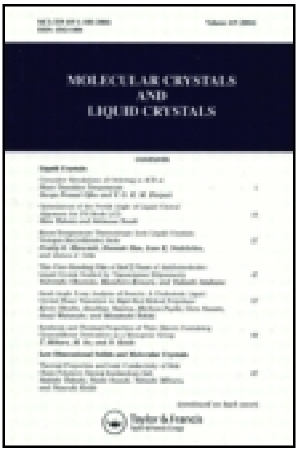

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# Biphotochromic Norbornadiene Systems

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# BIPHOTOCHROMIC NORBORNADIENE SYSTEMS

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Abstract Novel biphotochromic systems containing two norbornadiene moieties in one molecule or one norbornadienyl group in 2-[N-(3-phenylnorbornadiene-2-carbonyl)]-N-arylaminomethylene-(2H)benzo[b]thiophenones have been prepared. Under UV/VIS irradiation the latter compounds undergo Z/E-isomerization acompanied by N → O acyl rearrangement and valence isomerization in the norbornadiene fragment. Bis-norbornadienyl derivatives upon irradiation convert through stepwise isomerization into corresponding quadricyclanes. The back reactions are catalyzed with trifluoroacetic acid at room temperature.

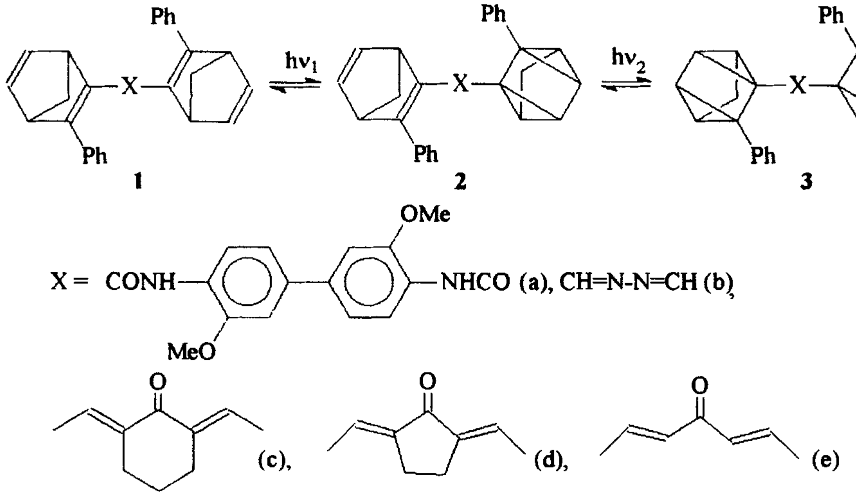
## INTRODUCTION

The reversible photoinduced isomerization of norbornadiene derivatives into corresponding quadricyclanes is one of the most efficient mechanisms of functioning molecular solar energy storage systems.[1,2]

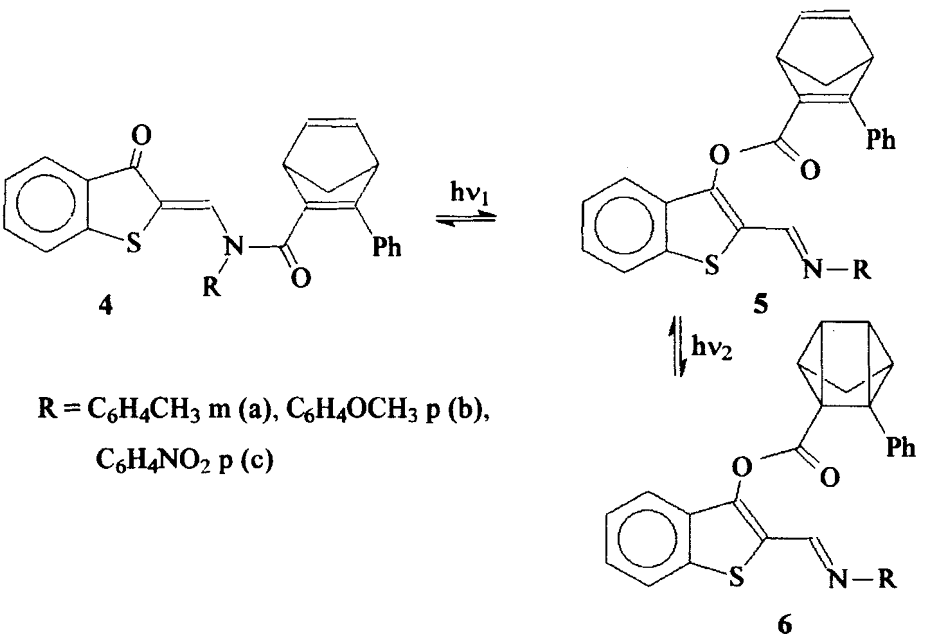
Here we report on the synthesis and spectral study of new biphotochromic compounds capable of either two stepwise valence isomerizations 1→ 2 → 3 (Scheme 1) or Z/E-isomerization accompanied by N→ O acyl rearrangement and valence isomerization 4→ 5→ 6 (Scheme 2).

