1,2,4,6-SUBSTITUTED PYRIDINIUM DERIVATIVES – SYNTHESIS AND PROPERTIES

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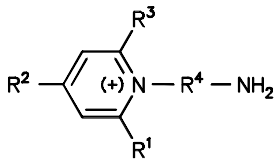
In relation to the investigation of their electrochemical properties[1,2,3] we prepared 24 pyridinium derivatives (*I*, *IV*, *V*, *VI*, *VII*) with alkyl and aryl substituents in positions 1, 2, 4 and 6, and 19 derivatives with two pyridinium nuclei (*II*, *III*, *VIII*, *IX*, *X*) connected by an aliphatic or an aromatic chain.

All the compounds were prepared from the corresponding pyrylium derivatives by reacting them with primary amines. The pyrylium derivatives were synthesized by aldolization and acylation followed by cyclization leading to a heteroaromatic pyrylium system[4–7]. In nucleophilic reactions with amines, the pyrylium derivatives yield pyridinium derivatives. The reaction was performed by adding the corresponding amine to an ethanolic suspension of the starting pyrylium salt[8,9].

Compounds with two pyridinium rings in the molecule were prepared by a similar procedure. The synthesis of a substance of the general formula *XI* by reaction with an excess of the diamine was found to be more convenient. This first step was followed by reaction with the equimolar amount of the starting pyrylium salt. This procedure was necessary for compounds with nonequally substituted pyridinium nuclei.



XI

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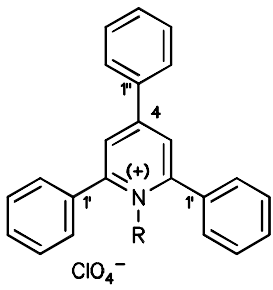
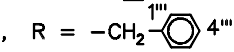
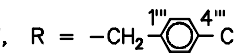
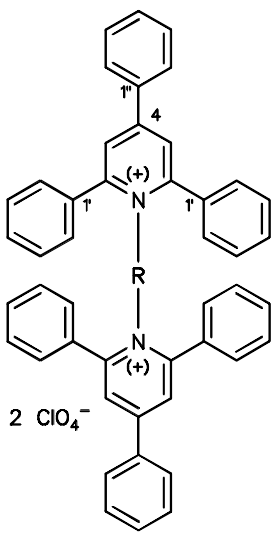


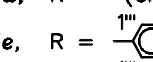
I

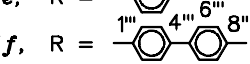
Ia, R = $-CH_3$
Ib, R = $-CH_2CH_3$
Ic, R = $-(CH_2)_2CH_3$
Id, R = $-(CH_2)_3CH_3$
Ie, R = $-CH_2CH(CH_3)_2$
If, R = $-(CH_2)_4CH_3$
Ig, R = $-CH_2CH{=}CH_2$
Ih, R = 
Ii, R = 

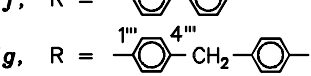
Ij, R = 

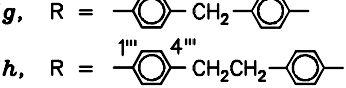


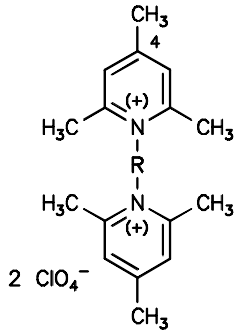
II

IIa, R = $-(CH_2)_2-$
IIb, R = $-(CH_2)_3-$
IIc, R = $-(CH_2)_4-$
IId, R = $-(CH_2)_6-$
IIe, R = 

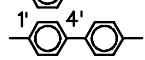
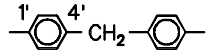
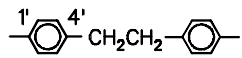
IIf, R = 

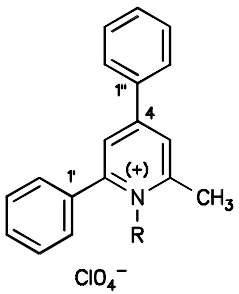
IIg, R = 

IIh, R = 

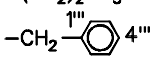


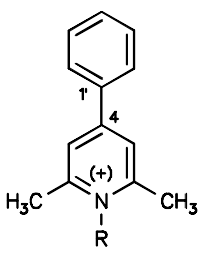
III

IIIa, R = $-(CH_2)_2-$
IIIb, R = $-(CH_2)_3-$
IIIc, R = $-(CH_2)_4-$
IIId, R = $-(CH_2)_6-$
IIIe, R = 
IIIf, R = 
IIIg, R = 
IIIh, R = 

