SYNTHESIS AND SPECTRAL PROPERTIES OF 4-SUBSTITUTED 2,6-BIS-(4-BIPHENYLYL)-3,5-DICYANO--1,4-DIHYDROPYRIDINES*

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Cyclocondensation of 3-amino-3-(4-biphenylyl)acrylonitrile (*Ie*) with benzaldehydes p-RC_6H_4.CHO, 2-furaldehyde and acetone produces 1,4-dihydropyridine derivatives *IIa*—*IIj*, *III*, and *IV*. 4-Cyanobiphenyl (*Id*) has been prepared and transformed into nitrile *Ie* by action of sodium powder and acetonitrile. Relation between structure and spectral properties of the dihydro derivatives prepared is discussed.

In the field of dihydropyridine chemistry there are only a small number of reports dealing with 2,6-diaryl-3,5-dicyano-1,4-dihydropyridines[1-6]. Within studies of physical and chemical properties of this type of compounds it was interesting to prepare derivatives with extended conjugation at 2 and 6 positions. Interesting optical properties could be expected with the synthetized 2,6-bis(4-biphenylyl)-1,4-dihydropyridines. The 2,6-bis(4-biphenylyl)-3,5-dicyano-1,4-dihydropyridines *IIa*–*IIj*, *III*, *IV* (Table I) were prepared by cyclocondensation of nitrile *Ie* with *para*-substituted benzaldehydes, 2-furaldehyde, and acetone on action of ethanolic hydrogen chloride in the yields of 11–79%. The lowest yield was observed in the reaction of compound *Ie* with 4-nitrobenzaldehyde and acetone. For the compound *IIf* we tried also the procedure using acetic acid as the reaction medium, and the yield increased from 11% to 79%. The starting 3-amino-3-(4-biphenylyl)acrylonitrile (*Ie*) was prepared by action of sodium powder on a mixture of 4-cyanobiphenyl (*Id*) and acetonitrile. This variant is simpler than the published procedure[7], the yields being comparable. 4-Cyanobiphenyl (*Id*) was prepared by dehydratation of 4-biphenylcarboxylic acid amide (*Ic*) with thionyl chloride or by the Sandmayer reaction from 4-aminonobiphenyl (*Ib*). Application of the general method using bromocyanogen[8] was unsuccessful.

The infrared spectra of the dihydro derivatives are given in Table II. The absorption maxima of stretching vibrations of C≡N and N—H groups are not much affected by nature of 4-substitutent in the dihydropyridine skeleton. With the 1,4-di-

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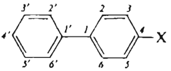
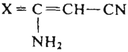
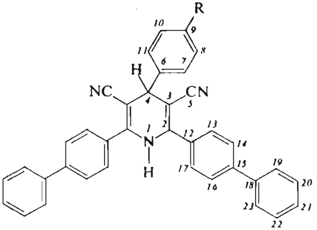
hydropyridines *IIa*–*IIj*, *III*, *IV* we observed overlap of bands of characteristic vibrations of the dihydropyridine skeleton (the region 1 500 to 1 700 cm^{-1}) with those of stretching vibrations $\nu(C{=}C)_{arom}$. The IR spectra show no bands of the associated N—H group due probably to steric requirements of bulky aromatic groups at 2 and 6 positions, which hinders formation of intermolecular hydrogen bonds.



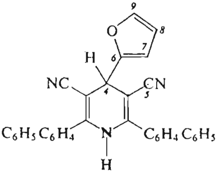
Ia, $X = NO_2$
Ib, $X = NH_2$
Ic, $X = CONH_2$
Id, $X = CN$
Ie,



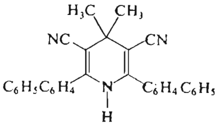
$X = \underset{\displaystyle NH_2}{C}{=}CH{-}CN$



