STERICALLY CROWDED HETEROCYCLES. IX. NEW α,β-UNSATURATED KETONES CONTAINING IMIDAZO[1,2-*a*]QUINOLINE, IMIDAZO[2,1-*a*]-ISOQUINOLINE, BENZO[*h*]IMIDAZO[1,2-*a*]QUINOLINE AND IMIDAZO[1,2-*a*]-1,10-PHENANTHROLINE MOIETIES

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(*Z*)-1,3-Diphenyl-3-(2-phenylimidazo[1,2-*a*]heteroaryl)prop-2-en-1-ones **2–6** and isomeric [1-heteroaryl-3,5-diphenylpyrrol-2-yl]phenylmethanones **17–20** were prepared by the ferricyanide oxidation of quaternary pyridinium salts **12–16**. Axial chirality and helicity of the molecules of **4** and **6** are discussed using various energy data obtained by the quantum chemical PM3 method.

Key words: Imidazo[1,2-*a*]quinolines; Imidazo[2,1-*a*]isoquinolines; Benzo[*h*]imidazo[1,2-*a*]quinolines; Imidazo[1,2-*a*]-1,10-phenanthrolines; Ferricyanide oxidation; Pyridinium salts; Axial chirality; Helicity.

An earlier reexamination[1] of products formed[2] by ferricyanide oxidation of 1-substituted 2,4,6-triphenylpyridinium salts led to the conclusion that the compound isolated after the reaction with 1-(quinolin-2-yl)-2,4,6-triphenylpyridinium perchlorate was undoubtedly imidazo[1,2-*a*]quinoline **1**. Substitution patterns in **1** and its molecular structure quite analogous to corresponding 2,3-disubstituted imidazo[1,2-*a*]pyridines[3] make it possible to conclude that the molecule of **1** is chiral due to the restricted rotation around the C1–C3′ bond. In connection with our interest in sterically crowded heterocyclic systems, we have tried to apply our extension of the Decker oxidation[4] to the synthesis of isomeric imidazo[2,1-*a*]isoquinoline **2** and its methyl derivative **3**. To examine effects of the 1,2-annelation in **1**-like molecules, the oxidative preparation of compounds **4–6** containing 2-phenylbenzo[*h*]imidazo[1,2-*a*]quinoline and 2-phenylimidazo[1,2-*a*]-1,10-phenanthroline has been also attempted. Some chemical transformations of the products demonstrating their molecular chirality have been carried out, too. In addition, approximate rotation barriers of compounds **4** and **6** have been calculated at the semiempirical PM3 level.

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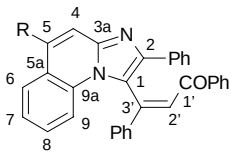
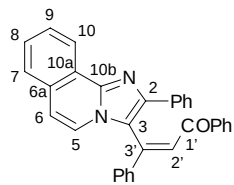
All preparative experiments started from heteroaromatic amines **7–11** which were converted to corresponding quaternary pyridinium salts **12–16** in high yields by heating with 2,4,6-triphenylpyrylium perchlorate in ethanol (Table I). Pyridinium salts **12–16** were subjected to the oxidation with potassium ferricyanide in the presence of potassium hydroxide in aqueous ethanol using the usual procedure[5]. The results are given in Table II. Except for 1-(isoquinolin-1-yl)pyridinium perchlorate **12** affording the expected ketone **2**, in all other cases the 1,3,3-trisubstituted (*Z*)-prop-2-en-1-ones **3–6** are accompanied by isomeric pyrrole derivatives **17–20** which correspond to typical products from simple 1-substituted 2,4,6-triphenylpyridinium salts[4]. It might be assumed that the four-ring fused system in **4** and **5** arises with certain steric difficulties and therefore the competing formation of isomeric compounds **17** and **18**, possessing only



1, R = H
3, R = Me



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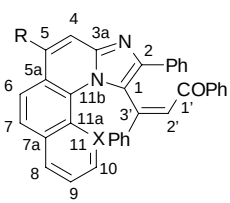
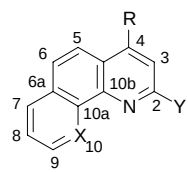


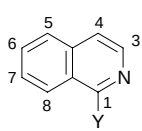
4-6

	R	X
4	H	CH
5	Me	CH
6	H	N

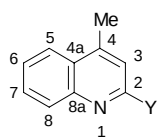


9-19

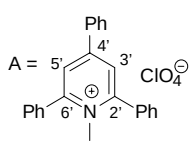
	R	X	Y
9	H	CH	NH_2
10	Me	CH	NH_2
11	H	N	NH_2
14	H	CH	A
15	Me	CH	A
16	H	N	A
17	H	CH	B
18	Me	CH	B
19	H	N	B



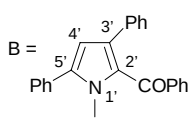
7, Y = NH_2
12, Y = A



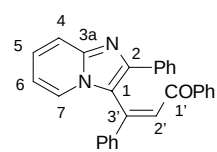
8, Y = NH_2
13, Y = A
20, Y = B



A = $ClO_4^{\ominus}$



B =



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the less fused three-ring subsystem, would be preferred. Contrary to the conclusion, the aza analog of **4** and **5**, ketone **6**, was found to be only the minor product besides the predominant isomeric pyrrole derivative **19** in the oxidation of 1-(1,10-phenanthrolin-2-yl) substituted pyridinium perchlorate **16**. Because the conversion is only negligibly influenced by temperature and inert atmosphere (Table II) and a detailed mechanism has not yet been known[4], only different coordination effects of the 1,10-phenanthroline moieties in both the competing pathways leading to products **6** and **19** might be expected.