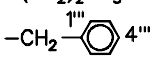


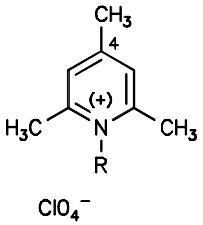
IV

IVa, R = $-CH_3$
IVb, R = $-(CH_2)_2CH_3$
IVc, R = 



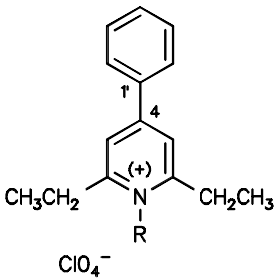
V

Va, R = $-CH_3$
Vb, R = $-(CH_2)_2CH_3$
Vc, R = 



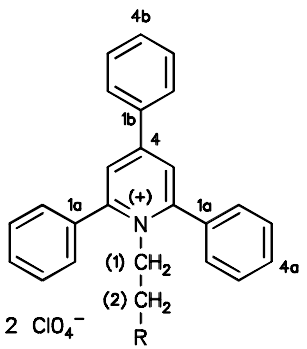
VI

VIa, R = $-CH_3$
VIb, R = $-(CH_2)_2CH_3$
VIc, R = $-CH_2$–C$_6$H$_5$ (1' 4')
VId, R = $-CH(CH_3)_2$
VIe, R = $-NH_2$



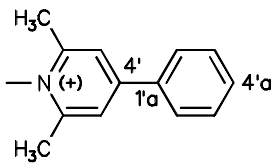
VII

VIIa, R = $-CH_3$
VIIb, R = $-(CH_2)_2CH_3$
VIIc, R = $-CH_2$–C$_6$H$_5$ (1' 4')

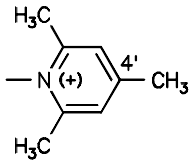


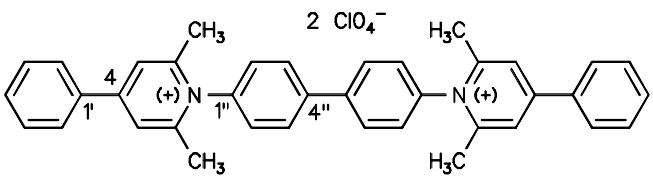
VIII, IX

VIII, R =



IX, R =





X

TABLE I
Physical characteristics of the pyridinium salts *I – X*

Compound	Formula M.w.	M.p., °C Yield, %	Calculated/Found			
			% C	% H	% Cl	% N
Ie	$C_{27}H_{26}ClNO_4$	232 – 234	69.89	5.66	7.64	3.02
	464.0	85	70.14	5.47	7.87	2.99
If	$C_{28}H_{28}ClNO_4$	215 – 218	70.34	5.92	7.42	2.93
	478.0	90	70.41	6.08	7.31	2.82
Ij	$C_{30}H_{23}Cl_2NO_4$	148 – 151	67.67	4.36	13.32	2.63
	532.4	88	67.42	4.51	13.11	2.54
IIa	$C_{48}H_{38}Cl_2N_2O_8$	207 – 210	68.48	4.56	8.42	3.33
	841.8	81	68.06	4.87	8.12	3.52
IIb	$C_{49}H_{40}Cl_2N_2O_8$	185 – 188	68.76	4.72	8.28	3.27
	855.8	62	68.21	4.99	7.87	3.56
IIc	$C_{50}H_{42}Cl_2N_2O_8$	323 – 325	69.04	4.88	8.15	3.22
	869.8	92	69.31	4.63	7.94	3.13
IId	$C_{52}H_{42}Cl_2N_2O_8$	295 – 297	69.55	5.17	7.90	3.12
	897.9	35	69.83	4.98	7.65	3.21
IIe	$C_{52}H_{38}Cl_2N_2O_8$	>360	70.18	4.31	7.97	3.15
	889.8	95	69.94	4.12	8.11	3.02
IIf	$C_{58}H_{42}Cl_2N_2O_8$	>360	72.12	4.39	7.34	2.90
	965.9	90	71.97	4.48	7.12	3.01
IIg	$C_{59}H_{44}Cl_2N_2O_8$	218 – 220	72.31	4.53	7.24	2.86
	980.0	85	72.74	4.57	7.07	2.98
IIh	$C_{60}H_{46}Cl_2N_2O_8$	327 – 329	72.50	4.67	7.13	2.82
	994.0	80	72.69	4.76	7.02	2.68
IIIa	$C_{18}H_{26}Cl_2N_2O_8$	295 – 297	46.06	5.59	15.11	5.97
	469.4	81	45.79	5.83	14.81	5.90
IIIb	$C_{19}H_{28}Cl_2N_2O_8$	288 – 289	47.21	5.85	14.67	5.80
	483.4	81	46.86	5.68	14.33	6.06
IIIc	$C_{20}H_{30}Cl_2N_2O_8$	266 – 268	48.29	6.09	14.25	5.63
	497.4	51	48.53	5.91	14.16	5.75
IIId	$C_{22}H_{34}Cl_2N_2O_8$	263 – 265	50.28	6.53	13.49	5.33
	525.4	50	50.47	6.39	13.12	5.41

TABLE I
(*Continued*)

