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




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Dedicated to the memory of Professor Nicholas Alexandrou

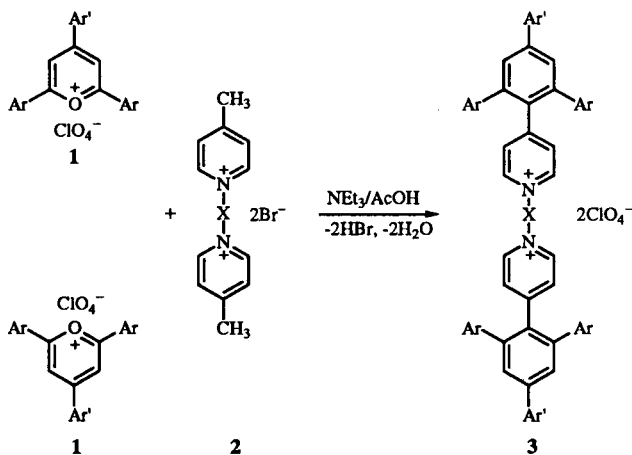
The synthesis of hitherto unknown 4,4'-bis(2,4,6-triarylphenyl) substituted bispyridinium diperchlorates **3**, in which the *N*-atoms are linked by a carbon chain, a heteroatom containing a carbon chain or a bis(methylene) substituted aromatic/heteroaromatic ring, from 4,4'-dimethylbispyridinium derivatives **2** by a double 2,6-[C₅+C] ring transformation of 2,4,6-triarylpyrylium and 2,4,6-triarylthiopyrylium salts **1/4** is reported. Spectroscopic data of the bispyridinium diperchlorates **3** and their mode of formation are discussed.

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Bispyridinium salts have been known as a class of substances with a wide range of biological activity [2]. Examples are their possible use for the reactivation of acetylcholinesterase, as neuromuscular and ganglionic blocking or antileukemic agents, as chemosterilants, bactericides, fungicides and herbicides or parasymphatheticomimetic, antisecretory and potential antitumor compounds. The ability of certain bispyridinium salts to form reversible two-step redox systems [3] have made them interesting study subjects not only in theoretical and physical organic chemistry but also in material sciences. Although a host of such substances have been described in the literature, a considerable demand for bispyridinium salts with novel structural features still exists. One possibility for the synthesis of these compounds is to start with an appropriate substituted bispyridinium salt and to vary its substitution pattern. In a preceding paper of this series [4] we described a new and simple method for the conversion of methyl substituted pyridinium salts [5] into 2,4,6-triarylphenyl derivatives *via*

1	2	Ar	Ar'	X	3
a	a	Ph	Ph	(CH ₂) ₂	a
b	a	Ph	4-MeC ₆ H ₄	(CH ₂) ₂	b
c	a	Ph	4-MeOC ₆ H ₄	(CH ₂) ₂	c
d	a	Ph	4-ClC ₆ H ₄	(CH ₂) ₂	d
e	a	Ph	4-BrC ₆ H ₄	(CH ₂) ₂	e
f	a	4-MeC ₆ H ₄	Ph	(CH ₂) ₂	f
g	a	4-ClC ₆ H ₄	Ph	(CH ₂) ₂	g
h	a	4-BrC ₆ H ₄	Ph	(CH ₂) ₂	h
a	b	Ph	Ph	(CH ₂) ₃	i
a	c	Ph	Ph	(CH ₂) ₄	j
a	d	Ph	Ph	(CH ₂) ₅	k
a	e	Ph	Ph	(CH ₂) ₆	l
a	f	Ph	Ph	(CH ₂) ₇	m
a	g	Ph	Ph	(CH ₂) ₈	n
a	h	Ph	Ph	(CH ₂) ₉	o
a	i	Ph	Ph	(CH ₂) ₁₀	p
a	j	Ph	Ph	(CH ₂) ₁₁	q
a	k	Ph	Ph	(CH ₂) ₁₂	r
a	l	Ph	Ph	(CH ₂) ₂ -O-(CH ₂) ₂	s
a	m	Ph	Ph	(CH ₂) ₂ -S-(CH ₂) ₂	t
a	n	Ph	Ph		u
a	o	Ph	Ph		v
a	p	Ph	Ph		w
a	q	Ph	Ph		x
a	r	Ph	Ph		y

Scheme I



pyrylium [6] or thiopyrylium [7] ring transformations. If this procedure could be applied to dimethylbispyridinium salts in a twofold manner then an easy access to former unknown bis(2,4,6-triarylphenyl) substituted bispyridinium salts should be possible. In this paper we wish to report on our investigations of such reactions.