Molecular structure of all investigated compounds has been verified using elemental analyses (Tables I and III) as well as ^{1}H and ^{13}C NMR spectra. Thus, pyridinium perchlorates **12–16** exhibit proton chemical shifts typical of such type of quaternary salts[3]. The signals at δ 8.14 to 8.19 assigned to the *ortho* protons at the 4′-phenyl groups can be found in most cases in addition to characteristic singlets of the 3′,5′-protons. Chemical shifts were almost entirely assigned not only to the position 1 or 2 in the 1′-heteroaryl groups but also to all carbons of the pyridinium ring in fragment A.

The pyrrole fragment B in compounds **17–20** can be readily recognized in the ^{1}H NMR spectra by the occurrence of the characteristic singlets at δ 6.6 to 6.7 of the 4′-protons and signals at δ 7.7 to 7.8 assigned most probably to the *ortho* protons in the 5′-phenyl

TABLE I
Yields and physical properties of perchlorates **12–16**

Compound	M.p., °C Yield, %	Formula M.w.	Calculated/Found			
			% C	% H	% Cl	% N
12	219–221[a]	$C_{32}H_{23}ClN_2O_4$	71.84	4.33	6.62	5.24
	84	535.0	71.55	4.44	6.35	5.18
13	261–262[b]	$C_{33}H_{35}ClN_2O_4$	72.19	4.59	6.46	5.10
	77	549.0	72.06	4.68	6.25	5.13
14	284–285[b]	$C_{36}H_{25}ClN_2O_4$	73.95	4.31	5.99	4.79
	99	584.2	73.68	4.30	6.28	4.75
15	312–314[b]	$C_{37}H_{27}ClN_2O_4$	74.23	4.55	5.85	4.68
	88	598.2	74.20	4.52	6.00	4.96
16[c]	189–191[d]	$C_{35}H_{26}ClN_3O_5$	69.59	4.34	5.87	6.96
	73	604.1	69.65	4.23	5.90	7.04

[a] From ethanol; [b] from ethanol–nitromethane; [c] monohydrate; [d] from dimethyl sulfoxide–ethanol–water.

groups in agreement with earlier findings[1]. Analogously, the 4′-carbons are seen in the ^{13}C NMR spectra at δ ≈112.7 and the presence of the carbonyl groups is proved by signals at δ 188 to 190.

The interpretation of the spectral characteristics of ketones **2–6** was found to be more difficult and only partial assignments could be accomplished empirically (see Experimental) using earlier complete interpretations[6] of ^{1}H and ^{13}C NMR spectra of a more simple **21**. More general assignments of ^{13}C signals are compared in Table IV. Some down-field shifted signals of compounds **3–6** in comparison with those of the standard **21** may be explained by more extensive π-electron currents in the more fused subfragments.

All studied ketones **2–6** are evidently axially chiral because of restricted rotation around the 3-3′ or 1-3′ bonds. For example, compound **3** can be reduced to mixtures of diastereoisomeric α,β-unsaturated alcohols[7]. In addition, a through-space repulsion between the 1- and 11-atomic centres might cause a helical shape of the fused four-ring system in **4–6** as the second chirality element. Although the phenomenon is well known in the hydrocarbon chemistry of helicenes, only limited number of corresponding aza analogues have been investigated[8]. Therefore, some PM3 calculations of molecules **4** and **6** were performed to estimate realistic geometries of the species. The torsion angle Φ (formula **22**) was used as an axial chirality criterion while the angle Ψ (formula **23**) as a measure of the helicity degree.

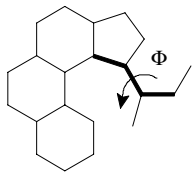
Plots of PM3-calculated heats of formation H_f of molecules **4** and **6** *versus* the torsion angle Φ are shown in Figs 1 and 2. Four more or less developed energy minima a–d are seen in both the cases. They may be attributed to four conformers **4a–4d** and **6a–6d**. The curves surprisingly involve almost discontinuous drops of energy at certain

TABLE II
Comparison of products obtained by ferricyanide oxidation of quaternary perchlorates **12**–**16** at 78 °C

Perchlorate	Reaction time min	Ketone	Yield, %	Pyrrole	Yield, %
12	5	**2**	52	–	–
13[a]	10	**3**	86	**20**	8
14	10	**4**	21	**17**	76
15	12	**5**	20	**18**	78
16	12	**6**	77	**19**	21
16	90[b]	**6**	73	**19**	23

[a] A yield of 75% of ketone **1** has been reported[2] from analogous non-methylated pyridinium salt; [b] at 0 °C.

Φ-values. The analysis of the problem has shown that these extreme energy changes are caused by jump-like inversions of helicity during relaxation of the molecular systems. Thus, the restricted rotation around the C1–C3′ bonds and the helicity of the fused π-electron systems operate together affecting final shapes of the molecules **4** and **6**. As a matter of fact, although the isomeric species **4a–4d** and **6a–6d** differ negligibly in their heats of formation H_f (Table V), all exhibit well-marked helicities (Ψ = 8.0–18.8°).