IIa, $R = H$
IIb, $R = N(CH_3)_2$
IIc, $R = OH$
IId, $R = OCH_3$
IIe, $R = CH_3$
IIf, $R = NO_2$
IIg, $R = NHCOCH_3$
IIh, $R = I$
IIi, $R = Br$
IIj, $R = F$



III



IV

The ultraviolet spectra of the dihydro derivatives *IIa*–*IIj*, *III*, *IV* in the region 200–400 nm (Table II) exhibit one band at 206–207 nm ($\log \varepsilon$ 4·74–5·02), one or two bands at 227–288 nm ($\log \varepsilon$ 4·09–4·76), and one band at 354–359 nm ($\log \varepsilon$ 3·40–4·09). The longest-wave band corresponds probably to the first $\pi \rightarrow \pi^*$ transition of the whole conjugated system which was studied on simpler 1,4-dihydropyridines[10]. Comparison of the absorption spectrum of compound *IV* with that of 2,6-diphenyl-4,4-dimethyl-3,5-dicyano-1,4-dihydropyridine[4] reveals a bathochromic shift of the longest-wave band by 5 nm only. The ultraviolet absorption spectra of the dihydro derivatives *IIa–IIj*, *IV* show considerable similarity with spectra of some 4-substituted and 4,4-disubstituted 2,6-diphenyl-3,5-dicyano-1,4-dihydropyridines[4] which indicates small effect of the second benzene ring of biphenyl on position of absorption maxima of the 1,4-dihydropyridine chromophore. Intensity of the

TABLE I

The substituted 2,6-bis(4-biphenylyl)-3,5-dicyano-1,4-dihydropyridines *II–IV*

Compound (yield, %)	R	M.p., °C (solvent)	Formula (mol. mass)	Calculated/Found		
				% C	% H	% N
IIa	H	270–272	$C_{37}H_{25}N_3$	86·85	4·94	8·21
(67)		(CH_3COCH_3)	(511·7)	86·83	5·00	8·03
IIb	$N(CH_3)_2$	277–279	$C_{39}H_{30}N_4$	84·43	5·46	10·10
(43)		(CH_3COCH_3)	(554·7)	84·60	5·63	10·27
IIc	OH	243–245	$C_{37}H_{25}N_3O$	84·22	4·79	7·97
(40)		$(n\text{-}C_6H_{14}—C_6H_6)$	(527·7)	83·97	4·77	7·79
IId	OCH_3	290–292	$C_{38}H_{17}N_3O$	84·25	5·03	7·76
(76)		$(C_2H_5OH—CH_3CN)$	(541·7)	84·43	5·31	7·64
IIe	CH_3	308–310	$C_{38}H_{27}N_3$	86·82	5·19	8·00
(79)		$(C_2H_5OH—CH_3CN)$	(525·7)	86·73	5·46	8·03
IIf	NO_2	288–290	$C_{37}H_{24}N_4O_2$	79·83	4·36	10·07
(11)		$(C_2H_5OH—DMF)$	(556·7)	79·87	4·60	9·96
IIg	$NHCOCH_3$	190–192	$C_{39}H_{28}N_4O$	82·36	4·97	9·85
(38)		(C_2H_5OH)	(568·7)	82·14	5·24	9·80
IIh	I	306–307	$C_{37}H_{24}IN_3$[a]	69·68	3·80	6·59
(70)		$(C_6H_6—CH_3CN)$	(637·7)	69·43	4·05	6·60
IIi	Br	313–315	$C_{37}H_{24}BrN_3$[b]	75·26	4·11	7·12
(65)		$(C_2H_5OH—C_6H_6)$	(590·5)	74·90	4·47	6·92
IIj	F	261–263	$C_{37}H_{24}FN_3$[c]	83·90	4·58	7·94
(68)		$(C_6H_6—CHCl_3)$	(529·6)	84·04	4·74	7·75
III	—	260–261	$C_{35}H_{23}N_3O$	83·80	4·63	8·38
(63)		(CH_3COCH_3)	(501·6)	83·54	4·64	8·47
IV	—	234–236	$C_{33}H_{25}N_3$	85·49	5·40	9·07
(33)		$(n\text{-}C_6H_{14}—C_6H_6)$	(463·6)	85·59	5·59	9·19

[a] Calculated: 19·90% I; found: 15·65% I; [b] calculated: 13·53% Br, found: 12·87% Br; [c] calculated: 3·59% F, found: 3·98% F.

