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Photoisomerization of Hydrazones of 2-Acetyl-3-hydroxy-benzo[*b*]furan and -benzo[*b*]thiophene

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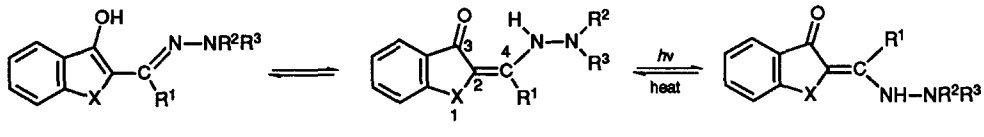
Under irradiation in the long-wave absorption band hydrazones of 2-acetyl-3-hydroxybenzo[*b*]furan and 2-acetyl-3-hydroxybenzo[*b*]thiophene undergo thermally reversible (*E*)/(*Z*) isomerization.



(1)

A (*E*)-**B** (*Z*)-**B**

1 X = S, R^1 = H; **a** R^2 = R^3 = Ph; **b** R^2 = R^3 = Me
2 X = O, R^1 = Me; **a** R^2 = R^3 = Ph; **b** R^2 = Me, R^3 = Ph
3 X = S, R^1 = Me; **a** R^2 = R^3 = Ph; **b** R^2 = Me, R^3 = Ph; **c** R^2 = R^3 = Et

Compounds capable of reversible (*E*)⇌(*Z*) photoisomerization have received much attention as molecular systems with a potential for solar energy storage.[1–3]

Recently we reported that the equilibrium of type (1) for *N*,*N*-disubstituted hydrazones of 2-formyl-3-hydroxybenzo[*b*]thiophene[4] is displaced to the ketohydrazine form **B** when passing from the *N*,*N*-diphenyl **1a** to the *N*,*N*-dimethyl derivative **1b**. (*E*)/(*Z*)-photoisomerization of compounds (*E*)-**B** was, however, discovered only in the series of hydrazones **2**, **3** possessing methyl groups instead of hydrogen at the exocyclic carbon atom C-4.[5]

In this communication the influence of the origin of the heteroatom X and substituents R^1, R^2 and R^3 on the probable (*E*)/(*Z*) photoisomerization process and the activation parameters of the reverse (*Z*)/(*E*) thermal reaction has been investigated.

Compounds **2**, **3** were obtained by condensation of 2-acetyl-3-hydroxybenzo[*b*]furan and 2-acetyl-3-hydroxybenzo[*b*]thiophene with the corresponding *N*,*N*-disubstituted hydrazines.† The ketohydrazine structure (*E*)-**B** of hydrazones **2**, **3** was elucidated on the basis of spectral data (UV, IR, NMR) and supported by X-ray crystallographic analysis (compounds **3a** and **3b**).

Irradiation of solutions of these compounds (DRS-250 lamp, λ 405 and 436 nm) having intense absorption bands at 390–400 nm (**2**) and 425–430 nm (**3**) results in the process of (*E*)/(*Z*) isomerization giving rise to a mixture of (*E*)- and (*Z*)-forms. Both non-polar solvents and alkyl substituents situated in the hydrazone part of the molecule increase the relative content of isomers (*Z*)-**B** in solution (**2b**: 30% and 59%;

† *Typical spectral data* for **2b**: ^{1}H NMR (CCl_4) δ 2.25 (s, 3H, CCH_3), 3.15 (s, 3H, NCH_3), 6.60–7.70 (m, 9H, arom.), 10.13 (s, 1H, NH); IR (Nujol) ν/cm^{-1} 3185, 1650, 1600, 1585; **3b**: ^{1}H NMR ([$^2H_6$]Me_2SO) δ 2.35 (s, 3H, CCH_3), 3.25 (s, 3H, NCH_3), 6.65–7.73 (m, 9H, arom.), 12.36 (s, 1H, NH); IR (Nujol) ν/cm^{-1} 1630, 1600, 1580.

