7.35—7.15 (m, 4 H, Ar); 6.92—6.10 (m, 2 H, Ar); 6.12 (s, 1 H, Ar); 4.82 and 4.52 (AB system, 2 H, CH_2, J_{AB} = 16.0 Hz); 3.98 (s, 3 H, OMe); 2.73 (s, 3 H, Me).

Acylated ketoenamines (1a,c—f, 2) were synthesized according to a procedure described earlier.[1]

2-[*N*-(2-Hydroxyphenyl)-*N*-(4-methyl-2-oxo-2*H*-benzopyran-7-yloxyacetyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (1a). The yield was 61%, m.p. 221 °C. Found (%): C, 66.67; H, 3.84; N, 2.70. $C_{27}H_{19}NO_6S$. Calculated (%): C, 66.79; H, 3.94; N, 2.89. IR, ν/cm^{-1}: 1760, 1720, 1630. UV, λ_{max}/nm (ε): 330 (19300), 470 (18500). ^{1}H NMR (DMSO-d_6), δ: 10.66 (br.s, 1 H, CH); 8.66 (s, 1 H, CH); 7.81—6.92 (m, 1 H, Ar); 6.10 (s, 1 H, Ar); 4.82 and 4.60 (AB system, 2 H, CH_2, J_{AB} = 16.0 Hz); 2.40 (s, 3 H, Me).

2-[*N*-3-Methoxyphenyl-*N*-(4-methyl-2-oxo-2*H*-benzopyran-7-yloxyacetyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (1c). The yield was 65%, m.p. 240 °C. Found (%): C, 67.12; H, 4.20; N, 2.72. $C_{28}H_{21}NO_6S$. Calculated (%): C, 67.32; H, 4.24; N, 2.79. IR, ν/cm^{-1}: 1720, 1710, 1680. UV, λ_{max}/nm (ε): 311 (30750), 427 (11750). ^{1}H NMR, δ: 8.84 (s, 1 H, CH); 7.82 (m, 1 H, Ar); 7.56—7.00, 7.26—7.16, and 7.07—6.83 (all m, 3 H each, Ar); 6.60 (d, 1 H, Ar, J = 2.5 Hz); 6.14 (s, 1 H, Ar); 4.62 (s, 2 H, CH_2); 3.90 (s, 3 H, OMe); 2.47 (s, 3 H, Me).

2-[*N*-4-Methoxyphenyl-*N*-(4-methyl-2-oxo-2*H*-benzopyran-7-yloxyacetyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-