## EXPERIMENTAL

UV-Vis absorption spectra were recorded on a Specord M-40 spectrophotometer. Irradiation of solutions was carried out by the light of a high-pressure mercury lamp DRSh (250 W)



Scheme1



R = $C_6H_4CH_3$ m (a), $C_6H_4OCH_3$ p (b), $C_6H_4NO_2$ p (c)

Scheme 2

supplied with a set of glass filters. IR spectra were measured with a Specord IR-75 spectrometer. $^1$H NMR spectra were recorded using Varian Unity 300 (300 MHz) instrument.

Compound 1a was prepared according to the method.[6]

Bis-3-phenylnorbornadiene-2-carbaldazine (1b). 3-Phenylnorbornadiene-2-carbaldehyde (0.5 g)[7] was dissolved in 2 ml of 2-propanol and 0.06 ml of 68% water solution of hydrazine was added at room temperature. The reaction mixture was heated to the boiling point and then allowed to stand at room temperature for 1 hour. The precipitate was filtered off and recrystallized from toluene to give 0.4 g (81%) of yellow crystals.

M.p. 274-275°C. Found: C 86.72; H 6.25; N 7.31%. $C_{28}H_{24}N_2$ requires: C 85.56 ; H 6.23; N 7.21%.

$^1$H NMR ($CDCl_3$, δ, ppm) 2.12 (d,2H,$H^7$), 2.22 (d, 2H, $H^{7'}$), 3.90 (s, 2H, $H^4$), 4.32 (s,2H,$H^1$), 6.92(m, 4H, $H^{5,6}$), 7.30-7.45 (m, 10H, $2C_6H_5$), 8.62 (s, 2H, 2H-C=).

IR (Nujol, ν, $cm^{-1}$): 1590, 1560, 1285.

Compounds 1c-e were obtained in the similar way.

2-[N-(3-phenylnorbornadiene-2-carbonyl)]-N-(3-methylphenyl)aminomethylene3(2H)-benzo[b]thiophenone (2a). 2-N-(m-methylphenyl)aminomethylene-3(2H)benzo[b]thiophenone[5] (0.54 g) was dissolved in 5 ml of toluene and 0.5 ml of 3-phenylnorbornadiene-2-carbonyl chloride was added. The reaction mixture was allowed to stand for 10 - 15 min and 0.4 ml of triethylamine was added dropwise with stirring. The mixture was boiled for 20 - 30 min. The insoluble materials were removed by filtration. The filtrate was diluted with ligroine. Yield 0.6 g (58%), M.p. 212 °C.

$^1$H NMR ($CDCl_3$, d, ppm) 2.00 (d, 1H, $H^7$), 2.13 (d, 1H, $H^{7'}$), 3.82 (s, 1H, $H^4$), 3.88 (s, 4H, $OCH_3$ + $H^1$), 6.81 (m, 6H, $C_6H_4$-p + $H^5C{=}CH^6$), 7.13 - 7.43 (m, 8H, $C_6H_5$ + $CH_{Ar}$), 7.80 (d, 1H, $CH_{Ar}$), 8.53 (c, 1H, $CH_{Ar}$).

The compounds 2b,c were synthesized in the similar way.

## RESULTS AND DISCUSSION

Bis-norbornadienes 1 were obtained by acylation of 3,3'-dimethoxy-4,4'-diaminodiphenyl with 3-phenylnorbornadiene-2-carbonyl chloride (a), by condensation of 3-phenylnorbornadiene-2-carbaldehyde with hydrazine (b), cyclohexanone (c), cyclopentanone (d) and acetone (e). Compounds 4 were synthesized by acylation of 3-hydroxybenzo[b]thiophene-2-carbaldehyde imines with 3-phenylnorbornadiene-2-

carbonyl chloride. Structure of the compounds **1**,**4** was elucidated on the basis of UV, IR and $^1$H NMR spectral data.