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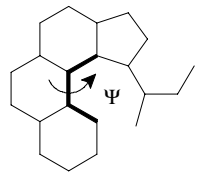

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Considering the recent findings[3,9], it may be expected that any chirality change is mainly associated with the C1–C3′ rotation barrier. The PM3 model of ketone **4** involves two higher barriers **b** → **c** and **d** → **a** (22 and 26 kcal/mol) conserving probably the axial chirality and two additional lower barriers **a** → **b** and **c** → **d** (7 and 9 kcal/mol) conjoint mainly to the changes of helicity (Fig. 1). On the other hand, the barriers **b** → **c** and **c** → **d** are little developed in the PM3 model of ketone **6** and only the rotation barriers **a** → **b** and **d** → **a** (24 and 27 kcal/mol) can be clearly interpreted (Fig. 2). The

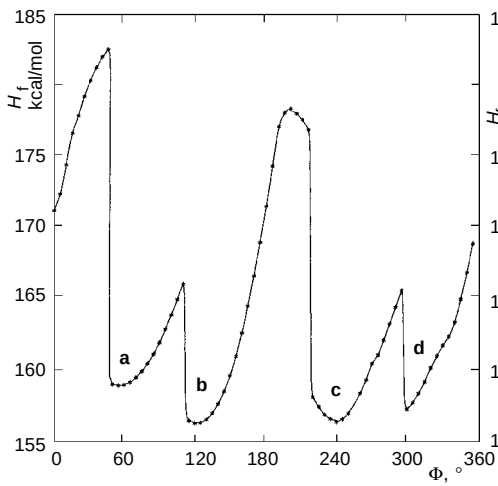

FIG. 1
Dependence of the PM3-calculated heats of formation for **4** on the torsion angle Φ (see formula **22**)

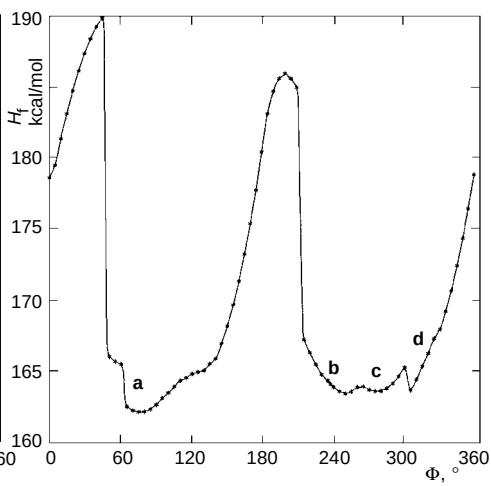

FIG. 2
Dependence of the PM3-calculated heats of formation for **6** on the torsion angle Φ (see formula **22**)

differences may be attributed to smaller steric requirements of the free electron pair at N11 in comparison with the C11–H bond.

EXPERIMENTAL

The temperature data are uncorrected. Melting points were determined on a Boetius block. NMR spectra (δ, ppm; *J*, Hz; $CDCl_3$ solutions) were taken on a GEMINI 300 HC instrument at 297 K. The working frequency was 300 MHz for ^1H and 75 MHz for ^{13}C. HPLC analyses were performed using an Ecom LCP 4000 chromatograph with LCD 2082 UV/VIS detector. Commercional Silufol and Alufol plates (Kavalier Sazava, Czech Republic) were used for TLC.

TABLE III
Characteristics of ferricyanide oxidation products **2**–**6** and **17**–**20**

Compound	M.p., °C solvent	Formula M.w.	Calculated/Found		
			% C	% H	% N
2	153–154	$C_{32}H_{22}N_2O$	85.31	4.92	6.22
	ether	450.5	85.42	4.88	6.02
3[a]	107–110[b]	$C_{35}H_{30}N_2O_2$	82.33	5.92	5.49
	ethanol–heptane	510.2	82.10	6.00	5.47
4	242–246[b]	$C_{36}H_{24}N_2O$	86.38	4.83	5.60
	ethanol–heptane	500.6	86.41	4.94	5.60
5	250–253[b]	$C_{37}H_{26}N_2O$	86.36	5.09	5.44
	ethanol–heptane	514.6	86.65	5.22	5.42
6[c]	133–136	$C_{35}H_{25}N_3O_2$	80.91	4.85	8.09
	ethanol–heptane	519.6	80.66	4.85	7.88
17	203–205	$C_{36}H_{24}N_2O$	86.38	4.83	5.60
	heptane–toluene	500.6	86.63	4.87	5.55
18	213–215	$C_{37}H_{26}N_2O$	86.36	5.09	5.44
	ethanol–toluene	514.6	86.53	5.32	5.57
19	191–193	$C_{35}H_{23}N_3O$	83.81	4.62	8.38
	heptane–toluene	501.6	83.60	4.78	8.31
20	174–175	$C_{33}H_{24}N_2O$	85.32	5.21	6.03
	heptane–toluene	464.6	85.13	5.26	5.90

[a] Monoethanolate; [b] decomposition; [c] monohydrate.

TABLE IV
Comparison of selected chemical shifts in the ^{13}C NMR spectra of ketones **3**–**6** and **21**

Assignment	**3**	**4**	**5**	**6**	**21**[a]
C4	117.30	117.36	116.97	119.25	117.27
C5a	125.35	125.06	125.05	125.39	–
C2′	127.95	127.95	127.81	[b]	127.97
m-Ph1′	130.06	129.67	129.62	129.61	129.05
p-Ph3′	130.22	129.80	129.66	[b]	130.23
p-Ph1′	132.76	133.05	132.97	132.23	132.14
i-Ph1′,3′	138.37	138.31	138.39	138.71	137.48
i-Ph1′,3′	138.60	138.38	138.48	139.03	137.73
C3′	144.22	145.26	145.41	146.60	141.49
C1	144.32	148.00	147.74	146.87	145.50
C3a	145.38	148.16	147.89	148.19	144.69
C1′	193.36	190.91	190.91	191.41	190.89

[a] Taken from ref.[3]; [b] the signal is overlapped.

TABLE V
PM3-calculated conformers of ketones **4** and **6**

Compound	ΔH_f, kcal/mol	Dihedral angles[a]	
		Φ, °	Ψ, °
4a	158.9	55.8	+18.8
4b	156.3	121.8	–18.6
4c	156.4	237.5	+18.5
4d	156.9	289.3	–19.8
6a	162.1	76.7	+8.8
6b	163.2	247.5	+9.0
6c	163.2	280.0	–8.0
6d	163.2	305.0	–10.0

[a] See formulae **22** and **23**.