When the 2,4,6-triarylpyrylium perchlorates **1** and the 4,4'-dimethylbispyridinium dibromides **2** were heated in the presence of triethylamine/acetic acid (molar ratio 1:2:

Table I
Physical and Analytical Data for the Bis(2,4,6-triarylphenyl)bispyridinium Diperchlorates 3

No.	-bispyridinium diperchlorate	Yield (%)	Mp (°C)	Molecular Formula (Molecular Weight)	Analysis (%)		
					C	H	N
3a	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-(1,2-ethanediyl)-	71	313-314	C ₆₀ H ₄₆ Cl ₂ N ₂ O ₈ (993.9)	72.51	4.66	2.82
					72.30	4.70	2.95
3b	4,4'-Bis[4-(4-methylphenyl)-2,6-diphenylphenyl]-1,1'-(1,2-ethanediyl)-	64	306-308	C ₆₂ H ₅₀ Cl ₂ N ₂ O ₈ (1022.0)	72.87	4.93	2.74
					72.86	4.85	2.71
3c	4,4'-Bis[4-(4-methoxyphenyl)-2,6-diphenylphenyl]-1,1'-(1,2-ethanediyl)-	68	291-292	C ₆₂ H ₅₀ Cl ₂ N ₂ O ₁₀ (1054.0)	70.65	4.78	2.66
					70.68	4.81	2.71
3d	4,4'-Bis[4-(4-chlorophenyl)-2,6-diphenylphenyl]-1,1'-(1,2-ethanediyl)-	72	306-308	C ₆₀ H ₄₄ Cl ₄ N ₂ O ₈ (1062.8)	67.81	4.17	2.64
					67.78	4.06	2.68
3e	4,4'-Bis[4-(4-bromophenyl)-2,6-diphenylphenyl]-1,1'-(1,2-ethanediyl)-	77	319-320	C ₆₀ H ₄₄ Br ₂ Cl ₂ N ₂ O ₈ (1151.8)	62.57	3.85	2.43
					62.65	3.90	2.50
3f	4,4'-Bis[2,6-bis(4-methylphenyl)-4-phenylphenyl]-1,1'-(1,2-ethanediyl)-	42	272-273	C ₆₄ H ₅₄ Cl ₂ N ₂ O ₈ (1050.1)	73.21	5.18	2.67
					73.18	5.20	2.72
3g	4,4'-Bis[2,6-bis(4-chlorophenyl)-4-phenylphenyl]-1,1'-(1,2-ethanediyl)-	85	309-311	C ₆₀ H ₄₂ Cl ₆ N ₂ O ₈ (1131.7)	63.68	3.74	2.48
					63.51	3.80	2.51
3h	4,4'-Bis[2,6-bis(4-bromophenyl)-4-phenylphenyl]-1,1'-(1,2-ethanediyl)-	67	294-296	C ₆₀ H ₄₂ Br ₄ Cl ₂ N ₂ O ₈ (1309.6)	55.03	3.23	2.14
					55.13	3.29	2.20
3i	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-(1,3-propanediyl)-	76	304-305	C ₆₁ H ₄₈ Cl ₂ N ₂ O ₈ (1008.0)	72.69	4.80	2.78
					72.72	4.81	2.85
3j	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-(1,4-butanediyl)-	87	316-317	C ₆₂ H ₅₀ Cl ₂ N ₂ O ₈ (1022.0)	72.87	4.93	2.74
					72.91	4.89	2.76
3k	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-(1,5-pentanediy)-	77	290-291	C ₆₃ H ₅₂ Cl ₂ N ₂ O ₈ (1036.0)	73.04	5.06	2.70
					73.10	5.20	2.70
3l	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-(1,6-hexanediy)-	78	293-294	C ₆₄ H ₅₄ Cl ₂ N ₂ O ₈ (1050.1)	73.21	5.18	2.67
					73.10	5.10	2.72
3m	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-(1,7-heptanediy)-	77	219-221	C ₆₅ H ₅₆ Cl ₂ N ₂ O ₈ (1064.1)	73.37	5.30	2.63
					73.40	5.31	2.67
3n	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-(1,8-octanediy)-	82	252-254	C ₆₆ H ₅₈ Cl ₂ N ₂ O ₈ (1078.1)	73.53	5.42	2.60
					73.58	5.48	2.70
3o	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-(1,9-nonanediy)-	80	157-159	C ₆₇ H ₆₀ Cl ₂ N ₂ O ₈ (1092.1)	73.69	5.54	2.57
					73.75	5.59	2.60
3p	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-(1,10-decanediyl)-	88	187-189	C ₆₈ H ₆₂ Cl ₂ N ₂ O ₈ (1106.2)	73.84	5.65	2.53
					73.96	5.61	2.48
3q	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-(1,11-undecanediyl)-	65	154-156	C ₆₉ H ₆₄ Cl ₂ N ₂ O ₈ (1120.2)	73.98	5.76	2.50
					73.88	5.71	2.43
3r	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-(1,12-dodecanediyl)-	82	133-135	C ₇₀ H ₆₆ Cl ₂ N ₂ O ₈ (1134.2)	74.13	5.87	2.47
					74.20	5.91	2.50
3s	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-(3-oxa-1,5-pentanediy)-	88	195-196	C ₆₂ H ₅₀ Cl ₂ N ₂ O ₉ (1038.0)	71.74	4.86	2.70
					71.71	4.93	2.72
3t	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-(3-thia-1,5-pentanediy)-	72	284-286	C ₆₂ H ₅₀ Cl ₂ N ₂ O ₈ S (1054.1)	70.65	4.78	2.66
					70.61	4.82	2.72
3u	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-[1,2-phenylenebis(methylene)]-	92	327-329	C ₆₆ H ₅₀ Cl ₂ N ₂ O ₈ (1070.0)	74.08	4.71	2.62
					74.01	4.78	2.70
3v	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-[1,3-phenylenebis(methylene)]-	85	271-272	C ₆₆ H ₅₀ Cl ₂ N ₂ O ₈ (1070.0)	74.08	4.71	2.62
					74.15	4.79	2.68
3w	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-[1,4-phenylenebis(methylene)]-	90	353-355	C ₆₆ H ₅₀ Cl ₂ N ₂ O ₈ (1070.0)	74.08	4.71	2.62
					73.95	4.77	2.72
3x	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-[2,2'-biphenylenebis(methylene)]-	81	305-306	C ₇₂ H ₅₄ Cl ₂ N ₂ O ₈ (1146.2)	75.45	4.75	2.44
					75.51	4.81	2.49
3y	4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-[2,3-quinoxalinylenebis(methylene)]-	75	360-361	C ₆₈ H ₅₀ Cl ₂ N ₄ O ₈ (1122.1)	72.79	4.49	4.99
					72.82	4.53	5.02