Photochromes **1** containing in one molecule two π-conjugated norbornadiene fragments absorb in longer wavelength spectral region than the majority of previously studied derivatives of norbornadiene (Table 1).

TABLE 1. Spectral characteristics of the compounds 1a-e and diquadricyclanes 3a-e in 2-propanol solution

| Compound | $1{:}\lambda_{max}$, nm ($\varepsilon \cdot 10^{-3}$) | 1: $\lambda_e{}^a$, nm | $3{:}\lambda_e{}^a$, nm | $\Phi^b{}_{1\to3}$ |
|---|---|---|---|---|
| a | 273 (14.6), 345 (17.0) | 435 | 400 | 0.011 |
| b | 278 (4.2), 382 (12.8) | 475 | 420 | 0.025 |
| c | 282 (11.2), 425 (24.0) | 530 | 455 | 0.039 |
| d | 285 (12.5), 451 (25.1) | 560 | 470 | 0.022 |
| e | 370 (14.3) | 530 | 500 | - |

[a] Absorption edge ($\varepsilon$~0)

[b] Aberchrome 540 was used as an actinometer

On irradiation of solutions of bis-norbornadienyl derivatives **1** in 2-propanol with the filtered 365 nm (**1a**,**b**) or 436 nm(**1c-e**) light of high-pressure mercury lamp valence isomerization of **1** into corresponding monoquadricyclanes **2a-e** and then - into the diquadricyclanes **3a-e** occurs. Two-stage character of this reaction postulated[3,4] for bis-norbornadienyl derivatives of diamides well examplified by the evolution of the UV spectra of 3-phenylnorbornadiene-2-carbaldazine **1b**. An appearence of the primary photoproduct, the quadricyclane **2b** is characterized by a new absorption band emerged at 380 nm [1] during irradiation of its 2-propanol solution ($\lambda_{irr}$ = 436 nm) (Figure 1a).On prolonged irradiation of the solution with the UV-light at 365 nm light formation of the compound **3b** which absorbs at $\lambda_{max}$= 300 nm is observed (Figure 1b).

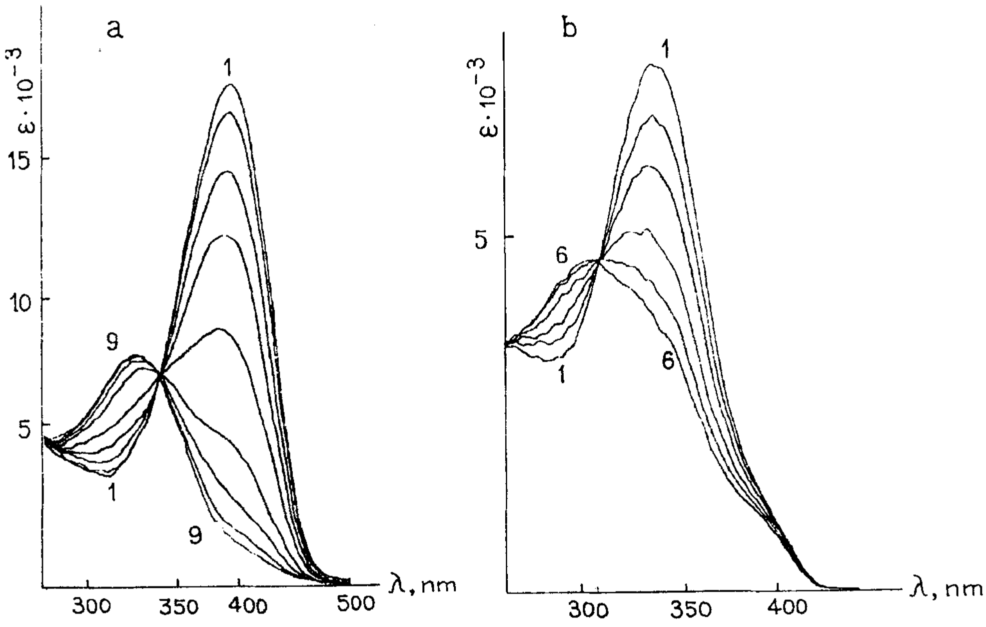


FIGURE 1. a)Electronic absorption spectra of the solution of the azine (1 b) in 2-propanol before (1) and after irradiation with the filtered ($\lambda_{irr}$=436 nm) light of a high-pressure mercury lamp: 0.5m (2), 2m (3), 4m(4), 8m (5),16m(6), 24m(7), 32m (8), 40m (9) and b) further irradiation with the UV-light ($\lambda_{irr}$= 365nm) before (1) and after irradiation: 3s (2),6s (3), 10s (4),15s (5),20s (6)

