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SYNTHESIS OF *tert*-BUTYL SUBSTITUTED POLYMETHINE 1-BENZOTHIOPYRYLIUM DYESTUFFS

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A series of polymethine thiopyrylium dyestuffs of symmetrical and unsymmetrical structure, containing one to four tert-*butyl groups, has been synthesized from 6-*tert-*butyl-2-(p-*tert-*butylphenyl)-4-methyl-, 4,6-di(*tert-*butyl)-2-methyl-, and 6-*tert-*butyl-2,4-dimethyl-1-benzothiopyrylium perchlorates.*

Pyrylo- and thiopyrylocyanines with three or five methine groups possess intense absorption in the 680-880 nm region and may be used in recording layers of optical disks of the WORM type. The presence of *tert*-butyl groups in their molecules increases solubility in organic media and improves film formation [1]. Previously we synthesized and investigated dyes from 6-*tert*-butyl-4-methylthioflavylium perchlorate (I) [2].

The aim of the present investigation was to extend the series of dyestuffs to 1-benzothiopyrylium salts containing one or two *tert*-butyl groups in the molecule. We used two approaches to prepare them.

First, the previously unknown thiochromone (IV) was synthesized from *p-tert*-butylthiophenol (II) and *p-tert*-butylbenzoylacetic ester (III) analogously to [3]. Compound (IV) was converted by reaction with methylmagnesium iodide according to [2] into 1-benzothiopyrylium perchlorate (V), the molecule of which contains an additional *tert*-butyl group compared with structure (I). Secondly, thiochromone (VI), containing a methyl group at position 2, was obtained by condensing compound (II) with acetoacetic ester according to [4]. Reaction of compound (VI) with *tert*-butylmagnesium bromide and with methylmagnesium iodide led to thiopyrylium salts (VII) and (VIII) respectively.

The reaction of compounds (V) and (VII) with ethyl orthoformate or with *p*-dialkylaminobenzaldehydes (IXa, b) by the usual methods gave the corresponding dyestuffs (X)-(XIII). The bistyryl derivative (XIV) was obtained from salt (VIII), an analog of which containing no *tert*-butyl group has an intense absorption at 836 nm [5].

The structures of the compounds synthesized were established from data of elemental analysis and spectroscopy. In the IR spectra of thiochromones (IV) and (VI) in addition to stretching vibrations of the *tert*-butyl groups (2880-3050) there were two intense absorption bands near 1600 corresponding to the stretching vibrations of a conjugated C=O group and two bands in the region of the thiopyrylium ring vibrations (1500 and 1560 cm^{-1}). The IR spectra of thiopyrylium salts (V), (VII), and (VIII) contain a very intense absorption band at 1100 cm^{-1} (perchlorate ion). The PMR spectral data corresponded completely with the structures of the synthesized compounds. The values of the coupling constants (13-15 Hz) for the Hα and Hβ protons in the spectra of dyestuffs (X)-(XIV) indicate their *trans* disposition unequivocally. All the dyestuffs absorb intensely in the 720-820 nm region. The introduction of a *tert*-butyl group at position 6 leads to a bathochromic shift of the λ_{max} by 5-18 nm in all cases except the bistyryl (XIV) (see [5-7]).

The results of the physicochemical investigations of layers based on the dyestuffs synthesized will be given in a separate paper.

EXPERIMENTAL

The IR spectra were drawn on a UR 20 instrument, and the electronic absorption spectra on a Specord M 40 spectrophotometer in dichloromethane (long-wave absorption bands are given). The PMR spectra were taken on a Bruker WP