TABLE II

UV and IR spectra of 4-substituted 2,6-bis(4-biphenylyl)-3,5-dicyano-1,4-dihydropyridines *II*—*IV*

Compound	UVspectrum[a]		IR spectrum[b]						
	λ_{max}	log ε	ν(N—H)	ν(=C—H)	ν(C—H)	ν(C≡N)	ν(C=C)		γ(C—H)
IIa[c]	206	4·95	3 265 m	3 028 w	2 880 w	2 201 s	1 628 s	1 558 w	843 s
	286	4·72					1 609 m	1 480 w	
	354	3·65					1 582 w	1 449 m	
IIb	206	4·93	3 435 m	3 008 w	2 890 w	2 204 s	1 648 m	1 475 s	849 m
	286	4·71					1 614 s	1 449 w	
	360	4·09					1 521 m		
IIc[c]	207	4·90	3 400 s[d]	3 020 w	2 925 w	2 204 s	1 640 m	1 478 s	842 s[e]
	228[i]	4·45					1 612 m	1 448 w	
	286	4·71					1 515 m		
	360	3·71							
IId[f]	206	4·88	3 268 w	3 026 w	2 998 w	2 200 s	1 628 s	1 555 w	851 s
	227[i]	4·48					1 608 m	1 510 s	
	286	4·68					1 580 w	1 478 s	
	358	3·66							
IIe	207	5·02	3 430 m	3 015 m	2 910 w	2 208 s	1 648 m	1 511 w	846 s
	287	4·76					1 612 w	1 474 s	
	359	3·85					1 582 w	1 448 w	
IIf[c]	206[g]	—	3 245 m	3 085 w	2 948 w	2 205 s	1 629 s	1 531 s	848 s[h]
	259[i]	—	3 200 m				1 612 m	1 488 s	
	288	—					1 558 w	1 452 w	
IIg[c]	207	4·89	3 422 w	3 029 w	—	2 202 s	1 638 s	1 489 m	845 s[j]
	249	4·52	3 345 w				1 609 w	1 475 m	
	287	4·74	3 262 w				1 595 m	1 449 w	
	357	3·76					1 512 w		
IIh	206[g]	—	3 425 m	3 010 m	2 970 w	2 203 s	1 645 s	1 472 s	845 s
	228[i]	—			2 922 w		1 610 m	1 448 w	
	288	—					1 587 w		
	356	—					1 555 w		
IIi	207	4·74	3 428 m	3 018 m	2 978 w	2 205 s	1 649 m	1 475 s	847 s
	288	4·54			2 925 w		1 610 w	1 450 w	
	356	3·40					1 592 w		
IIj	206	4·87	3 425 m	3 010 m	2 978 w	2 203 s	1 648 m	1 475 s	845 m
	286	4·69					1 607 m	1 450 w	
	360	3·60					1 510 s		
III	207	4·90	3 435 m	3 019 m	2 930 w	2 210 s	1 649 m	1 477 s	848 m
	287	4·69					1 620 w	1 450 w	
							1 583 w		

TABLE II
(*Continued*)