Compound	Formula M.w.	M.p., °C Yield, %	Calculated/Found			
			% C	% H	% Cl	% N
IIIe	$C_{22}H_{26}Cl_2N_2O_8$	>380	51.07	5.08	13.70	5.42
	517.4	83	51.36	4.91	13.42	5.66
IIIf	$C_{28}H_{30}Cl_2N_2O_8$	270 – 275	56.67	5.11	11.95	4.72
	593.5	decomp. 85	56.88	5.02	11.81	4.90
IIIg	$C_{29}H_{32}Cl_2N_2O_8$	275 – 277	57.33	5.32	11.67	4.61
	607.5	90	57.60	5.21	11.46	4.54
IIIh	$C_{30}H_{34}Cl_2N_2O_8$	172 – 174	57.97	5.52	11.41	4.51
	621.6	90	58.12	5.63	11.47	4.39
IVa	$C_{19}H_{18}ClNO_4$	189 – 190	63.42	5.05	9.85	3.89
	359.8	68	63.35	5.18	10.04	3.93
IVb	$C_{21}H_{22}ClNO_4$	183 – 185	65.02	5.73	9.14	3.61
	387.9	71	64.89	5.85	9.24	3.79
IVc	$C_{25}H_{22}ClNO_4$	233 – 234	68.88	5.10	8.13	3.21
	435.9	70	68.59	5.01	8.01	3.32
Va	$C_{14}H_{16}ClNO_4$	121	56.47	5.43	11.91	4.71
	297.8	55	56.28	5.57	11.69	4.62
Vb	$C_{16}H_{20}ClNO_4$	236 – 238	58.98	6.20	10.88	4.30
	325.8	55	59.16	6.31	10.75	4.17
Vc	$C_{20}H_{20}ClNO_4$	220 – 221	64.25	5.40	9.48	3.75
	373.9	75	64.37	5.49	9.75	3.51
VIa	$C_9H_{14}ClNO_4$	208 – 209	45.86	6.00	15.04	5.95
	235.7	77	45.66	6.15	14.75	5.81
VIb	$C_{11}H_{18}ClNO_4$	122	50.09	6.89	13.44	5.31
	263.8	65	50.22	6.77	13.26	5.28
VIc	$C_{15}H_{18}ClNO_4$	140	57.78	5.83	11.37	4.49
	311.8	80	57.91	6.12	11.22	4.54
VId	$C_{11}H_{18}ClNO_4$	163 – 164	50.09	6.89	13.44	5.31
	263.8	20	49.89	7.03	13.56	5.38
VIIa	$C_{16}H_{20}ClNO_4$	212 – 213	58.98	6.20	10.88	4.30
	325.8	83	59.21	6.42	10.71	4.24

TABLE I
(*Continued*)

Compound	Formula M.w.	M.p., °C Yield, %	Calculated/Found			
			% C	% H	% Cl	% N
VIIb	$C_{18}H_{24}ClNO_4$	185 – 186	61.09	6.85	10.02	3.96
	353.9	64	60.87	6.99	9.86	3.84
VIIc	$C_{22}H_{24}ClNO_4$	151	65.74	6.03	8.82	3.49
	401.9	76	65.29	6.18	8.74	3.38
VIII	$C_{38}H_{34}Cl_2N_2O_8$	310 – 311.5	63.59	4.79	9.88	3.90
	717.6	79	63.34	4.68	9.59	4.10
IX	$C_{33}H_{32}Cl_2N_2O_8$	348	60.46	4.93	10.82	4.27
	655.6	74	60.31	4.87	10.69	4.16
X	$C_{38}H_{34}Cl_2N_2O_8$	295 – 297	63.59	4.79	9.88	3.90
	717.6	92	63.81	4.62	9.67	3.99

EXPERIMENTAL

The melting points were measured on a Boetius block. The NMR spectra were measured on Varian XL-200 and Varian Unity-200 instruments (working frequency 200.057 MHz for ^1H and 50.309 MHz for ^{13}C). The reported spectra (δ, ppm; *J*, Hz) were measured in $(CD_3)_2SO$. Hexamethyldisiloxane (0.05 ppm) was used as the internal standard in ^1H NMR spectroscopy, whereas the signals of the solvents (39.7 ppm in $(CD_3)_2SO$; 77.0 ppm in $CDCl_3$) served as reference in ^{13}C NMR spectroscopy. The numbering of the carbon atoms for the NMR signal assignment is given in the respective formulae. The aliphatic chain in position 1 is numbered as usual; where it connects two pyridinium nuclei, the numbering is from CH_2-1 to CH_2-3.

Synthesis of Compounds *I*, *IV*, *V*, *VI*, *VII*

2,4,6-Substituted pyrylium perchlorate (0.012 mol) was suspended in ethanol (18 ml) and the amine (0.015 mol) was added. The suspension was stirred for 4 h at room temperature. The crystalline salt was then filtered off, washed twice with ethanol and recrystallized from ethanol.