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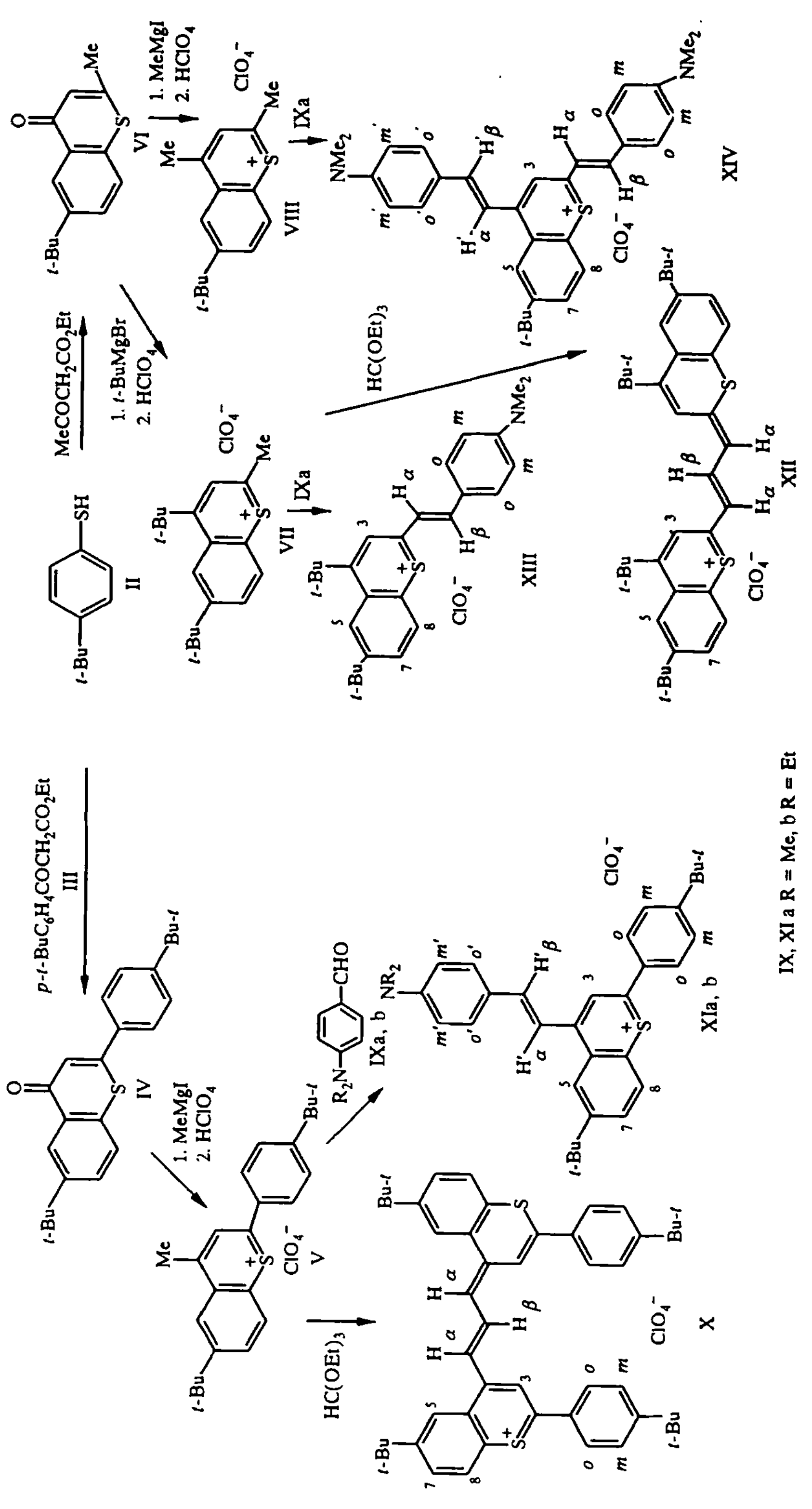
II
III
IV
V
VI
VII
VIII
X
XII
XIII
XIV
IXa, b
XIa, b
p-t-BuC$_6$H$_4$COCH$_2$CO$_2$Et
MeCOCH$_2$CO$_2$Et
1. t-BuMgBr
2. HClO$_4$
1. MeMgI
2. HClO$_4$
IXa
HC(OEt)$_3$
ClO$_4^-$
IX, XI a R = Me, b R = Et

TABLE 1. Characteristics of 1-Benzothiopyrylium Perchlorates (V), (VII), and (VIII)

Compound	Empirical formula	Found, % / Calculated, %				mp, (decomp.), °C	Yield, %
		C	H	Cl	S		
V	$C_{24}H_{29}ClO_4S$	64,78 64,20	6,80 6,51	7,92 7,90	7,10 7,14	140	73
VII	$C_{18}H_{25}ClO_4S$	58,05 57,97	6,89 6,76	9,60 9,51	8,40 8,60	180	22
VIII	$C_{15}H_{19}ClO_4S$	54,62 54,46	5,99 5,79	10,70 10,72	9,15 9,69	210	59