(*Z*)-1,3-Diphenyl-3-(2-phenylimidazo[2,1-*a*]isoquinolin-3-yl)prop-2-en-1-one (**2**)

A solution of potassium ferricyanide (1.6 g) and potassium hydroxide (0.4 g) in water (8 ml) was portionwise added to a boiling solution of pyridinium salt **12** (0.8 g, 1.5 mmol) in ethanol (80 ml) during 1 min. After 5 min refluxing, the reaction mixture was poured into cold water (100 ml) and extracted with chloroform (4 × 16 ml). Collected organic extracts were washed with water (2 × 50 ml), dried over magnesium sulfate and evaporated *in vacuo*. The residue was subjected a column chromatography (80 g of silica gel, $CHCl_3$) affording a yellow oil which crystallized on treatment with ether. The yield was 0.35 g (52%) (see Table III). ^{1}H NMR spectrum: 6.97 d, 1 H, *J* = 9.0 (H-6); 7.14–7.77 m, 20 H (H-2′, H-7, H-8, H-9, H-10 and Ph); 8.72 d, 1 H, *J* = 9.0 (H-5). ^{13}C NMR spectrum: 112.63 CH, 119.82 C, 122.06 CH, 122.62 CH, 122.91 C, 126.67 CH, 127.12 CH, 127.17 CH, 127.53 CH, 128.07 CH, 128.08 CH, 128.14 CH, 128.18 CH, 128.39 CH, 128.46 CH, 129.04 CH, 129.31 C, 130.33 CH, 132.87 CH, 132.87 CH, 133.66 C, 137.34 C, 137.45 C, 140.49 C, 141.97 C, 189.64 C (C-3).

(*Z*)-3-(5-Methyl-2-phenylimidazo[1,2-*a*]quinolin-1-yl)-1,3-diphenylprop-2-en-1-one (**3**)
and 1-(4-Methylquinolin-2-yl)-3,5-diphenyl-1*H*-pyrrol-2-yl)phenylmethanone (**20**)

A solution of potassium ferricyanide (1.8 g, 5.37 mmol) and potassium hydroxide (4.4 g, 78.7 mmol) in water (10 ml) was added to a stirred and refluxed suspension of perchlorate **13** in ethanol (50 ml). After 10 min the reaction mixture was poured onto crushed ice (200 g), extracted with 3 × 25 ml of dichloromethane and the collected organic extracts were dried with sodium sulfate and evaporated. Crystallization of the residue from ethanol afforded the major portion of ketone **3**. ^{1}H NMR spectrum: 2.61 s, 3 H (Me-5); 7.08 dd, 2 H, *J* = 8.0 and 7.5 (Ph); 7.14–7.25 m, 3 H (H-2′ and Ph); 7.29 ddd, 1 H, *J* = 8.0, 7.5 and 1.5 (H-8); 7.32–7.48 m, 8 H (Ph); 7.54–7.65 m, 5 H (H-4, H-7 and Ph); 7.86 ddd, 1 H, *J* ≈ 8.0, ≈ 4.0 and ≈ 1.0 (H-6); 8.18 ddd, 1 H, *J* ≈ 8.0, ≈ 4.0 and ≈ 1.0 (H-9). ^{13}C NMR spectrum: 20.02 CH_3 (C-5), 117.30 CH (C-4), 117.72 CH, 120.51 C (C-2), 124.82 CH, 125.35 C, 126.04 CH, 127.95 CH (C-2′), 127.98 2 × CH (Ph), 128.42 2 × CH (Ph), 128.48 2 × CH (Ph), 128.58 2 × CH (Ph), 128.63 CH (*p*-Ph2), 128.74 2 × CH (Ph), 130.06 2 × CH (*m*-Ph1′), 130.22 CH (*p*-Ph3′), 130.96 CH, 132.76 CH (*p*-Ph1′), 134.27 2 × C (*i*-Ph2 or C-9a), 138.37 C (*i*-Ph3′ or *i*-Ph1′), 144.22 C (C-3′), 144.32 C (C-1), 145.38 C (C-3a), 192.36 C (C-1′). The mother liquor was subjected to a column chromatography on silica gel (10 g). The dichloromethane fractions contained pyrrole derivative **20**. ^{1}H NMR spectrum: 2.58 s, 3 H (Me-4); 6.64 s, 1 H (H-4′); 7.03–7.15 m, 6 H (Ph); 7.16–7.29 m, 8 H (H-3 and Ph); 7.54 dd, 1 H, *J* = 8.0 and 7.0 (H-7); 7.61–7.71 m, 3 H (Ph, H-6); 7.88 d, 1 H, *J* = 8.0 (H-5); 7.94 d, 1 H, *J* = 8.0 (H-8). ^{13}C NMR spectrum: 19.40 CH_3 (C-4), 112.80 CH (C-4′), 122.00 CH (C-3), 124.36 CH, 127.25 CH, 127.36 CH, 127.96 (C-4a), 128.21 2 × CH, 128.35 CH, 128.52 2 × CH, 128.89 2 × CH, 129.58 2 × CH, 130.03 2 × CH, 130.31 CH, 130.51 2 × CH, 131.08 C, 132.44 C, 132.51 CH (*p*-Ph2), 133.79 C, 135.79 C (*i*-Ph), 139.17 C (*i*-Ph), 139.29 C (*i*-Ph), 146.98 C (C-4), 147.44 C (C-8a), 151.47 C (C-2), 188.89 C (CO). The elution with the dichloromethane–diethyl ether (9 : 1) solvent gave the second portion of the isomeric ketone **3**. Total yields and other characteristics of compounds **3** and **20** are given in Table III.