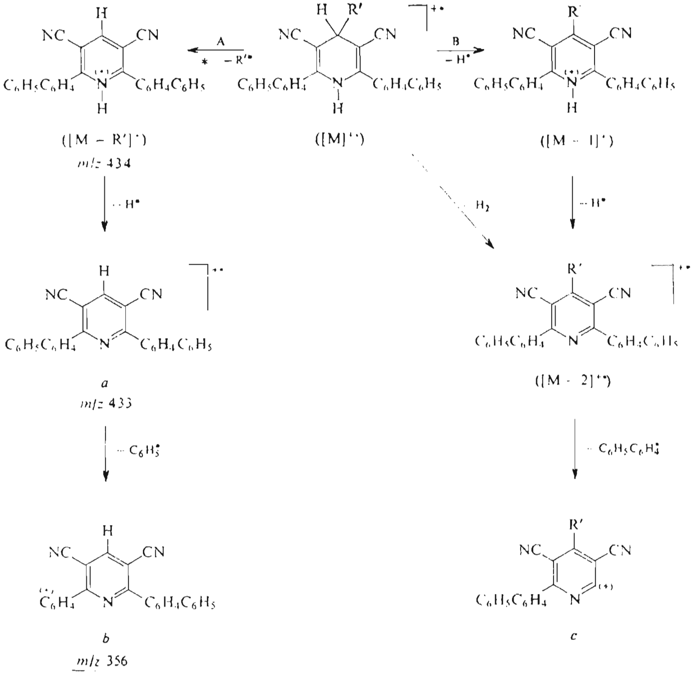
Compound	UV spectrum[a]		IR spectrum[b]						
	λ_{max}	log ε	ν(N—H)	ν(=C—H)	ν(C—H)	ν(C≡N)	ν(C=C)		γ(C—H)
IV	206	4·86	3 432 m	3 018 m	2 970 w	2 201 s	1 648 m	1 478 s	845 m
	283	4·68			2 935 w		1 620 w	1 468 s	
	359	3·66					1 588 w		

[a] Concentration 8 . 10^{-6} mol l^{-1}, ethanol; [b] measured in chloroform; [c] measured in KBr disc; [d] the associated absorption band ν(N—H) and ν(O—H), $\Delta\tilde{\nu}_{1/2}$ = 320 cm^{-1}; [e] in the IR spectrum of compound *IIc* an absorption band at 1 128 m ν(C—O) was recorded; [f] in the IR spectrum of compound *IId* the following absorption bands were identified: 1 305 m δCH_3 in OCH_3 group, 1 249 m and 1 032 m ν(=C—O—C), 1 178 s, ωCH_3 in aromatic OCH_3 group; [g] measured as saturated solution in ethanol; [h] in the IR spectrum of compound *IIf* an absorption band at 1 350 s $\nu_s(NO_2)$ was recorded; [i] inflexion; [j] in the IR spectrum of compound *IIg* the following absorption bands were recorded: 1 695 s and 1 688 s ν(C=O).

longest-wave band is, on average, ten times lower than that of the 2,6-diphenyl derivatives. This phenomenon is due obviously to more intensive absorption of the partial chromophores of the biphenyl substituents as compared with the 1,4-dihydropyridine chromophore itself as a consequence of small importance of plane conformation of the molecules *IIa*–*IIj*, *IV* for excitations of π electrons.

^{1}H NMR spectra of the compounds *IIa*–*IIj*, *III*, *IV* are given in Table III. The values of chemical shifts as well as the integral intensities correspond to structures *II*–*IV*. The values of chemical shift of methine group at 4-position of the dihydro derivatives *IIa*–*IIj* are shifted downfield by 0·25 ppm (on the average) as compared with analogous signals in ^{1}H NMR spectra of 2,6-dimethyl-3,5-dicyano-1,4-dihydropyridines[11]. The ^{13}C NMR spectra (Table IV) show theoretical number of signals. The chemical shifts of the dihydropyridine and phenyl carbon atoms were assigned by comparison with ^{13}C NMR spectra of other 1,4-dihydropyridines[12] and with application of the additivity rule[13]. The values of chemical shifts of biphenyl residues were identified on the basis of comparison with spectra of 4-substituted biphenyls[14] and compound *Ie*. Whereas the assignment of the quaternary carbon atoms was unambiguous, the off resonance technique being applied, in the region of signals of the aromatic CH carbon atoms 128·0–130·1 ppm there appears an overlap of signals of the aromatic ring at 4-position of the compounds *IIa*–*IIj* with the signals of carbon atoms of biphenyl. The signals of C(7) and C(8) carbon atoms were determined by application of the additivity rule and on the basis of the fact that spectra of *III* and *IV* do not show these signals. The C(4) carbon of the dihydro derivative *IIa* is shifted downfield by 7·0 ppm as compared with *III*, which indicates a stronger electron-acceptor effect of phenyl ring as compared with furane ring.