Another biphotochromic system studied in this work is 2-[N-(3-phenylnorbornadiene-2-carbonyl)]-N-arylaminomethylene-3(2H)benzo[b]thiophenones, whose photochemical transformations are featured by Scheme 2. Recently we described the mechanism of the photoisomerization of 2-N-acyl-N-arylaminimethylene-3(2H)benzo[b]thiophenones as the Z/E-photoisomerization accompanied with the thermal N→ O acyl migration [5]. In accordance with this mechanism, formation of O-acyl derivatives of 4, the compounds 5a,b were observed on irradiation of 2-propanol solutions of compounds 4 with the quantum yield of 0.5 ($\lambda_{irr}$=436 nm) (Figure 2a) . The compound possessing p- $NO_2$ phenyl group exists under all conditions

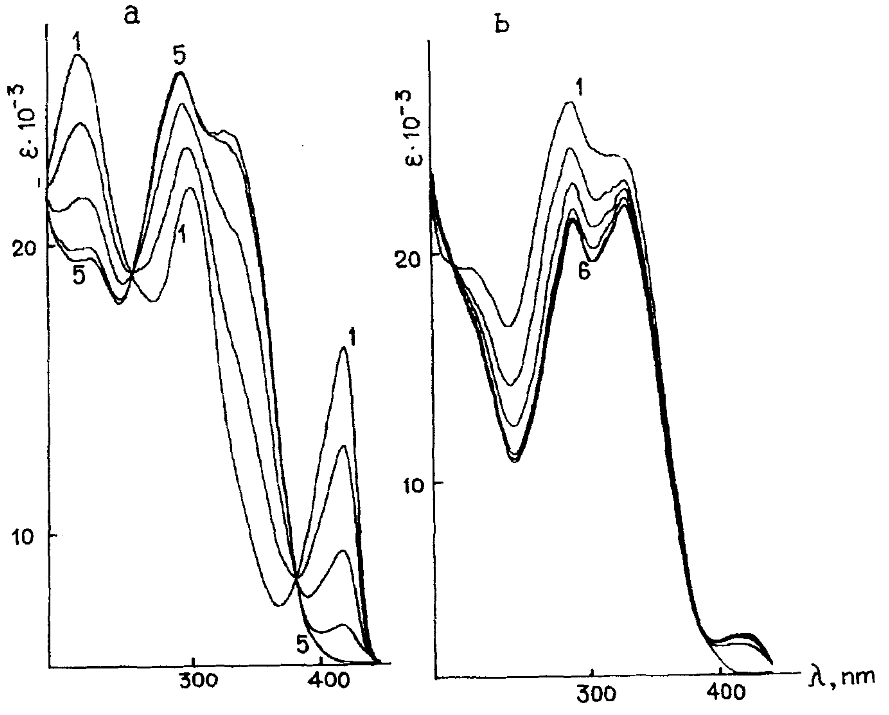


FIGURE 2. a)Electronic absorption spectra of the solution of the compound (3 b) in 2-propanol before (1) and after irradiation with the filtered ($\lambda_{irr}$=436 nm) light of a high- pressure mercury lamp: 5s (2), 20s (3), 60s (4), 120s (5), and b) further irradiation with the UV-light ($\lambda_{irr}$= 365 nm): 0.5m (1), 2m (2), 5m (3), 10m (4), 15m (5).

in the stable O-acyl form 5c and doesn't undergo photorearrangements. On the contrary, O-acyl isomers 5a,b which absorb at $\lambda_{max}$ 350 - 370 nm upon irradiation with the light at 365 nm undergo partial valence isomerization into the quadricyclane derivatives 6a,b, respectively(Figure 2b). According to the $^1$H NMR spectral data the mixture obtained on irradiation of the solution of 4a contains 50% of 5a and 50% of 6a, correspondingly.

The back reactions 3 → 1 and 6 → 4 are catalyzed by $CF_3COOH$.

## CONCLUSIONS

1.Irradiation of solutions 2-[N-(3-phenylnorbornadiene-2-carbonyl)-N-arylaminomethylene]-3(2H)benzo[b]thiophenones results in Z/E-isomerization accompanied with N→O acyl migration and following valence isomerization of norbornadiene into quadricyclane.

2. Upon UV-irradiation bis-norbornadienyl derivatives undergo stepwise isomerization first to monoquadricyclanes and then to bis-quadricyclanes.

3. The back reactions are catalyzed by protic acids.

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