(*Z*)-1,3-Diphenyl-3-(2-phenylbenzo[*h*]imidazo[1,2-*a*]quinolin-1-yl)prop-2-en-1-one (**4**)
and [1-(Benzo[*h*]quinolin-2-yl)-3,5-diphenyl-1*H*-pyrrol-2-yl]phenylmethanone (**17**)

The reaction of perchlorate **14** (1 g, 1.71 mmol) in ethanol (45 ml) with potassium ferricyanide (1.69 g, 5.13 mmol) and potassium hydroxide (0.44 g, 7.96 mmol) in water (9 ml) was carried out in the same way as above mentioned but the products were extracted with 3 × 50 ml chloroform. Crystallization of the crude mixture from ethanol and heptane–toluene (1 : 1) afforded the major amount of

pyrrole derivative **17**. ^{1}H NMR spectrum: 6.74 s, 1 H (H-4′); 7.10–7.33 m, 12 H (H-3 and Ph); 7.42–7.47 m, 2 H (Ph); 7.49 ddd, 1 H, *J* = 8.0, 8.0 and 1.0 (H-9); 7.59 d, 1 H, *J* = 9.0 (H-6); 7.63 ddd, 1 H, *J* = 7.5, 8.0 and 1.0 (H-8); 7.77 d, 1 H, *J* = 9.0 (H-5); 7.79 d, 2 H, *J* ≈ 8.5 (Ph); 7.85 d, 1 H, *J* = 8.0 (H-7); 7.98 d, 1 H, *J* = 8.5 (H-4); 8.67 d, 1 H, *J* = 8.0 (H-10). ^{13}C NMR spectrum: 112.72 CH (C-4′), 120.78 CH (C-3), 125.22 CH, 125.44 CH, 125.50 C (C-4a), 127.31 CH, 127.58 CH, 128.16 CH, 128.33 CH, 128.43 2 × CH, 128.58 CH, 128.70 2 × CH, 128.94 3 × CH, 129.66 2 × CH, 129.78 2 × CH, 130.29 2 × CH, 130.99 C, 131.63 C, 131.97 C, 132.71 C, 132.77 CH (*p*-Ph2), 134.38 C, 135.43 C, 137.84 C, 137.91 CH (C-4), 139.21 C, 145.91 C (C-10b), 149.83 C (C-2), 190.18 C (CO). The mixture obtained from collected mother liquors was chromatographed on a silica gel column (15 g, 80/25 μm, 8% H_2O, chloroform–diethyl ether 9 : 1). In addition to a smaller portion of pyrrole **17**, the following coloured fractions contained a red light-sensitive substance identified as ketone **4**. ^{1}H NMR spectrum: 6.56 d, 2 H, *J* = 7.5 (Ph); 6.83 dd, 2 H, *J* = 8.0 and 7.5 (Ph); 6.90–7.01 m, 3 H (H-2′ and Ph); 7.07 dd, 2 H, *J* = 7.5 and 7.5 (Ph); 7.27 dd, 2 H, *J* = 7.5 and 7.5 (Ph); 7.36 ddd, 1 H, *J* = 7.5, 7.5 and 1.5 (H-9); 7.40–7.57 m, 8 H (H-5, H-8. H-10 and Ph); 7.60 d, 1 H, *J* = 9.0 (H-4); 7.67 d, 1 H, *J* = 8.0 (H-7); 7.79 d, 1 H, *J* = 9.0 (H-6); 9.02 d, 1 H, *J* = 8.5 (H-11). ^{13}C NMR spectrum: 117.36 CH (C-4), 123.02 CH, 124.90 C, 124.97 CH, 125.06 C, 125.40 CH, 126.10 (C-5), 126.21 CH, 127.44 2 × CH (*o*-Ph), 127.61 CH (*p*-Ph2), 127.95 CH (C-2′), 128.01 2 × CH (Ph), 128.56 2 × CH (Ph), 128.62 2 × CH (Ph), 128.70 4 × CH, 129.67 2 × CH (*m*-Ph1′), 129.80 CH (*p*-Ph3′), 131.13 C, 133.05 CH (*p*-Ph1′), 133.35 C, 135.46 C (*i*-Ph2), 138.31 and 138.38 (*i*-Ph1′ and *i*-Ph3′), 145.26 C (C-3′), 148.00 C (C-1), 148.16 C (C-3a), 190.91 C (C-1′). Total yields and other characteristics of compounds **4** and **17** are given in Table III.

(*Z*)-3-(5-Methyl-2-phenylbenzo[*h*]imidazo[1,2-*a*]quinolin-1-yl)-1,3-diphenylprop-2-en-1-one (**5**) and [1-(4-Methylbenzo[*h*]quinolin-2-yl)-3,5-diphenyl-1*H*-pyrrol-2-yl]phenylmethanone (**18**)