The mass spectra of 2,6-diaryl-1,4-dihydropyridines, dihydro derivatives *IIa*–*IIc*, *III*, *IV* can be interpreted by two fragmentation processes *A* and *B* (Scheme 1). The



(R' = p-HOC$_6$H$_5$, p-(CH$_3$)$_2$NC$_6$H$_{48}$, C$_6$H$_5$, 2-furyl)

Scheme 1

molecular ion $[M]^{+\cdot}$ which was observed in all the spectra, can lose either the R' substituent from C(4) carbon atom or a hydrogen atom to form stable pyridinium ion $[M-R']^+$ or ion $[M-1]^+$, respectively. The latter loses another hydrogen atom to give the ion $[M-2]^{+\cdot}$ which represents the most intensive ionic species in spectra of compounds *IIa*, *IIb*. Alternatively, formation of this fragmentation ion can be explained by loss of a hydrogen molecule from the molecular ion $[M]^{+\bullet}$. The ion $[M-R']^{+}$ is further fragmentated to give the ions *a* and *b*. The ions $[M-R']^{+}$, $[M-1]^{+}$, $[M-2]^{+\bullet}$, *a*, and *b* formed by these fragmentation processes are independent of the nature of 4-substituent, and, hence, the dihydro derivatives *IIa*–*IIc*, *III*, *IV* give series of typical ionic species which make this class of organic compounds identifiable. In the dihydro derivatives *IIb* and *IIc* it is possible to observe splitting off of the substituent from the phenyl nucleus: *IIb* ($[M-44]^{+}$), *IIc* ($[M-17]^{+}$). The two processes *A* and *B* can only take place with the derivative *IIa*. From compounds *IIb*, *IIc*, *III*, *IV*, the fragmentation ion *c* is not formed. The fragmentation of the 4,4-dimethyl derivative *IV* goes by the path *A*.

TABLE III

^{1}H NMR spectral characteristics of the 1,4-dihydropyridines *II*–*IV*

Compound	Chemical shifts δ, ppm (C^2HCl_3, 35°C)			
	H—C(4)	N—H	H-arom.	R
IIa	4·58 s	6·51 s	7·24–7·94 m	—
IIb	4·49 s	6·43 s	7·24–7·80 m 6·79 d (H_{ortho})	2·96 s
IIc[a]	4·59 s	8·93 s	7·32–8·02 m 6·96 d (H_{ortho})	8·50 s
IId	4·54 s	6·42 s	7·18–7·83 m 6·94 d (H_{ortho})	3·80 s
IIe	4·58 s	6·39 s	7·20–7·80 m	2·38 s
IIf[b]	5·04 s	10·10 s	7·40–7·92 m 8·40 d (H_{ortho})	—
IIg[b]	4·65 s	12·02 s 12·13 s	7·32–7·88 m	2·07 s
IIh	4·60 s	6·57 s	7·32–7·90 m 7·24 d (H_{meta})	—
IIi	4·59 s	6·62 s	7·25–7·84 m	—
IIj	4·65 s	6·62 s	7·15–7·70 m	—
III	4·68 s	6·41 s	7·20–7·68 m	6·28–6·36 m[c]
IV	—	6·15 s	7·05–7·64 m	1·66 s[d]

[a] Measured in hexadeuterioacetone; [b] measured in hexadeuteriodimethyl sulphoxide; [c] δ_H of furane skeleton; [d] $(CH_3)_2$—C.