Synthesis of Compounds *II*, *III*, *VIII*, *IX*, *X*

The corresponding 2,4,6-substituted pyrylium perchlorate (0.008 mol) was suspended in ethanol (20 ml) and the diamine (0.016 mol) was added. The suspension was stirred for 5 h at room temperature. The deposited intermediate *XI* was sucked off, washed twice with ethanol and dried in air. To the product so obtained was added an equimolar amount of the corresponding pyrylium perchlorate in ethanol (20 ml) and the constantly stirred suspension was refluxed for 5 h. After cooling, the deposited substance was filtered off, washed twice with ethanol and dried in air. Physical characteristics of the prepared compounds are given in Table I. Melting points of the compounds *Ia – Id*, *Ig – Ii* and *VIe* are in accordance with the published data[8,9]. NMR spectra of the compounds *I – X* are given in Tables II – XV.

TABLE II
^{13}C NMR spectra of the compounds *I*

Position	*Ia*	*Ib*	*Ic*	*Id*	*Ie*	*If*	*Ig*	*Ih*	*Ii*	*Ij*
2, 6	156.6	155.9	156.1	156.0	156.6	156.0	156.4	156.3	156.7	156.7
3, 5	125.3	126.3	126.2	126.2	126.4	126.2	126.3	125.3	126.4	126.5
4	154.3	154.2	154.3	154.3	154.6	154.3	154.7	155.7	155.1	155.3
1′	133.2	133.1	133.2	133.1	133.5	133.1	132.9	133.2	133.1	133.0
2′, 6′	129.2	129.2	129.2	129.1	129.3	129.2	129.0	129.8	129.0	129.0
3′, 5′	129.6	129.2	129.3	129.3	129.8	129.3	129.3	128.2	129.3	129.3
4′	131.2	131.0	131.0	131.0	131.2	131.0	131.1	130.0	131.0	131.0
1″	133.6	133.3	133.4	133.3	133.3	133.3	133.3	133.6	133.3	133.3
2″, 6″	128.7	128.8	128.8	128.8	128.9	128.9	128.9	128.8	128.6	128.6
3″, 5″	129.6	129.7	129.7	129.7	129.6	129.7	129.7	129.8	129.7	129.7
4″	132.3	132.4	132.4	132.4	132.5	132.4	132.6	132.5	132.6	132.67
C1	45.8	50.3	56.0	54.1	61.2	54.4	56.7	–	57.9	57.3
C2	–	14.7	22.6	30.8	28.8	28.3	126.3	–	–	–
C3	–	–	10.5	18.8	19.3	27.6	118.8	–	–	–
C4	–	–	–	12.5	–	20.7	–	–	–	–
C5	–	–	–	–	–	13.3	–	–	–	–
1‴	–	–	–		–	–	–	139.2	134.1	132.74
2‴	–	–	–	–	–	–	–	128.6	129.0	128.1
3‴	–	–	–	–	–	–	–	128.9	126.3	129.0
4‴	–	–	–	–	–	–	–	–	128.1	133.1

TABLE III
^{1}H NMR spectra of the compounds *I*

Compound	Arom.	2″	3	The other positions
Ia	7.58 – 7.70 m, 9 H; 7.85 m, 4 H	8.22 dd, 2 H, ^3J = 10.3, ^4J = 2.5	8.41 s, 2 H	3.77 s, 3 H (CH_3)
Ib	7.57 – 7.70 m, 9 H; 7.83 m, 4 H	8.21 dd, 2 H, ^3J = 7.7, ^4J = 2.5	8.41 s, 2 H	0.94 t, 3 H, J = 7.3 (CH_3); 4.34 q, 2 H, J = 7.3 (CH_2)
Ic	7.57 – 7.71 m, 9 H; 7.86 m, 4 H	8.21 dd, 2 H, ^3J = 8.9, ^4J = 2.5	8.41 s, 2 H	0.32 t, 3 H, J = 7.4 (CH_3); 1.39 qt, 2 H, J = 7.4 (CH_2-1); 4.28 t, 2 H, J = 7.4 (CH_2-2)
Id	7.58 – 7.71 m, 9 H; 7.86 m, 4 H	8.21 dd, 2 H, ^3J = 8.1, ^4J = 2.0	8.42 s, 2 H	0.34 t, 3 H, J = 6.5 (CH_3); 0.72 qt, 2 H, J = 6.5, 7.3(CH_2-3); 1.36 tt, 2 H, J = 7.3, 7.6 (CH_2-2); 4.31 t, 2 H, J = 7.6 (CH_2-1)
Ie	7.64 – 7.71 m, 9 H; 7.96 m, 4 H	8.29 dd, 2 H, ^3J = 8.0, ^4J = 2.0	8.48 s, 2 H	0.38 d, 6 H, J = 6.8 (CH_3); 1.51 septet of t, 1 H, J = 6.8, 7.3 (CH); 4.45 d, 2 H, J = 7.3 (CH_2)
If	7.44 – 7.71 m, 8 H; 7.84 m, 4 H; 8.05 t, 1 H, J = 7 (H-4″)	8.25 dd, 2 H, ^3J = 8.0, ^4J = 2.0	8.46 s, 2 H	0.52 t, 3 H, J = 7 (CH_3); 0.71 m, 4 H (CH_2-3,4); 1.38 tt, 2 H, J = 8.0, 7.5 (CH_2-2); 4.30 t, 2 H, J = 8.0 (CH_2-1)
Ig	7.59 – 7.67 m, 9 H; 7.77 m, 4 H	8.24 dd, 2 H, ^3J = 8.2, ^4J = 2.0	8.47 s, 2 H	4.57 d, 1 H, J = 17.5 (H-*trans*, =CH_2); 4.94 d, 2 H, J = 5.7 (CH_2–N); 5.04 d, 1 H, J = 11.3 (H-*cis*, =CH_2); 5.61 ddt, 1 H, J = 17.5, 11.3, 5.7 (–CH=)
Ih	7.14 m, 3 H; 7.33 m, 6 H; 7.45 m, 6 H; 7.64 m, 3 H	8.31 dd, 2 H, ^3J = 8.0, ^4J = 2.5	8.62 s, 2 H	
Ii	7.53 – 7.73 m, 13 H	8.28 dd, 2 H, ^3J = 8.1, ^4J = 2.2	8.51 s, 2H	5.67 s, 2 H (CH_2); 6.58 d, 2 H, J = 6.8 (H-2‴, 6‴); 7.10 m, 3 H (H-3‴, 4‴, 5‴)
Ij	7.55 – 7.73 m, 13 H	8.28 dd, 2 H, ^3J = 8.0, ^4J = 0.8	8.52 s, 2 H	5.66 s, 2 H (CH_2); 6.66 d, 2 H, J = 8.5 (H-3‴, 5‴); 7.10 d, 2 H, J = 8.5 (H-2‴, 6‴)