Reaction of perchlorate **15** (0.5 g, 0.84 mmol) in ethanol (25 ml) with potassium ferricyanide (0.81 g, 2.46 mmol) and potassium hydroxide (0.24 g, 4.28 mmol) in water (3 ml) was carried out by the standard procedure using 100 g of ice and extraction with 3 × 25 ml chloroform. The crude reaction mixture (0.47 g) was chromatographed on a silica gel column (10 g, 80/25 μm, 8% H_2O). Yellow chloroform fractions contained pyrrole derivative **18** which was recrystallized from ethanol–toluene (5 : 2). ^{1}H NMR spectrum: 2.55 s, 3 H (Me-4); 6.69 s, 1 H (H-4′); 7.02 s, 1 H (H-3); 7.08–7.30 m, 11 H (Ph); 7.38 dd, 2 H, *J* = 8.0 and 1.5 (Ph); 7.44 dd, 1 H, *J* = 8.5 and 7.0 (H-9); 7.60 dd, 1 H, *J* = 8.5 and 7.0 (H-8); 7.76 dd, 2 H, *J* = 8.0 and 1.5 (H-5 and H-6); 7.79 s, 2 H (Ph); 7.84 d, 1 H, *J* = 7.5 (H-7); 8.64 d, 1 H, *J* = 8.0 (H-10). ^{13}C NMR spectrum: 19.64 CH_3 (Me-4), 112.60 CH (C-4′), 121.51 CH, 121.75 CH, 125.27 C (C-4a), 125.97 CH, 127.29 CH, 127.54 CH, 128.03 CH, 128.22 CH, 128.29 CH, 128.41 2 × CH, 128.71 2 × CH, 128.77 CH, 128.87 2 × CH, 129.74 2 × CH, 129.84 2 × CH, 130.42 2 × CH, 131.15 C, 131.97 C, 132.20 C, 132.97 C, 134.25 C, 135.67 C, 138.06 C, 139.45 C, 145.78 C (C-10b), 146.56 C (C-4), 149.68 C (C-2′), 190.20 C (CO). The following red eluates (chloroform–diethyl ether 95 : 5) contained a light-sensitive substance identified as ketone **5** which was recrystallized from ethanol–heptane (4 : 1). ^{1}H NMR spectrum: 2.67 s, 3 H (Me-5); 6.52 d, 2 H, *J* = 7.5 (Ph); 6.81 dd, 2 H, *J* = 8.0 and 7.5 (Ph); 6.89–7.00 m, 3 H (H-2′ and Ph); 7.06 dd, 2 H, *J* = 7.5 and 7.5 (Ph); 7.27 dd, 2 H, *J* = 7.5 and 7.5 (Ph); 7.35 dd, 1 H, *J* = 7.5 and 7.5 (H-9); 7.40–7.60 m, 7 H (H-8, H-10 and Ph); 7.62 s, 1 H (H-4); 7.66 d, 1 H, *J* = 7.5 (H-7); 7.68 d, 1 H, *J* = 9.0 (H-6); 9.04 d, 1 H, *J* = 9.0 (H-11). ^{13}C NMR spectrum: 116.97 CH (C-4), 121.80 CH, 122.73 CH, 123.05 C, 124.43 C, 125.00 CH, 125.05 C, 125.81 CH, 126.29 CH, 127.19 2 × CH (*o*-Ph), 127.42 CH (*p*-Ph2), 127.81 CH (C-2′), 127.97 2 × CH (*o*-Ph), 128.51 2 × CH (Ph), 128.66 2 × CH (Ph), 128.69 2 × CH (Ph), 129.62 2 × CH (*m*-Ph1′), 131.03 C, 132.97 CH (*p*-Ph1′), 133.03 C, 134.68 C (C-5), 138.39 C

(*i*-Ph1′), 138.48 C (*i*-Ph3′), 145.41 C (C-3′), 147.74 C (C-1), 147.89 C (C-3a), 190.91 C (C-1′). Yields and other characteristics of compounds **5** and **18** are given in Table III.

(*Z*)-1,3-Diphenyl-3-(2-phenylimidazo[1,2-*a*]-1,10-phenanthrolin-1-yl)prop-2-en-1-one* (**6**) and [1-(1,10-Phenanthrolin-2-yl)-3,5-diphenyl-1*H*-pyrrol-2-yl]phenylmethanone (**19**)

Method A. The reaction of perchlorate **16** (0.1 g, 0.166 mmol) in ethanol (7 ml) with potassiumn ferricyanide (0.11 g, 0.334 mmol) and potassium hydroxide (50 mg, 0.85 mmol) in water (1 ml) was carried out by the standard procedure, using ice (50 g) and extraction with chloroform. The preparative separation of products was performed by TLC on a loose silica gel layer (20 g, <80 μm, deactivated with 6% aqueous NH_3) using dichloromethane–toluene–1% ethanolic ammonia (15 : 15 : 2.2) as an eluent. A more mobile yellow zone was extracted with dichloromethane–methanol (1 : 1) and afforded pyrrole derivative **19** which was crystallized from heptane–toluene (3 : 1). ^{1}H NMR spectrum: 6.62 s, 1 H (H-4′); 6.99–7.13 m, 5 H (Ph); 7.15–7.24 m, 6 H (Ph); 7.28–7.33 m, 2 H (Ph); 7.42 d, 1 H, *J* = 8.0 (H-3); 7.51 dd, 1 H, *J* = 8.0 and 4.5 (H-8); 7.69 dd, 2 H, *J* = 7.5 and 1.5 (H-5 and H-6); 7.75 s, 2 H (Ph); 8.15 d, 2 H, *J* ≈ 8.0 (H-4 and H-7); 8.98 dd, 1 H, *J* = 4.5 and 1.5 (H-9). ^{13}C NMR spectrum: 112.72 CH (C-4′), 123.54 CH (C-5), 126.54 CH, 123.64 CH (C-6), 127.15 CH, 127.65 CH, 128.06 2 × CH, 128.32 CH, 128.37 C, 128.41 2 × CH, 128.87 2 × CH, 129.58 C, 129.85 2 × CH, 130.14 2 × CH, 130.63 2 × CH, 131.40 C, 132.26 CH (*p*-PhCO2′), 132.36 C, 134.16 C, 135.95 C, 136.33 CH (C-4), 138.28 CH (C-7), 139.25 C, 139.59 C, 145.98 C (C-10a), 146.45 (C-10b), 150.80 CH (C-9), 152.07 C (C-2), 188.81 C (CO). A less mobile orange zone was repeatedly chromatographed until no traces of minor component **19** were detected in extracts. After the procedure only ketone **6** was present in the extract; it was recrystallized from ethanol–heptane (1 : 2). ^{1}H NMR spectrum: 6.85 s, 1 H (H-2′); 7.04 dd, 2 H, *J* = 8.0 and 7.5 (Ph); 7.09–7. 28 m, 9 H (Ph); 7.31 dd, 1 H, *J* = 8.0 and 4.0 (H-9); 7.56–7.65 m, 4 H (H-4, H-5 and Ph); 7.71–7.81 m, 4 H (H-6, H-7 and Ph); 8.06 dd, 1 H, *J* = 8.0 and 1.5 (H-8); 8.25 dd, 1 H, *J* = 4.0 and 1.5 (H-10). ^{13}C NMR spectrum: 119.25 CH (C-4), 122.07 CH (C-7), 122.19 CH (C-6), 124.92 CH, 125.39 C, 125.94 C, 126.37 CH (C-5), 127.46 CH, 127.73 CH, 127.79 2 × CH (Ph), 127.87 C, 128.12 2 × CH (Ph), 128.17 2 × CH (Ph), 128.52 2 × CH, 129.61 4 CH (Ph), 130.92 C, 132.23 (*p*-Ph1′), 135.18 C (*i*-Ph2), 135.57 CH (C-8), 138.71 and 139.03 (*i*-Ph1′ and *i*-Ph3′), 140.48 C, 145.54 CH (C-10), 146.60 C (C-3′), 146.87 C (C-1), 148.19 C (C-3a), 191.41 C (C-1′). Other characteristics of the products are given in Table III, yields are shown in Table II.