Compound	PMR spectrum, δ, ppm						
	Me, sec	*t*-Bu, sec	3-H, sec	5-H, d, (*J*, Hz)	7-H, d.d (J_1, J_2, Hz)	8-H, d (*J*, Hz)	H_{arom}, d (*J*, Hz)
V	3,30	1,31 1,43	8,91	8,46 (1,5)	8,19 (8,5; 1,5)	8,61 (8,5)	7,65 (8,5), 8,18 (8,5)
VII	3,16	1,32 1,65	8,39	8,85 (2)	8,04 (9; 2)	8,33 (9)	
VIII	3,26 3,29	1,51	8,55	8,60 (2)	8,32 (9; 2)	8,50 (9)	

200 SY instrument at 200 MHz in $CDCl_3$ or in CD_2Cl_2. Yields, physicochemical and spectral characteristics, and data of elemental analysis of the thiopyrylium salts and dyestuffs are given in Tables 1 and 2.

***p-tert*-Butylbenzoylacetic ester (III)** was obtained from *p-tert*-butylbenzoyl chloride by the procedure of [8]. The reaction product was an oil containing 65% ester (III) (according to PMR and GLC data) and was used without further purification in the following stages. PMR spectrum of ester (III) ($CDCl_3$): 1.23 (3H, t, $C\underline{H}_3CH_2$); 1.30 (9H, s, *t*-Bu); 3.95 (2H, s, $COCH_2$); 4.17 (2H, q, $CH_3C\underline{H}_2$); 7.46 (2H, d, H_{arom}); 7.86 ppm (2H, d, H_{arom}).

6-*tert*-Butyl-2-(p-*tert*-butylphenyl)-4H-1-benzothiopyran-4-one (IV). A solution of thiophenol (II) (26.0 ml) and unpurified ester (III) (20.0 g) from the previous experiment was added dropwise to polyphosphoric acid, prepared from H_3PO_4 (d = 1.87 g/cm^3) (100 ml) and P_2O_5 (200 g), at a rate such that the temperature of the reaction mixture did not rise above 100°C. The mixture was then stirred at 90-100°C for a further 20 min. The mixture was cooled to 40-45°C, poured onto crushed ice, the viscous yellow product was extracted with ether, the extract washed with 2% NaOH, then with water, dried over $MgSO_4$, and evaporated, and the residue washed with hexane. Thiochromone (IV) (9.3 g, 61%) was obtained having mp 172-174°C (from alcohol). IR spectrum ($CHCl_3$): 1590 s, 1620 s (conjugated C=O), 2850-3050 cm^{-1} (*t*-Bu). PMR spectrum ($CDCl_3$): 1.35 (9H, s, *t*-Bu); 1.39 (9H, s, *t*-Bu); 7.24 (1H, s, 3-H); 7.45-7.70 (6H, m, $4H_{arom}$, 7-H, 8-H); 8.55 ppm (1H, d, 5-H, *J* = 2 Hz). Found, %: C 78.64; H 7.46; S 9.10. $C_{23}H_{26}OS$. Calculated, %: C 78.81; H 7.48; S 9.15.

6-*tert*-Butyl-2-(*p-tert*-butylphenyl)-4-methyl-1-benzothiopyrylium perchlorate (V) was obtained from thiochromone (IV) and methylmagnesium iodide according to [2].

2-(*p-tert*-Butylphenyl)-4-{3-[2-(*p-tert*-butylphenyl)-6-*tert*-butyl-1-benzothiopyran-4-ylidene]-1-propenyl}-6-*tert*-butyl-1-benzothiopyrylium perchlorate (X) was synthesized by boiling perchlorate (V) (1.9 g) with ethyl orthoformate (2 ml) and CH_3COONa (0.7 g) in a mixture (2 ml) of acetic acid and acetic anhydride (1:1) for 20 min.

6-*tert*-Butyl-2-methyl-4H-1-benzothiopyran-4-one (VI) was obtained by reacting equimolar quantities of thiophenol (II) and acetoacetic ester in polyphosphoric acid at 90°C for 1 h (see [4]). The reaction product, isolated analogously to compound (IV), was chromatographed on Al_2O_3 collecting the colorless fraction eluted after two colored zones (eluent benzene). The yield of thiochromone (VI) was 57% as a bright yellow oil. IR spectrum ($CHCl_3$): 1595 s, 1630 s (C=O conjugated), 2950-3050 cm^{-1} (*t*-Bu). PMR spectrum (CCl_4): 1.35 (9H, s, *t*-Bu); 2.35 (3H, d, Me, *J* = 1 Hz); 6.63 (1H, m, 3-H); 7.32 (1H, d, 8-H, *J* = 8 Hz); 7.52 (1H, d.d, 7-H, J_1 = 8, J_2 = 2 Hz); 8.34 ppm (1H, d, 5-H, *J* = 2 Hz). Found, %: C 72.87; H 6.96. $C_{14}H_{16}OS$. Calculated, %: C 72.37; H 6.94.