NEt₃:AcOH = 2:1:4:6) in boiling ethanol the desired double pyrylium ring transformation smoothly occurred and the 4,4'-bis(2,4,6-triarylphenyl)bispyridinium diperchlorates **3** in yields up to 92% were formed. The structure of the bispyridinium salts **2** can be varied in a wide range: Thus, the transformation is possible with salts, in which the *N*-atoms are linked by a carbon chain (**2a-k**), an heteroatom containing carbon chain (**2l,m**) and a bis(methylene) substi-

tuted aromatic (**2n-q**) or heteroaromatic ring (**2r**). A detailed study of the transformation of the pyrylium perchlorate **1a** with the bispyridinium dibromide **2a** indicated that a mono-transformation by reacting **1a** with **2a** in a 1:1-molar ratio could not be observed. Under these conditions the product isolated was a mixture of the bis(2,4,6-triphenylphenyl)-bispyridinium diperchlorate **3a** and unchanged **2a**.

Table 2
Spectral Data for the Bis(2,4,6-triarylphenyl)bispyridinium Diperchlorates 3

Compound	IR (KBr) (cm ⁻¹) ClO ₄	UV (CH ₃ CN) λ _{max} (nm) (log ε)	¹ H-NMR (DMSO-d ₆) [a] δ (ppm)
3a [b]	1078	242 (4.92), 343 (4.34)	5.04 (s, 4H, NCH ₂), 7.15-7.85 (m, 38H, arom-H), 8.26 (d, J = 6.3 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3b	1089	242 (4.98), 350 (4.42)	2.32 (s, 6H, CH ₃), 5.02 (s, 4H, NCH ₂), 7.12-7.76 (m, 36H, arom-H), 8.24 (d, J = 6.6 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3c	1088	243 (4.92), 362 (4.41)	3.77 (s, 6H, OCH ₃), 5.04 (s, 4H, NCH ₂), 7.01-7.80 (m, 36H, arom-H), 8.26 (d, J = 6.4 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3d	1091	245 (4.97), 342 (4.42)	5.02 (s, 4H, NCH ₂), 7.12-7.92 (m, 36H, arom-H), 8.24 (d, J = 6.6 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3e	1080	246 (4.98), 342 (4.50)	5.02 (s, 4H, NCH ₂), 7.12-7.86 (m, 36H, arom-H), 8.24 (d, J = 6.5 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3f	1095	248 (5.00), 3.50 (4.38)	2.16 (s, 12H, CH ₃), 5.06 (s, 4H, NCH ₂), 6.95-7.82 (m, 34H, arom-H), 8.38 (d, J = 6.6 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3g	1092	246 (4.99), 343 (4.37)	5.08 (s, 4H, NCH ₂), 7.12-7.87 (m, 34H, arom-H), 8.45 (d, J = 6.6 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3h	1080	249 (5.04), 343 (4.40)	5.10 (s, 4H, NCH ₂), 7.07-7.86 (m, 34H, arom-H), 8.45 (d, J = 6.5 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3i	1097	241 (4.97), 334 (4.44)	2.33 (m, 2H, CH ₂), 4.35 (t, 4H, NCH ₂), 7.15-7.84 (m, 38H, arom-H), 8.61 (d, J = 6.7 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3j	1091	240 (4.90), 332 (4.38)	1.52 (m, 4H, CH ₂), 4.40 (t, 4H, NCH ₂), 7.15-7.85 (m, 38H, arom-H), 8.64 (d, J = 6.8 