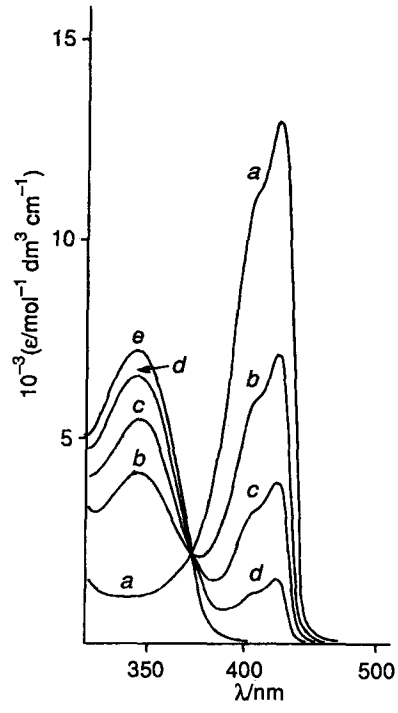


Fig. 1 Electronic absorption spectra of compound **3c** in heptane before (*a*) and after irradiation with 436 nm light: 0.5 min (*b*), 2 min (*c*), 6 min (*d*), 12 min (*e*).

3b: 4% and 50% in acetonitrile and heptane, respectively, at 293 K). On irradiation of hydrazone **3c** the percentage of isomer (*Z*)-**B** reached its peak of 100% (Fig. 1).

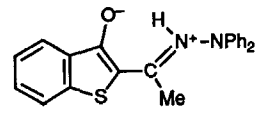
The activation parameters of the thermal $Z \rightarrow E$ isomerization, listed in Table 1, demonstrate that under identical conditions the photoinduced (*Z*)-**B**-isomer is kinetically more stable in the case of the benzofuran derivative **2b** than with the benzothienyl derivative **3b**. Surprisingly, in contrast to the above-mentioned compounds the diphenylhydrazones **2a** and **3a** were found to be photostable at room temperature both in solution and in the solid state. In this case (*E*)/(*Z*) (λ 436 nm) and (*Z*)/(*E*) (λ 365 nm) photoisomerizations in heptane can be conducted only at low temperature (193 K). In both cases a photostationary state with a small amount (less than 5%) of the (*Z*)-isomer was established. The values of selected bond distances‡ O—C(3), C(3)—C(2), C(2)—C(4), C(4)—N in molecule **3a** (1.326, 1.386, 1.415 and 1.308 Å, respectively) were found to be intermediate in comparison with the corresponding distances for the hydroxyhydrazone **A**[4] and ketohydrazine (*E*)-**B** structures. Thus, interatomic distances O—C(3), C(3)—C(2), C(2)—C(4), C(4)—N in hydrazone **3b** are 1.264, 1.441, 1.357 and 1.348 Å, respectively.

‡ The X-ray structural data were obtained by S. M. Aldoshin and L. O. Atovmyan (Institute of Chemical Physics, Academy of Science of the USSR, Chernogolovka) and will be published elsewhere.

Table 1 Activation parameters of thermal (*Z*)→(*E*) isomerization of hydrazones **2b**, **3b** and **3c**[a]

Compound	*T*/K	k/s^{-1}	$\Delta G^{\ddagger}$ /kJ mol^{-1}	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /J K^{-1} mol^{-1}
2b	292	6.1×10^{-4}	89.3	38.9	− 172.6
3b	293	1.2×10^{-3}	87.9	38.5	− 168.6
3c	293	6.1×10^{-5}	95.4	38.5	− 194.2

[a] Temperature range 252–293 K.



3a

Taking into consideration both the similarity of the UV spectra of hydrazone **3a** and its anion and also the absence of photo- and solvato-chromism in the case of compound **3a**, the bipolar structure appears to be the most stable one for these molecules both in solution and in the solid state.

In conclusion it should be noted that the results reported here provide a useful approach to the development of organic materials for solar energy storage. The following observations are of particular interest. (*i*) The (*E*,*Z*)-isomers in the benzofuran series (X = O) are kinetically more stable than the corresponding benzothiophene derivatives. However, the spectral features of the latter compounds are more suitable for solar energy storage. (*ii*) The percentage of the (*Z*)-**B** isomer in solution after irradiation depends on the type of substituents R^2 and R^3, being greatest in the case of $R^2 = R^3$ = Et (**3c**).

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