TABLE IV
^{13}C NMR spectra of the compounds *II*

Position	*IIa*	*IIb*	*IIc*	*IId*	*IIe*	*IIf*	*IIg*	*IIh*	*IIe* (60 °C)
2, 6	156.0	155.8	155.8	155.9	157.3 170.6	156.5 170.1	156.4	156.5	156.8
3, 5	127.3	126.2	126.1	126.2	125.7 115.6	127.4 115.2	125.3	125.3	125.1
4	156.0	154.6	154.4	154.3	155.6 165.9	155.8 165.3	155.7	155.6	155.0
1′	132.0	132.5	132.7	133.0	133.9 129.5	133.3 129.2	133.3	133.3	133.3
2′, 6′	129.5	128.9	129.0	129.1	130.2 130.5	130.3 130.5	129.9	129.8	129.7
3′, 5′	129.6	129.3	129.2	129.2	128.7 130.5	129.2 130.5	128.2	128.3	127.8
4′	131.8	131.1	131.2	131.0	130.4 130.3	130.4	130.0	130.0	129.8
1″	132.9	133.1	133.2	133.3	134.0 129.0	133.7 132.6	133.7	133.7	133.5
2″, 6″	129.2	128.8	128.8	128.8	129.1 129.2	128.8 129.4	128.9	129.0	128.6
3″, 5″	129.9	129.7	129.7	129.7	130.2 128.7	129.3	129.9	129.8	129.4
4″	133.2	132.6	132.5	132.4	135.7 132.9	135.7	132.6	132.6	134.8
C1	53.2	50.9	53.1	53.9	–	–	39.3	37.1	–
C2	–	28.9	31.9	28.4	–	–	–	–	–
C3	–	–	–	24.1	–	–	–	–	–
1‴	–	–	–	–	148.2	141.4	142.3	142.2	148.8
2‴	–	–	–	–	129.7	126.3	128.8	128.3	112.7
3‴	–	–	–	–	114.1	125.8	129.0	129.8	–
4‴	–	–	–	–	133.0	140.5	137.3	137.2	–
5‴	–	–	–	–	–	138.8	–	–	–
6‴	–	–	–	–	–	123.0	–	–	–
7‴	–	–	–	–	–	121.4	–	–	–
8‴	–	–	–	–	–	138.5	–	–	–