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3k	1095	241 (4.93), 330 (4.41)	0.91 (m, 2H, CH ₂), 1.73 (m, 4H, CH ₂), 4.37 (t, 4H, NCH ₂), 7.14-7.84 (m, 38H, arom-H), 8.68 (d, J = 6.6 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3l	1088	241 (4.92), 330 (4.39)	0.95 (m, 4H, CH ₂), 1.68 (m, 4H, CH ₂), 4.42 (t, 4H, NCH ₂), 7.15-7.74 (m, 38H, arom-H), 8.70 (d, J = 6.8 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3m	1091	242 (4.95), 329 (4.41)	0.96 (m, 4H, CH ₂), 1.19 (m, 2H, CH ₂), 1.72 (m, 4H, CH ₂), 4.43 (t, 4H, NCH ₂), 7.14-7.83 (m, 38H, arom-H), 8.70 (d, J = 6.8 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3n	1085	240 (4.93), 329 (4.40)	0.96 (m, 4H, CH ₂), 1.17 (m, 4H, CH ₂), 1.73 (m, 4H, CH ₂), 4.44 (t, 4H, NCH ₂), 7.14-7.82 (m, 38H, arom-H), 8.71 (d, J = 6.6 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3o	1090	240 (4.89), 329 (4.35)	0.95 (m, 4H, CH ₂), 1.17 (m, 6H, CH ₂), 1.72 (m, 4H, CH ₂), 4.43 (t, 4H, NCH ₂), 7.13-7.82 (m, 38H, arom-H), 8.71 (d, J = 6.6 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3p	1097	240 (4.92), 329 (4.38)	0.94 (m, 4H, CH ₂), 1.17 (m, 8H, CH ₂), 1.73 (m, 4H, CH ₂), 4.43 (t, 4H, NCH ₂), 7.13-7.82 (m, 38H, arom-H), 8.71 (d, J = 6.8 Hz, 2-, 6-, 2'-, 6'-H)
3q	1086	241 (4.92), 329 (4.38)	0.95 (m, 4H, CH ₂), 1.20 (m, 10H, CH ₂), 1.73 (m, 4H, CH ₂), 4.42 (t, 4H, NCH ₂), 7.13-7.80 (m, 38H, arom-H), 8.69 (d, J = 6.7 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3r [b]	1102	241 (4.89), 329 (4.36)	0.93 (m, 4H, CH ₂), 1.20 (m, 12H, CH ₂), 1.71 (m, 4H, CH ₂), 4.41 (t, 4H, NCH ₂), 7.13-7.82 (m, 38H, arom-H), 8.68 (d, J = 6.6 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3s [b]	1097	241 (4.92), 3.31 (4.38)	3.58 (m, 4H, OCH ₂), 4.49 (m, 4H, NCH ₂), 7.15-7.83 (m, 38H, arom-H), 8.53 (d, J = 6.5 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3t	1089	240 (4.94), 333 (4.42)	2.94 (t, 4H, SCH ₂), 4.61 (t, 4H, NCH ₂), 7.14-7.82 (m, 38H, arom-H), 8.68 (d, J = 6.6 Hz, 2-, 6-, 2'-, 6'-H)
3u	1094	240 (4.94), 339 (4.39)	5.77 (s, 4H, NCH ₂), 6.36-7.84 (m, 42H, arom-H), 8.71 (d, J = 6.3 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3v	1095	241 (4.95), 336 (4.41)	5.69 (s, 4H, NCH ₂), 6.88-7.84 (m, 42H, arom-H), 8.75 (d, J = 6.2 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3w [b]	1082	240 (4.97), 336 (4.43)	5.71 (s, 4H, NCH ₂), 7.15-7.82 (m, 42H, arom-H), 8.80 (d, J = 6.6 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3x	1096	239 (4.94), 336 (4.40)	5.51, 5.58 (d, J = 15.1 Hz, 4H, NCH ₂), 6.48-7.82 (m, 46H, arom-H), 8.48 (d, J = 6.5 Hz, 4H, 2-, 6-, 2'-, 6'-H)
3y	1100	239 (5.06), 330 (4.45)	6.18 (s, 4H, NCH ₂), 7.24-8.01 (m, 42H, arom-H), 8.68 (d, J = 6.6 Hz, 4H, 2-, 6-, 2'-, 6'-H)