Method B. A solution of potassium ferricyanide (0.11 g, 0.334 mmol) and potassium hydroxide (50 mg, 0.85 mmol) in water (1.5 ml) was added to an ice-cold solution of perchlorate **16** (0.1 g, 0.166 mmol) and the mixture was stirred for 1.5 h under argon. The isolation of products **6** and **19** was accomplished in the same way as above (see Table II).

Heterocyclic Amines **7–11**

Isoquinolin-1-ylamine (**7**) was a commercial product (Aldrich), 4-methylquinolin-2-ylamine (**8**) and benzo[*h*]quinolin-2-ylamine (**9**) were prepared by the described[10,11] procedures. An analogous Tschitschibabin reaction was used for the preparation of 4-methylbenzo[*h*]quinolin-2-ylamine (**10**): A mix-

* For numbering compatibility of compounds **4–6**, needed for correlation of NMR signals, incorrect name of **6** was used. Correct IUPAC name is (*Z*)-1,3-diphenyl-3-(10-phenylimidazo[1,2-*a*]-1,10-phenanthrolin-11-yl)prop-2-en-1-one.

ture of 4-methylbenzo[*h*]quinoline[12] (4.15 g), sodium amide (5.5 g) and freshly distilled *N*,*N*-dimethylaniline (30 ml) was stirred in a closed apparatus at 125 °C for 24 h. The reaction mixture was then decomposed with water (100 ml), extracted with chloroform and the combined organic layers were evaporated to dryness. The residue (4.2 g) was chromatographed on a silica gel column (120 g) with a toluene–chloroform (6 : 4) mixture saturated with dry ammonia. Amine **10** (2.8 g) was recrystallized from heptane–toluene (10 : 1), m.p. 129–131 °C, and used without additional purification (ref.[13] reported m.p. 133–134 °C). ^{1}H NMR spectrum: 2.65 s, 3 H (Me-4); 4.77 bs, 2 H (NH_2-2); 6.68 s, 1 H (H-3); 7.58–7.67 m, 3 H (H-6, H-8 and H-9); 7.77 d, 1 H, *J* = 9.0 (H-5); 7.85 ddd, 1 H, *J* = 8.0, ≈ 4.0 and 1.0 (H-7); 9.15 ddd, 1 H, *J* = 8.0, ≈ 4.0 and 1.0 (H-10). 1,10-Phenanthrolin-2-ylamine (**11**) was obtained by the reaction of ammonia and phenol with the 2-chloro derivative[14].

1-(Isoquinolin-1-yl)-2,4,6-triphenylpyridinium Perchlorate (**12**)

A mixture of 2,4,6-triphenylpyrylium perchlorate[15] (1 g, 2.6 mmol) and 1-aminoisoquinoline (0.5 g, 3.5 mmol) in ethanol (40 ml) was refluxed for 8 h. The crystals precipitated after cooling were sucked off, washed with ether and crystallized from ethanol. Yield 1.1 g of perchlorate **12**, see Table I. ^{1}H NMR spectrum ($(CD_3)_2SO$): 7.15–7.30 m, 6 H (*m*,*p*-Ph2 and *m*,*p*-Ph6); 7.32–7.37 m, 4 H (*o*-Ph2′ and *o*-Ph6′); 7.64–7.79 m, 6 H (H-4, H-5, H-7 and *m*,*p*-Ph4′); 7.87–7.95 m, 3 H (H-6 and *o*-Ph4′); 8.35–8.38 m, 1 H (H-8); 8.43–8.47 m, 1 H (H-3); 8.85 s, 2 H (H-3 and H-5). ^{13}C NMR spectrum ($(CD_3)_2SO$): 123 CH, 123.90 C, 124.46 CH, 125.97 CH, 127.09 CH, 127.94 CH, 129.23 CH, 129.38 CH, 129.64 CH, 130.01 CH, 130.45 CH, 131.78 C, 132.01 CH, 132.91 CH, 133.35 C, 136.98 C, 140.02 CH, 149.18 C, 155.62 C, 157.27 C.