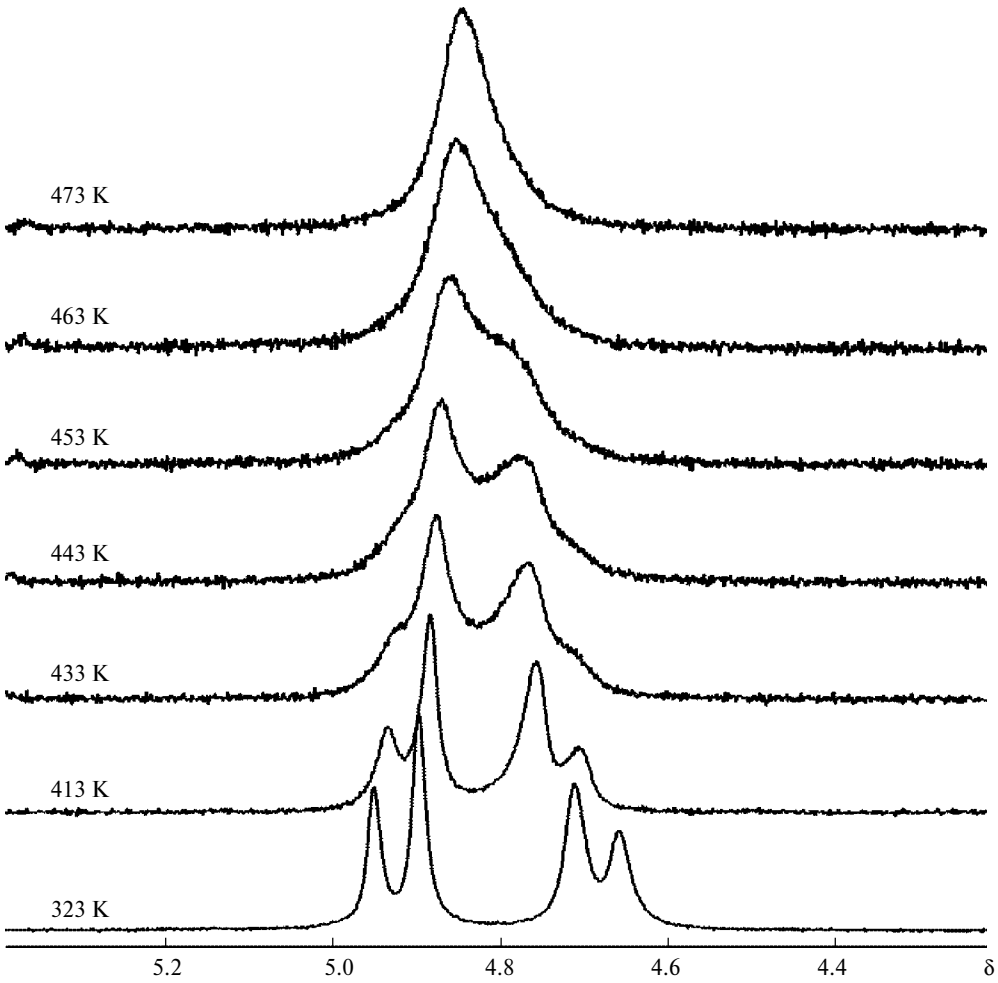


Fig. 4. Temperature dependence of the line shapes in the ^{1}H NMR spectra of solutions of compound **2** in deuterionitrobenzene.

one (1d). The yield was 63%, m.p. 279 °C. Found (%) : C, 67.15; H, 4.19; N, 2.69. $C_{28}H_{21}NO_6S$. Calculated (%): C, 67.32; H, 4.24; N, 2.79. IR, ν/cm^{-1}: 1710, 1660. UV, λ_{max}/nm (ε): 311 (28500), 377 (17250), 427 (10250). ^{1}H NMR, δ: 8.86 (s, 1 H, CH); 7.84 (m, 1 H, Ar); 7.52—7.07 (m, 8 H, Ar); 6.92—6.84 (m, 1 H, Ar); 6.38 (d, 1 H, Ar); 6.14 (s, 1 H, Ar); 4.45 (s, 2 H, CH_2); 3.98 and 2.38 (both s, 3 H each, OMe).

2-[*N*-(4-Methyl-2-oxo-2*H*-benzopyran-7-yloxyacetyl)-*N*-(2-methylphenyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (1e). The yield was 64%, m.p. 203 °C. Found (%): C, 69.50; H, 4.07; N, 2.54. $C_{28}H_{21}NO_5S$. Calculated (%): C, 69.57; H, 4.34; N, 2.89. IR, ν/cm^{-1}: 1710, 1675. UV, λ_{max}/nm (ε): 310 (28500), 427 (14000). ^{1}H NMR, δ: 8.92 (br.s, 1 H, CH); 7.84 (m, 1 H, Ar); 7.64—7.16 (m, 8 H, Ar); 6.93—6.86 (m, 1 H, Ar); 6.58 (br.s, 1 H, Ar); 6.12 (s, 1 H, Ar); 4.60 and 4.34 (AB system, 2 H, CH_2, J_{AB} = 16.0 Hz); 2.36 and 2.26 (both s, 3 H each, Me).

2-[*N*-(4-Methyl-2-oxo-2*H*-benzopyran-7-yloxyacetyl)-*N*-(2,4,6-trimethylphenyl)aminomethylene]benzo[*b*]thiophen-3(2*H*)-one (1f). The yield was 12.2%, m.p. 215 °C. Found (%): C, 70.06; H, 4.77; N, 2.63. $C_{30}H_{25}NO_5S$. Calculated (%): C, 70.46; H, 4.88; N, 2.74. IR, ν/cm^{-1}: 1720, 1680. UV, λ_{max}/nm (ε): 310 (37000), 425 (14000). ^{1}H NMR, δ: 8.98 (s, 1 H, CH); 7.84 (m, 1 H, Ar); 7.52—7.40 (m, 2 H, Ar); 7.16—7.12 (m, 2 H, Ar); 7.08 (s, 2 H, Ar); 6.90 (m, 1 H, Ar); 6.57 (br.s, 1 H, Ar); 6.14 (s, 1 H, Ar); 4.38 (s, 2 H, CH_2); 2.46 and 2.27 (both s, 3 H each, Me); 2.17 (s, 6 H, 2 Me).