TABLE V
^{1}H NMR spectra of the compounds *II*

Compound	Arom.	2″	3	The other positions
IIa	7.27 d, 8 H, J = 7.2 (H-2′); 7.57 dd, 8 H, J = 7.5 (H-3′); 7.73 m, 10 H	8.32 dd, 4 H, ^3J = 7.2, ^4J = 1.6	8.27 s, 4 H	4.80 s, 4 H (CH_2)
IIb	7.54 – 7.67 m, 26 H	8.16 d, 4 H, J = 7.8	8.26 s, 4 H	1.71 bs, 2 H (CH_2-2); 3.77 bs, 4 H (CH_2-1)
IIc	7.62 – 7.72 m, 26 H	8.24 d, 4 H, J = 6.8	8.40 s, 4 H	0.77 bs, 4 H (CH_2-2); 3.82 bs, 4 H (CH_2-1)
IId	7.55 – 7.76 m, 26 H	8.20 d, 4 H, J = 8.7	8.39 s, 4 H	0.09 bs, 4 H (CH_2-3); 1.05 bs, 4 H (CH_2-2); 4.05 t, 4 H, J = 7.1 (CH_2-1)
IIe	7.41 m, 11 H; 7.65 m, 4 H; 7.83 m, 9 H	8.32 dd, 2 H, ^3J = 8.0, ^4J = 2.0; 8.48 d, 2 H, J = 8.0	8.57 s, 2 H; 9.17 s, 2 H	6.23 d, 2 H, J = 8.7 (H-2‴); 6.97 d, 2 H, J = 8.7 (H-3‴)
IIf	7.33 – 7.83 m, 30 H; 8.57 m, 6 H	8.31 dd, 2 H, ^3J = 8.0, ^4J = 2.0	8.59 s, 2 H; 9.09 s, 2 H	
IIg	7.30 – 7.44 m, 24 H; 7.66 m, 6 H	8.32 d, 4 H, J = 8.3	8.64 s, 4 H	3.63 s, 2 H (CH_2); 6.57 d, 4 H, J = 8.5 (H-3‴)
IIh	7.42 m, 20 H; 7.67 m, 6 H	8.33 dd, 4 H, ^3J = 8.3, ^4J = 3.0	8.63 s, 4 H	2.43 s, 4 H (CH_2); 6.30 d, 4 H, J = 8.0 (H-3‴); 7.23 d, 4 H, J = 8.0 (H-2‴)
IIe (60 °C)	7.31 s, 6 H; 7.42 – 7.68 m, 20 H	8.24 dd, 4 H, ^3J = 7.9, ^4J = 2.0	8.39 s, 4 H	7.28 s, 4 H (H-2‴, 3‴)

TABLE VI
^{13}C NMR spectra of the compounds *III*

Position	*IIIa*	*IIIb*	*IIIc*	*IIId*	*IIIe*	*IIIf*	*IIIg*	*IIIh*
2, 6	155.4	154.7	154.4	154.2	154.8	155.0	154.9	154.9
3, 5	129.0	128.3	128.3	128.3	129.0	129.0	127.3	127.3
4	159.1	157.6	157.3	157.1	159.7	159.4	159.1	159.1
CH_3-2	21.1	20.8	20.6	20.4	21.7	21.8	21.7	21.6
CH_3-4	21.15	21.0	21.0	20.9	21.5	21.6	21.4	21.4
CH_2-1	49.2	48.6	51.2	51.8	–	–	40.0	36.3
CH_2-2	–	25.6	24.7	27.4	–	–	–	–
CH_2-3	–	–	–	25.5	–	–	–	–
1′	–	–	–	–	140.0	140.8	143.5	144.3
2′	–	–	–	–	127.4	127.0	126.2	125.7
3′	–	–	–	–	–	127.5	131.2	131.0
4′	–	–	–	–	–	138.6	136.8	136.5

TABLE VII
^{1}H NMR spectra of the compounds *III*

Compound	3, 5	CH_3-2	CH_3-4	The other positions
IIIa	7.82 s, 4 H	2.77 s, 12 H	2.52 s, 6 H	5.04 s, 4 H (2 × CH_2-1)
IIIb	7.72 s, 4 H	2.83 s, 12 H	2.47 s, 6 H	2.33 m, 2 H (CH_2-2); 4.67 t, 4 H, J = 8.0 (2 × CH_2-1)
IIIc	7.73 s, 4 H	2.82 s, 12 H	2.48 s, 6 H	1.96 bs, 4 H (2 × CH_2-2); 4.45 bs, 4 H (2 × CH_2-1)
IIId	7.72 s, 4 H	2.79 s, 12 H	2.47 s, 6 H	1.54 bs, 4 H (2 × CH_2-3); 1.80 bs, 4 H (2 × CH_2-2); 4.39 bs, 4 H (2 × CH_2-1)
IIIe	7.96 s, 4 H	2.38 s, 12 H	2.62 s, 6 H	7.99 s, 4 H (H-2′,3′,5′,6′)
IIIf	7.95 s, 4 H	2.38 s, 12 H	2.63 s, 6 H	7.78 d, 4 H, J = 6.4 (H-3′,5′); 8.19 d, 4 H, J = 6.4 (H-2′,6′)
IIIg	7.89 s, 4 H	2.29 s, 12 H	2.58 s, 6 H	4.27 s, 2 H (CH_2); 7.56 and 7.64 ABq, 8 H, J = 8.1 (H-2′,3′,5′,6′)
IIIh	7.89 s, 4 H	2.27 s, 12 H	2.59 s, 6 H	3.11 s, 4 H (2 × CH_2) ; 7.46 and 7.50 ABq, 8 H, J = 8.6 (H-2′,3′,5′,6′)