Typical manifestation of compounds *IIa–IIc* in the mass spectra is the formation of bivalent ions $[M-2]^{2+}$. Intensity of these fragmentation ions is substantially higher than that of analogous doubly charged ions observed in spectra of aromatic hydrocarbons and some nitrogen heterocyclic systems[15]. The intensity ratio $[M-2]^{2+}/[M-2]^{+\bullet}$ is 20·8 (*IIa*), 17·1 (*IIb*), 16·7 (*IIc*). The tendency of molecules to produce the doubly charged ions rather than fragmentation was suggested as a criterion of aromaticity of organic compounds[15]. The distinct intensity of $[M-2]^{2+}$ ions in our case indicates a relatively high π electron density, which agrees with the π donor character of 1 4-dihydropyridines.

As the crystalline dihydro derivatives *II–IV* exhibit marked fluorescence after irradiation with UV light there appeared attempts to measure fluorescence spectra

TABLE IV

^{13}C NMR chemical shifts of 1,4-dihydropyridines *IIa–IIe*, *IIh–IIj*, *III*. The data in ppm with respect to tetramethylsilane; saturated solutions in C^2HCl_3

Carbon	*IIa*[a]	*IIb*	*IIc*[a]	*IId*	*IIe*	*IIh*	*IIi*	*IIj*	*III*
C(2)	145·2	146·4	148·6	146·8	147·0	147·5	147·7	147·3	148·1
C(3)	85·7	85·8	86·0	85·8	85·6	84·7	84·8	85·3	82·5
C(4)	45·0	43·0	44·1	43·4	43·7	43·7	43·6	43·4	38·0
C(5)	120·0	119·3	120·0	119·2	119·0	118·7	118·9	118·8	118·6
C(6)	149·3	131·0	136·3	135·3	138·3	142·3	141·9	138·6	153·9
C(7) C(11)	130·3	128·5	129·9	129·0	127·8	129·7	129·5	129·6	110·9
C(8) C(10)	130·1	113·1	116·8	115·0	130·2	138·6	132·7	116·4	107·9
C(9)	128·1	150·5	158·4	159·8	135·5	103·4	123·0	162·8	143·6
C(12)	132·8	131·5	132·8	131·5	131·5	131·1	131·1	131·2	131·3
C(13) C(17)	130·1	129·0	130·1	129·2	129·2	129·2	129·2	129·2	129·2
C(14) C(16)	128·9	128·1	128·9	128·1	128·2	128·2	128·2	128·2	128·3
C(15)	140·9	139·7	140·7	139·8	139·8	139·7	139·9	139·7	139·8
C(18)	144·5	144·2	144·2	144·5	144·5	144·6	144·6	144·6	144·6
C(19) C(23)	128·1	127·2	127·9	127·3	127·3	127·3	127·3	127·3	127·3
C(20) C(22)	129·1	128·1	129·2	128·3	128·5	128·5	128·4	128·5	128·3
C(21)	128·1	127·9	127·9	128·1	128·1	128·0	128·2	128·1	128·0
Others	—	40·5	—	55·4	21·2	—	—	—	—

[a] Measured in hexadeuterioacetone.

of these compounds in solution and to evaluate effects of the 4-substituent of the dihydropyridine skeleton on quantum yield of the fluorescence. Fluorescence spectra of compounds *II*–*IV* were measured[16] in various solvents (methanol, ethanol, acetonitrile, toluene) at the excitation wavelength $\lambda_{max} = 355$ nm. The found quantum yield of fluorescence, compared with the standard quinine sulphate solution in 0·2M-H_2SO_4, was below 1% in all the derivatives. Only the dihydroderivative *IIb* exhibited a more distinct emission in toluene with $\lambda_{max} = 520$ nm (quantum yield $\varphi = 0{\cdot}02$).