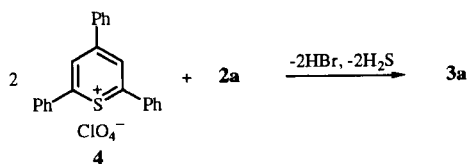
[a] 2-, 6-, 2'-, 6'-H Denotes the protons in 2-, 6-, 2'- and 6'-position, respectively, and arom-H the other protons bonded to the aromatic/heteroaromatic rings. [b] Mass spectra (FAB): m/z **3a** 893 [C₆₀H₄₆ClN₂O₄⁺] (M⁺-ClO₄), **3r** 1033 [C₇₀H₆₆ClN₂O₄⁺] (M⁺-ClO₄), **3s** 937 [C₆₂H₅₀ClN₂O₅⁺] O₄⁺ (M⁺-ClO₄), **3w** [C₆₆H₅₀ClN₂O₄⁺] (M⁺-ClO₄).

2,4,6-Triarylthiopyrylium salts, the sulfur analogues of the pyrylium salts **1**, reacted with the bispyridinium dibromides **2** in the same way: When the 2,4,6-triphenylthiopyrylium perchlorate (**4**) was refluxed with the 4,4'-dimethyl-1,1'-(1,2-ethanediy)bispyridinium dibromide (**2a**) in the presence of triethylamine/acetic acid in ethanol a compound was isolated which was identical with the product of the transformation **1a** + **2a** → **3a**. Since the yield was significantly lower (39% vs 71%) and the thiopyrylium salts have to be prepared from the appropriate pyrylium salts by heteroatom exchange with

sodium sulfide in acetone according to the Wizinger procedure [8] it is evident that the bis(2,4,6-triarylphenyl)-bispyridinium diperchlorates **3** can be synthesized more effectively *via* the pyrylium route.

The formation of the ring transformation products **3** can be explained in analogy to the related transformation of the pyrylium/thiopyrylium salts **1/4** with methyl substituted monopyridinium salts [4]. Under the action of triethylamine the 4,4'-dimethylbispyridinium salts **2** are deprotonated to anhydrobases which as carbon nucleophiles of the enamine type are added to the preferred position 2 of the

Scheme 2



pyrylium/thiopyrylium system [6,7,9]. Then *via* ring opening/ring closure two new benzene rings are formed [10]. Since each of these rings is built up from five carbon atoms of the pyrylium/thiopyrylium cation 1/4 and the C-atom of one methyl group of the 4,4'-dimethylbispyridinium salt 2 by connection of the former positions 2 and 6 of 1/4 by one carbon atom the reaction has to be classified as a 2,6-[C₅+C] transformation [11].