TABLE VIII
^{1}H NMR spectra of the compounds *V*

Position	*Va*	*Vb*	*Vc*
3, 5	8.20 s, 2 H	8.26 s, 2 H	8.42 s, 2 H
2′, 6′	7.94 dd, 2 H, ^3J = 8.0, ^4J = 2.5	7.99 dd, 2 H, ^3J = 8.0, ^4J = 2.8	8.09 dd, 2 H, ^3J = 6.5, ^4J = 3.4
3′, 4′, 5′	7.58 m, 3 H	7.63 m, 3 H	7.66 m, 3 H
CH_3 (2, 6)	2.77 s, 6 H	2.89 s, 6 H	2.79 s, 6 H
The other positions	3.97 s, 3 H (CH_3)	1.05 t, 3 H, J = 7.1 (CH_3); 1.84 qt, 2 H, J = 7.1, 8.6 (CH_2-2); 4.40 t, 2 H, J = 8.6 (CH_2-1)	5.89 s, 2 H (CH_2); 7.10 dd, 2 H, ^3J = 7.8, ^4J = 1.9 (H-2″, 6″); 7.40 m, 3 H (H-3″, 4″, 5″)

TABLE IX
^{13}C NMR spectra of the compounds *IV* and *V*

Position	*IVa*	*IVb*	*IVc*	*Va*	*Vb*	*Vc*
2	156.0	155.8	156.4	155.9	155.4	156.1
3	124.0	124.8	125.1	123.5	124.3	124.7
4	153.5	153.6	154.5	153.1	153.3	154.2
5	124.8	125.8	126.2	–	–	–
6	156.8	155.9	156.5	–	–	–
1′	133.2	133.2	133.4	133.7	133.6	133.6
2′, 6′	129.2	129.1	128.9	127.9	127.9	128.2
3′, 5′	129.3	129.1	128.5	129.7	129.7	129.8
4′	131.0	130.8	130.9	131.9	131.9	132.2
1″	133.6	133.5	133.6	–	–	–
2″, 6″	128.3	128.3	128.5	–	–	–
3″, 5″	129.7	129.7	129.7	–	–	–
4″	132.1	132.2	132.4	–	–	–
CH_3-2 (6)	21.5	21.0	21.4	21.5	20.7	21.1
C1	42.3	54.5	56.3	39.8	53.4	54.9
C2	–	22.2	–	–	21.3	–
C3	–	10.8	–	–	11.0	–
1‴(1″)	–	–	132.9	–	–	132.7
2‴(2″)	–	–	125.8	–	–	125.7
3‴(3″)	–	–	129.2	–	–	129.5
4‴(4″)	–	–	128.3	–	–	128.4

TABLE X
^{1}H NMR spectra of the compounds *VI*

Compound	3	CH_3-2, 6	CH_3-4	The other positions
VIa	7.68 s, 2 H	2.71 s, 6 H	2.46 s, 3 H	3.96 s, 3 H (CH_3)
VIb	7.71 s, 2 H	2.79 s, 6 H	2.46 s, 3 H	1.01 t, 3 H, J = 6.7 (CH_3); 1.78 qt, 2 H, J = 6.7, 8.8 (CH_2-2); 4.35 t, 2 H, J = 8.8 (CH_2-1)
VIc	7.83 s, 2 H	2.68 s, 6 H	2.54 s, 3 H	5.83 s, 2 H (CH_2); 7.01 d, 2 H, J = 7.9 (H-2′, 6′); 7.37 m, 3 H (H-3′, 4′ 5′)
VId	7.69 s, 2 H	2.82 s, 6 H	2.45 s, 3 H	1.65 d, 6 H, J = 7.2 (2 × CH_3); 5.35 septet, 1 H, J = 7.2 (CH)
VIe	7.66 s, 2 H	2.70 s, 6 H	2.45 s, 3 H	6.87 bs, 2 H (NH_2)

TABLE XI
^{13}C NMR spectra of the compounds *VI* and *VII*

Position	*VIa*	*VIb*	*VIc*	*VId*	*VIe*	*VIIa*	*VIIb*	*VIIc*
2, 6	154.9	154.2	154.9	154.7	153.8	160.3	159.8	160.5
3, 5	127.5	128.3	128.6	128.7	127.4	122.1	122.7	123.1
4	156.9	157.1	158.4	156.8	154.6	153.8	153.9	154.8
1′	–	–	–	–	–	134.1	134.0	134.0
2′, 6′	–	–	–	–	–	128.1	128.2	128.4
3′, 5′	–	–	–	–	–	129.7	129.6	129.7
4′	–	–	–	–	–	131.8	131.8	132.1
CH_2-2	–	–	–	–	–	27.1	26.3	26.8
CH_3-2(6)	21.2	20.4	20.8	20.2	19.8	12.1	13.2	12.9
CH_3-4	21.0	20.8	21.2	20.6	20.9	–	–	–
C1	39.7	53.2	54.8	57.9	–	38.7	52.1	53.8
C2	–	21.3	–	22.1	–	–	23.0	–
C3	–	10.8	–	–	–	–	10.8	–
1′ (1″)	–	–	132.7	–	–	–	–	133.8
2′ (2″)	–	–	125.6	–	–	–	–	125.6
3′ (3″)	–	–	129.5	–	–	–	–	129.4
4′ (4″)	–	–	128.3	–	–	–	–	128.3