EXPERIMENTAL

The temperature data are not corrected. The melting temperatures were determined with a Boetius apparatus. The spectral characteristics were measured with the following apparatus: Perkin-Elmer 325 (IR), Carl Zeiss, Jena Specord UV VIS (UV), Varian XL-100 (^{1}H NMR), Tesla BS 567 (^{13}C NMR), LKB 9 000, AEI MS 902 S (mass spectra, 70 eV), and Perkin-Elmer MPF 44A (fluorescence spectra). The compound *Ia* was prepared by nitration of biphenyl with 100% nitric acid, m.p. 111–113°C (ref.[17] m.p. 114–115°C), and the compound *Ic* was prepared by reaction of 4-biphenylcarboxylic acid chloride with aqueous ammonia, m.p. 222–225°C (ref.[18] m.p. 222–223°C).

4-Aminobiphenyl (*Ib*)

Solution of 79·7 g 4-nitrobiphenyl in 200 ml ethanol was stirred and treated with 49 ml hydrazine hydrate (80%). The solution was heated at 30–40°C, and ethanolic suspension of Raney nickel (prepared from 5 g of the alloy) was added thereto in small portions. When further addition of the catalyst caused no gas evolution, the mixture was boiled 1 h. The catalyst was filtered off, the solution was decolourized by addition of charcoal, and the solvent was distilled off under reduced pressure. The raw product was recrystallized from benzene-n-heptane mixture; yield 58·5 g *Ib* (86%), mp. 52–53°C (ref. 19; m.p. 53°C). The compound *Ib* was diazotized and submitted to the Sandmayer reaction[20] to give 4-cyanobiphenyl (*Id*), m.p. 82–84°C (ref.[20] m.p. 85–86°C).

4-Cyanobiphenyl (*Id*)

Mixture of 140 g 4-biphenylcarboxyl amide (*Ic*) and 167 g thionyl chloride was refluxed 6 h (until the end of gas evolution). The excess thionyl chloride was distilled off, and the residue was distilled under reduced pressure, the fraction 178–182°C/1·6 kPa being taken. The distillate was recrystallized from n-heptane to give 75 g *Id* (59%),m.p. 85–86°C. IR spectrum (KBr): 2 225 cm^{-1} ν(C≡N). ^{1}H NMR spectrum (C^2HCl_3), δ, ppm: 7·30–7·82 m.

3-(4-Biphenylyl)-3-aminoacrylonitrile (*Ie*)

Solution of 60 g 4-cyanobiphenyl (*Id*) and 36 ml acetonitrile in 200 ml benzene was added drop by drop to suspension of 15·4 g sodium powder in 150 ml toluene at 40–50°C with stirring during 2 h. Then the mixture was boiled 5 h and left to stand overnight. Using outer cooling with ice, the mixture was decomposed by addition of 300 ml water, the separated solid was coollected by suction, washed with ethanol, and recrystallized from 1,2-dimethoxyethane. Yield 15·5 g (21%), m.p. 188–190°C (ref.[7] m.p. 187–189°C). UV spectrum (ethanol): λ_{max} 299 nm (log ε 4·18).

IR spectrum (KBr disc), $\tilde{\nu}_{max}$, cm^{-1}: 3 425, 3 330, 3 248 (NH_2), 2 200 (C≡N). ^{1}H NMR spectrum (hexadeuteriodimethyl sulphoxide), δ, ppm: 4·27 s (=CH), 6·83 s (NH_2), 7·26—7·79 m ($C_6H_5.C_6H_4$). ^{13}C NMR spectrum (hexadeuteriodimethyl sulphoxide), δ, ppm: 59·3 (=CH), 120·6 (C≡N), 126·9 (C(2')), 127·1 (C(4')), 128·2 (C(2), C(6), C(3'), C(5')), 129·2 (C(3), C(5)), 134·6 (C(4)), 139·2 (C(1)), 142·2 (C(1')), 161·5 ($-CNH_2$).