2-[*N*-(2-Methylphenyl)-*N*-phenoxyacetylaminomethylene]benzo[*b*]thiophen-3(2*H*)-one (2). The yield was 67%, m.p. 185 °C. Found (%): C, 71.12; H, 4.08; N, 3.33. $C_{24}H_{17}NO_3S$. Calculated (%): C, 71.79; H, 4.77; N, 3.49. IR, ν/cm^{-1}: 1710, 1675. UV, λ_{max}/nm (ε): 309 (38800), 426 (18800). ^{1}H NMR, δ: 8.95 (s, 1 H, CH); 7.84 (m, 1 H, Ar); 7.60—7.16 (m, 8 H, Ar); 7.05—6.71 (m, 1 H, Ar); 4.68 и 4.36 (AB system, 2 H, CH_2, J_{AB} = 16.0 Hz); 2.36 and 2.24 (both s, 3 H each, Me).

X-ray diffraction study. Compound **2** crystallized as transparent crystals of poor quality belonging to the orthorhombic system. The principal crystallographic data for **2**: $C_{24}H_{11}NO_3S$ at T = 23 °C, a = 6.581(1), b = 13.420(10), c = 11.194(4) Å, V = 1960.4(6) Å^3, Z = 4, d = 1.360(3) g cm^{-3}, space group $P2_12_12_1$.

The intensities of 1653 independent observed reflections were measured on an automated four-circle KM-4 diffractometer (Mo-Kα radiation). Absorption was ignored. The structure was solved by direct methods using the SHELXS-93 program package and refined by the full-matrix least-squares method with anisotropic thermal parameters (nonhydrogen atoms). The R factor was 0.055.

The complete data of X-ray diffraction analysis, including atomic coordinates and thermal parameters, were deposited with the Cambridge Structural Database.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 02-03-32527), the Federal Program for the Support of Leading Scientific Schools of the Russian Foundation for Basic Research (Project No. 945.2003.3), and jointly by the US Civilian Research and Development Foundation (CRDF) and the Ministry of Education of the Russian Federation (Grant REC-004).

References

1. V. P. Rybalkin, L. L. Popova, A. D. Dubonosov, E. N. Shepelenko, Yu. V. Revinskii, V. A. Bren´, and V. I. Minkin, *Zh. Org. Khim.*, 2001, **37**, 1384 [*Russ. J. Org. Chem.*, 2001, **37**, 1318 (Engl. Transl.)].
2. B. L. Feringa, *Chem. Rev.*, 2000, **5**, 1789.
3. V. I. Minkin, *Ross. Khim. Zh.* (*Zh. Ross. Khim. Obshch. im. D. I. Mendeleeva)* 2000, **6**, 3 [*Mendeleev Chem. J.*, 2000, **6** (Engl. Transl.)].
4. Y. Yokoyama, S. Uchida, Y. Yokoyama, T. Sagisaka, Y. Uchida, and T. Inada, *Enantiomer*, 1998, **3**, 123.
5. Y. Yokoyama, *Chem. Rev.*, 2000, **100**, 1717.
6. S. M. Aldoshin, O. A. Dyachenko, and L. O. Atovmyan, *Z. Kristallogr.*, 1982, **159**, 143.
7. L. M. Sitkina, A. D. Dubonosov, V. A. Bren´, S. M. Aldoshin, V. V. Bubnova, V. I. Minkin, and L. O. Atovmyan, *Zh. Org. Khim.*, 1987, **23**, 803 [*J. Org. Chem. USSR*, 1987, **23**, 769 (Engl. Transl.)].
8. A. E. Lyubarskaya, G. D. Palui, V. A. Bren´, Yu. A. Zhdanov, M. I. Knyazhanskii, V. I. Minkin, and L. P. Olekhnovich, *Zh. Org. Khim.*, 1976, **12**, 918 [*J. Org. Chem. USSR*, 1976 (Engl. Transl.)].
9. H. Günther, *NMR Spectroscopy an Introduction*, 1980, p. 248.

Received February 6, 2003;
in revised form May 23, 2003