4,6-Di-*tert*-butyl-2-methyl-1-benzothiopyrylium Perchlorate (VII). A solution of *t*-BuMgBr prepared from Mg (4.1 g) and freshly distilled *t*-BuBr (19 ml) in dry ether (170 ml) was added dropwise to a solution of thiochromone (VI) (13.3 g) in dry ether (60 ml). The mixture was boiled for 1 h, some of the ether (~ 120 ml) was boiled off, dry benzene (120 ml) was

TABLE 2. Characteristics of 1-Benzothiopyrylium Dyestuffs (X)-(XIV)

Compound	Empirical formula	Found, % / Calculated, % C	H	Cl	N	S	mp (decomp.), °C	Absorption spectrum, λ_{max} nm. (log ε)	PMR spectrum, δ, ppm	Yield, %
X	$C_{49}H_{55}ClO_4S_2$	72,78 72,88	6,86 6,86	4,27 4,39		7,84 7,94	280	743 sh (4,54), 812 (5,20)	1.32 (18H, s, *t*-Bu); 1.41 (18H, s, *t*-Bu); 7.56 (4H, d, *m*-H, *J* = 8 Hz); 7.73 (6H, m, α-H, 7-H, 8-H); 7.88 (4H, d, *o*-H, *J* = 8 Hz); 8.38 (4H, m, 3-H, 5-H); 8.88 (1H, t, β-H, *J* = 13 Hz)	46
XIa	$C_{33}H_{38}ClNO_4S$	68,26 68,31	6,55 6,60	6,20 6,11	2,44 2,41	5,70 5,53	270	727 (5,06)	1.41 (9H, s, *t*-Bu); 1.52 (9H, s, *t*-Bu); 3.29 (6H, s, NMe_2); 6.93 (2H, d, *m'*-H, *J* = 9 Hz); 7.70 (2H, d, *m*-H, *J* = 8 Hz); 7.90-8.04 (7H, m, α-H, *o*-H, *o'*-H, 7-H, 8-H); 8.41 (1H, d, β-H, *J* = 14 Hz); 8.57 (1H, br. s, 5-H); 8.59 (1H, s, 3-H)	68
XIb	$C_{35}H_{42}ClNO_4S$	68,70 69,11	7,09 6,96	6,16 5,82	2,06 2,30	5,60 5,27	200	735 (5,05)	1.27 (6H, t, $C\underline{H}_3CH_2$, *J* = 7 Hz); 1.34 (9H, s, *t*-Bu); 1.45 (9H, s, *t*-Bu); 3.55 (4H, q, $CH_3C\underline{H}_2$, *J* = 7 Hz); 6.86 (2H, d, *m'*-H, *J* = 9 Hz); 7.62 (2H, d, *m*-H, *J* = 8 Hz); 7.81 (1H, d, α-H, *J* = 13 Hz); 7.81-7.91 (2H, m, 7-H, 8-H); 7.97 (2H, d, *o*-H, *J* = 8 Hz), 8.02 (2H, d, *o'*-H, *J* = 9 Hz); 8.42 (1H, br. s, 5-H); 8.54 (1H, d, β-H, *J* = 13 Hz); 8.57 (1H, s, 3-H)	65
XII	$C_{37}H_{47}ClO_4S_2$	67,50 67,81	7,54 7,22	5,70 5,41	—	9,60 9,79	170	776 (5,03), 805 sh (5,01)	1.42 (18H, s, *t*-Bu); 1.66 (18H, s, *t*-Bu); 6.86 (2H, d, α-H, *J* = 13 Hz); 7.56 (2H, s, 3-H); 7.70 (2H, d.d, 7-H, J_1 = 8, J_2 = 2 Hz); 7.78 (2H, d, 8-H, *J* = 8 Hz); 8.27 (1H, t, β-H, *J* = 13 Hz); 8.44 (2H, d, 5-H, *J* = 2 Hz)	32
XIII	$C_{27}H_{34}ClNO_4S$	64,23 64,33	6,79 6,80	6,86 7,03	2,87 2,78	6,20 6,36	220	718 (4,92)	1.36 (9H, s, *t*-Bu); 1.65 (9H, s, *t*-Bu); 3.11 (6H, s, NMe_2); 6.70 (2H, d, *m*-H, *J* = 8.5 Hz); 7.44 (1H, d, α-H, *J* = 15 Hz); 7.69 (1H, d, 7-H, *J* = 8.5 Hz); 7.78 (2H, d, *o*-H, *J* = 8.5 Hz); 7.85-7.91 (2H, m, 3-H, 8-H); 7.96 (1H, d, β-H, *J* = 15 Hz); 8.44 (1H, br. s, 5-H)	60
XIV	$C_{33}H_{37}ClN_2O_4S$	66,49 66,82	6,46 6,29		4,59 4,72		205	809 (4,93)	1.47 (9H, s, *t*-Bu); 3.09 (6H, s, NMe_2); 3.14 (6H, s, NMe_2); 6.68 (2H, d, *m*-H, *J* = 9 Hz); 6.75 (2H, d, *m'*-H, *J* = 9 Hz); 7.38 (1H, d, α-H, *J* = 15 Hz); 7.59-7.63 (4H, m, *o*-H, α'-H, β-H); 7.77 (3H, m, *o'*-H, 8-H); 7.81 (1H, d.d, 7-H, J_1 = 8, J_2 = 2 Hz); 8.19 (1H, d, β'-H, *J* = 15 Hz); 8.25 (1H, s, 3-H); 8.31 (1H, d, 5-H, *J* = 1.5 Hz)	28