4-Substituted 2,6-Bis(4-biphenylyl)-3,5-dicyano-1,4-dihydropyridines *IIa—IIj, III, IV*

Suspension of 0·005 mol compound *Ie* and 0·0025 mol corresponding aldehyde in 25 ml methanol was treated with the methanol saturated with hydrogen chloride until acid reaction (pH 3—4). The mixture was stirred 4 h, boiled 15 min, and left to stand at room temperature 12 h. The precipitated solid was collected by suction, washed with 20 ml 5% NaOH and with water until neutral. The dihydropyridines *IIa—IIj, III, IV* were recrystallized from suitable solvent until constant melting temperature. Table I summarizes the derivatives prepared. For the fluorescence measurements, the compounds *IIa—IIj, III* were purified chromatographically (silica gel, chloroform).

4-Nitrophenyl-2,6-bis(4-biphenylyl)-3,5-dicyano-1,4-dihydropyridine (*IIf*)

Solution of 0·38 g 4-nitrobenzaldehyde and 1·1 g nitrile *Ie* in 15 ml acetic acid was boiled 4 h. After 10 min the mixture changed its colour, and a precipitate began to separate. Thereafter the mixture was left to stand 24 h. The precipitate was collected by suction and recrystallized from ethanol–dioxane mixture to give 1·1 g compound *IIf* (79%), m.p. 289—290°C.

Mass spectra (ions and relative intensities, %)

IIa: 511 (21, $[M]^{+\cdot}$), 510 (35, $[M-1]^{+}$), 509 (100, $[M-2]^{+\cdot}$), 508 (96), 435 (28), 434 (79, $[M-R']^{+}$), 433 (10,a), 356 (5, b, c), 329 (6), 255 (10), 254 (21), 253 (11), 153 (6), 152 (16), 131 (7), 105 (9), 92 (38), 91 (58), 78 (15), 77 (29), 69 (18), 67 (10), 65 (14).

IIb: 554 (25, $[M]^{+\cdot}$), 553 (46, $[M-1]^{+}$), 552 (100, $[M-2]^{+\cdot}$), 551 (26), 508 (11), 434 (23, $[M-R']^{+}$), 433 (46, a), 432 (32), 356 (9, b), 276 (17), 275 (16), 181 (11), 152 (12), 131 (14), 121 (32), 120 (33), 105 (19), 96 (11), 91 (31), 85 (32), 83 (24), 81 (26), 77 (36), 71 (27), 69 (38), 67 (30), 64 (21), 60 (24).

IIc: 527 (33, $[M]^{+\cdot}$), 526 (20, $[M-1]^{+}$), 525 (62, $[M-2]^{+\cdot}$), 524 (43), 509 (17), 434 (100, $[M-R']^{+}$), 433 (48, a), 432 (29), 374 (12), 356 (9, b), 262 (17), 181 (11), 179 (11), 152 (114), 97 (12), 95(12), 94 (38), 83 (12), 77 (12), 71 (14), 69 (17), 66 (10), 65 (14).

III: 501 (100, $[M]^{+\cdot}$), 500 (28, $[M-1]^{+}$), 499 (17, $[M-2]^{+\cdot}$), 498 (9), 474 (48), 473 (40), 472 (28), 448 (9), 446 (13), 434 (39, $[M-R']^{+}$), 433 (26, a), 432 (13), 397 (10), 359 (22), 358 (65), 356 (65, b), 263 (5), 250 (7), 236(9), 181 (6), 165 (6), 153 (6), 152 (15), 151 (10), 77 (13), 63 (5).

IV: 463 (1, $[M]^{+\cdot}$), 462 (1, $[M-1]^{+}$), 448 (100, $[M-CH_3]^{+}$), 447 (4), 446 (1), 371 (2), 370 (1), 293 (1), 268 (1), 240 (2), 232 (1), 224 (13), 215 (2), 204 (1), 181 (1), 177 (1), 153 (2), 152 (4), 151 (2), 115 (1), 77 (4).

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