The structure of the transformation products can be unequivocally deduced from the spectroscopic data and the results of the elemental analyses (*cf.* Tables 1 and 2). In the ¹H nmr spectra the protons of the pyridinium rings in position 2, 6, 2' and 6' cause doublets in the same region (8.24-8.80 ppm) where the comparable protons of the monopyridinium analogues (1-alkyl-4-(2,4,6-triarylphenyl)pyridinium perchlorates A [4]) resonates (8.57-8.64 ppm); these signals are significantly downfield shifted in comparison to the signals of the aryl protons and the other protons of the pyridinium system. The most downfield shifted signal of the aliphatic protons is the signal of the CH₂-group bonded directly to the pyridinium nitrogens (4.35-6.18 ppm); the other signals caused by the protons of the 1,1'-linking groups are in agreement with the expected pattern. The characteristic feature of the uv spectra is also comparable to that one of the spectra of the salts A [4]: A strong absorption is observed at 239-249 nm (A: 240-255 nm) together with a band of lower intensity at 329-362 nm (A: 309-340 nm). From the results of the elemental analyses and the characteristic perchlorate ir absorption [12] at 1078-1102 cm⁻¹ it can be concluded that the bispyridinium diperchlorates were isolated.

EXPERIMENTAL

The melting points were measured on a Boëtius apparatus. The ¹H nmr spectra were recorded on Varian Gemini 200 spectrometer (199.975 MHz, DMSO-d₆, 25°, HMDSO as internal standard), ir spectra were obtained on a Perkin-Elmer FTIR 2000 spectrophotometer (in potassium bromide) and uv spectra on a Zeiss M 40 instrument (acetonitrile, 25°). Mass spectra were determined on a Finnigan MAT 701A spectrometer (FAB, 8 keV, argon, matrix: nitrobenzyl alcohol). The pyrylium salts 1a [13], 1b [14], 1c [15], 1d [16], 1e [17], 1f-h [18] and the thiopyrylium salt 4 [8] were prepared according to literature procedures; the 4,4'-dimethylbispyridinium dibromides 2 were synthesized applying the standard method for the bisalkylation of pyridines with α,ω-dibromides described in ref [19].

Preparation of 4,4'-Bis(2,4,6-triarylphenyl) Substituted

Bispyridinium Dipperchlorates 3 from 2,4,6-Triarylpyrylium Perchlorates 1 and 4,4'-Dimethylbispyridinium Dibromides 2. General Procedure (*cf.* Tables 1 and 2).

To absolute ethanol (30 ml) 5 mmoles pyrylium perchlorate 1, 2.5 mmoles bispyridinium dibromide 2, triethylamine (1.51 g, 15 mmoles) and acetic acid (0.60 g, 10 mmoles) were added. The reaction mixture was then heated under reflux for 2 hours. The bis(2,4,6-triarylphenyl)bispyridinium diperchlorates formed crystallized in some cases from the hot reaction mixture; otherwise their crystallization was initiated by cooling. They were filtered off by suction, washed with ethanol and diethyl ether and purified by dissolving in a minimal amount of hot acetonitrile and subsequent precipitation with diethyl ether.

When the bispyridinium dibromide 2a was treated with only one equivalent of 2,4,6-triphenylpyrylium perchlorate (1a) the product isolated contained, as ¹H nmr and FAB mass spectra indicated, the bis(2,4,6-triphenylphenyl)bispyridinium diperchlorate 3a and unreacted 2a (as perchlorate salt).

Synthesis of the 4,4'-Bis(2,4,6-triphenylphenyl)-1,1'-(1,2-ethanediy)bispyridinium Dipperchlorate (3a) from 2,4,6-Triphenylthiopyrylium Perchlorate (4) and 4,4'-Dimethyl-1,1'-(1,2-ethanediy)bispyridinium Dibromide (2a).

According to the general procedure for the transformation of the pyrylium salts 1 2,4,6-triphenylthiopyrylium perchlorate (4) (2.12 g, 5 mmoles) was reacted with 4,4'-dimethyl-1,1'-(1,2-ethanediy)bispyridinium dibromide (2a) and triethylamine/acetic acid in ethanol. The product was isolated and purified as described there. Yield: 39%; the compound was identical in all respects with that one obtained from 1a and 2a.

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