added, and the mixture then boiled for 1 h further. After the reaction was complete some of the solvent (~ 100 ml) was distilled off, the reaction mass was cooled to −20°C, and 20% $HClO_4$ (50 ml) added dropwise with vigorous stirring and cooling. The cooling was removed, a top layer (dark oil) separated from the reaction mixture, this was removed, and rubbed under ether. The precipitated solid was filtered off, washed with ether, dried, and then reprecipitated from CH_2Cl_2 with ether.

6-*tert*-Butyl-2,4-dimethyl-1-benzothiopyrylium perchlorate (VIII) was synthesized from thiochromone (VI) analogously to salt (V).

Styryl derivatives (XIa, b) and (XIII) were obtained by heating salts (V) or (VII) with an equimolar quantity of the appropriate aromatic aldehyde in acetic anhydride at 100°C.

6-*tert*-Butyl-2,4-bis[(*p*-dimethylaminophenyl)ethenyl]-1-benzothiopyrylium perchlorate (XIV) was obtained by boiling perchlorate (VIII) (1.0 g) with benzaldehyde (IXa) (1.0 g) in alcohol (6 ml) for 4 h (see [5]).

4,6-Di-*tert*-butyl-2-[3-(4,6-di-*tert*-butyl-1-benzothiopyranylidene)propenyl]-1-benzothiopyrylium Perchlorate (XII). Perchlorate (VII) (0.5 g), ethyl orthoformate (1.9 ml), and dry pyridine (0.5 ml) in a mixture (5 ml) of acetonitrile and acetic anhydride (4:1) were boiled for 5 min, then 10% $HClO_4$ was poured in. The precipitated solid was filtered off, air-dried, and reprecipitated from CH_2Cl_2 with hexane.

REFERENCES

1. T. N. Gerasimova and V. V. Shelkovnikov, Usp. Khim., **61**, 102 (1992).
2. N. A. Orlova, N. V. Pavlova, Z. M. Ivanova, V. V. Shelkovnikov, and T. N. Gerasimova, Sib. Khim. Zh., No. 1, 57 (1993).
3. F. Bossert, Justus Liebigs Ann. Chem., **680**, 40 (1964).
4. H. Nakazumi, T. Ueyama, and T. Kitao, J. Heterocycl. Chem., **21**, 193 (1984).
5. H. Nakazumi, S. Watanabe, S. Kado, and T. Kitao, Chem. Lett., No. 6, 1039 (1989).
6. A. I. Tolmachev, N. A. Derevyanko, and A. A. Ishchenko, Khim. Geterotsikl. Soedin., No. 9, 1173 (1992).
7. M. A. Kudinova, V. V. Kurdyukov, A. A. Ishchenko, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 3, 339 (1992).
8. Organic Syntheses [Russian translation], Mir, Moscow (1959), No. 9, p. 84 (in Russian version).