TABLE XII
^{1}H NMR spectra of the compounds *IV*

Position	*IVa*	*IVb*	*IVc*
3	8.22 bs, 1 H	8.20 d, 1 H, J = 2.5	8.33 s, 1 H
5	8.49 bs, 1 H	8.51 d, 1 H, J = 2.5	8.60 s, 1 H
2″, 6″	8.11 dd, 2 H, ^{3}J = 9.0, ^{4}J = 2.4	8.11 dd, 2 H, ^{3}J = 9.4, ^{4}J = 2.0	8.18 dd, 2 H, ^{3}J = 8.0, ^{4}J = 2.0
Arom.	7.59 – 7.68 m, 8 H	7.59 – 7.68 m, 8 H	7.60 m, 8 H
CH_3 (2)	2.91 s, 3 H	2.99 s, 3 H	2.82 s, 3 H
The other positions	3.92 s, 3 H (CH_3)	0.68 t, 3 H, J = 7.1 (CH_3); 1.68 qt, 2 H, J = 7.1 (CH_2-2); 4.27 t, 2 H, J = 8.0 (CH_2-1)	5.73 s, 2 H (CH_2); 7.01 d, 2 H, J = 8.0 (H-2‴); 7.31 m, 3 H (H-3‴, 4‴, 5‴)

TABLE XIII
^{13}C NMR spectra of the compounds *VIII* – *X*

Position	*VIII*	*IX*	*X*
2, 6	156.5	156.5	156.16, 156.2
3, 5	127.0	127.0	123.5
4	155.5	155.5	155.1, 155.2
2′, 6′	155.7	154.5	128.4
3′, 5′	124.3	128.3	128.3
4′	154.2	158.3	130.0
1a	132.7	132.6	–
2a, 6a	129.76	129.8	–
3a, 5a	129.79	130.3	–
4a	131.7	131.7	–
1b	133.1	133.1	–
2b, 6b	129.1	129.0	–
3b, 5b	130.3	129.8	–
4b	132.9	132.9	–
1′a	133.3	–	–
2′a, 6′a	128.0	–	–
3′a, 5′a	129.9	–	–
4′a	132.3	–	–
CH_3-2′, 6′	19.1	18.8	–
CH_3-4′	–	20.9	–
CH_2(1)	49.8	49.7	–
CH_2(2)	48.5	48.3	–
1′	–	–	133.9
1″	–	–	140.8, 142.0
2″, 6″	–	–	120.8
3″, 5″	–	–	126.6
4″	–	–	137.5, 138.6
CH_3-2, 6	–	–	22.1

TABLE XIV
^{1}H NMR spectra of the compounds *VIII – X*

Position	*VIII*	*IX*	*X*
3, 5	8.53 s, 2 H	8.52 s, 2 H	8.59 s, 2 H; 8.62 s, 2 H
3′, 5′	8.05 s, 2 H	7.48 s, 2 H	
2b, 6b	8.30 d, 2 H, J = 7.3	8.28 dd, 2 H, ^3J = 7.3, ^4J = 1.6	
2′a, 6′a	7.91 d, 2 H, J = 7		
2″, 6″			7.25 d, 2 H, J = 8.5
3″, 5″			7.86 d, 2 H, J = 8.5
Ar–H	7.61 m, 7 H; 7.79 m, 5 H; 8.05 s, 6 H	7.64 m, 3 H; 7.77 m, 6 H; 8.00 m, 4 H	7.77 m, 8 H; 8.06 – 8.34 m, 6 H
CH_2 (1)	4.37 t, 2 H, J = 8.6	4.33 t, 2 H, J = 8.5	
CH_2 (2)	5.11 t, 2 H, J = 8.6	5.04 t, 2 H, J = 8.5	
CH_3-2′, 6′	1.78 s, 6 H	1.66 s, 6 H	2.46 s, 6 H[a]; 2.49 s, 6 H[a]
CH_3-4		2.34 s, 3 H	

[a] CH_3-2, 6.

TABLE XV
^{1}H NMR spectra of the compounds *VII*

Position	*VIIa*	*VIIb*	*VIIc*
3	8.15 s, 2 H	8.15 s, 2 H	8.30 s, 2 H
2′	8.07 dd, 2 H, ^3J = 7.5, ^4J = 2.1	8.07 dd, 2 H, ^3J = 7.4, ^4J = 2.4	8.15 dd, 2 H, ^3J = 7.2, ^4J = 2.5
3′, 4′, 5′	7.63 m, 3 H	7.62 m, 3 H	7.66 m, 3 H
CH_3-2	1.38 t, 6 H, J = 7.1	1.43 t, 6 H, J = 7.7	1.33 t, 6 H, J = 7.2
CH_2-2	3.17 q, 4 H, J = 7.1	3.19 q, 4 H, J = 7.7	3.09 q, 4 H, J = 7.2
The other positions	4.11 s, 3 H (CH_3)	1.07 t, 3 H, J = 6.8 (CH_3); 1.84 qt, J = 6.8, 8.3 (CH_2-2); 4.42 t, 2 H, J = 8.3 (CH_2-1)	5.93 s, 2 H (CH_2); 7.09 d, 2 H, J = 7.3 (H-2″, 6″); 7.39 m, 3 H (H-3″, 4″, 5″)

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