1-(4-Methylquinolin-2-yl)-2,4,6-triphenylpyridinium Perchlorate (**13**)

A solution of amine **8** (4.22 g, 10.36 mmol) in ethanol (10 ml) was added to a boiling solution of 2,4,6-triphenylpyrylium perchlorate[15] in ethanol (80 ml). The mixture was refluxed for 8.5 h and then cooled. The crystals of product **13** contained traces of the starting salt and therefore were purified by crystallization from ethanol and ethanol–nitromethane (10 : 1) (see Table I). ^{1}H NMR spectrum: 2.50 s, 3 H (Me-4); 7.15–7.24 m, 6 H (*m*,*p*-Ph2′ and *m*,*p*-Ph6′); 7.18 d, 1 H, *J* = 8.5 (H-8); 7.54–7.63 m, 9 H (H-7, *m*,*p*-Ph4′, *o*-Ph2′ and *o*-Ph6′); 7.65 s, 1 H (H-3); 7.70 ddd, 1 H, *J* = 7.5, 8.5 and 1.5 (H-6); 7.93 dd, 2 H, *J* = 8.0 and 2.5 (*o*-Ph4′); 8.14 s, 2 H (H-3′ and H-5′). ^{13}C NMR spectrum: 19.20 CH_3 (Me-4), 122.13 CH (C-3), 124.80 CH (C-6), 127.07 2 × CH (C-3′ and C-5′), 128.30 C (C-4a), 129.00 4 × CH (*m*-Pha2′ and *m*-Ph6′), 129.24 2 × CH (*o*-Ph4′), 130.00 CH (C-5), 130.43 2 × CH (*m*-Ph4′), 130.54 4 × CH (*o*-Ph2′ and *o*-Ph6′), 130.93 2 × CH (*p*-Ph2′ and *p*-Ph6′), 131.33 CH (C-7), 132.81 CH (*p*-Ph4′), 133.14 2 × C (*i*-Ph2′ and *i*-Ph 6′), 135.49 C (*i*-Ph4′), 145.91 C (C-8a), 149.91 C (C-4), 151.23 C (C-4′), 156.70 2 × C (C-2′ and C-6′), 158.97 C (C-2).

1-(Benzo[*h*]quinolin-2-yl)-2,4,6-triphenylpyridinium Perchlorate (**14**)

The reaction of 2,4,6-triphenylpyrylium perchlorate[15] (3 g, 7.25 mmol) in ethanol (90 ml) with amine **9** (1.55 g, 7.98 mmol) in ethanol (10 ml) was performed as mentioned above and completed after 7.5 h. Almost quantitative yield of product **14** was obtained (see Table I). ^{1}H NMR spectrum: 7.10–7.18 m, 6 H (*m*,*p*-Ph2′ and *m*,*p*-Ph6′), 7.52–7.63 m, 8 H (H-3, *o*-Ph2′, *o*-Ph6′ and *m*,*p*-Ph4′); 7.72–7.78 m, 2 H (H-8 and H-9); 7.84 d, 2 H, *J* ≈ 9.0 and ≈ 9.0 (H-4 and H-6); 7.92 dd, 1 H, *J* = 8.0 and 4.0 (H-7); 7.97 d, 3 H, *J* = 8.0 (*o*-Ph4′ and H-5); 8.19 s, 2 H (H-3′ and H-5′); 8.88 dd, 1 H, *J* = 8.0 and 4.1 (H-10). ^{13}C NMR spectrum: 122.49 CH (H-3), 124.72 CH, 125.14 CH (C-6′), 126.91 C (C-4a), 127.07 2 × CH (C-3′ and C-5′), 128.31 CH, 128.75 CH, 129.00 4 × CH (*m*-Ph2′ and *m*-Ph6′), 129.25 2 × CH (*o*-Ph4′), 129.85 CH (C-7), 130.41 2 × CH (*m*-Ph4′), 130.48 4 × CH (*o*-Ph2′ and *o*-Ph6′),

130.60 CH, 130.88 2 × CH (*p*-Ph2′ and *p*-Ph6′), 131.01 C (C-10a), 132.81 CH (*p*-Ph4′), 133.22 2 × C (*i*-Ph2′ and *i*-Ph6′), 134.56 C (C-6a), 135.43 C (*i*-Ph4′), 139.56 CH (C-4), 145.00 C (C-10b), 150.18 C (C-4′), 156.86 2 C (C-2′ and C-6′), 159.00 C (C-2).

1-(4-Methylbenzo[*h*]quinolin-2-yl)-2,4,6-triphenylpyridinium Perchlorate (**15**)

The reaction of 2,4,6-triphenylpyrylium perchlorate[15] (3.3 g, 8.07 mmol) and amine **10** (1.85 g, 8.88 mmol) in ethanol (100 ml) was performed by the standard procedure for 9 h. The precipitated salt **15** was washed with ethanol and recrystallized from ethanol–nitromethane (1 : 20) (see Table I). ^{1}H NMR spectrum: 2.50 s, 3 H (Me-4); 7.10–7.22 m, 6 H (*m*,*p*-Ph2′ and *m*,*p*-Ph6′); 7.54–7.64 m, 7 H (*o*-Ph2′, *o*-Ph6′ and *m*,*p*-Ph4′); 7.68–7.77 m, 4 H (H-3, H-6, H-8 and H-9); 7.85 d, 1 H, *J* = 9.0 (H-5); 7.91 dd, 1 H, *J* = 8.0 and 4.0 (H-7); 7.96 dd, 2 H, *J* = 7.9 and 2.2 (*o*-Ph4′); 8.17 s, 2 H (H-3′ and H-5′); 8.91 dd, 1 H, *J* = 8.0 and 4.0 (H-10). ^{13}C NMR spectrum: 19.55 CH_3 (Me-4), 121.42 CH (C-3), 122.95 CH, 125.08 CH, 126.46 C (C-4a), 127.00 2 × CH (C-3′ and C-5′), 128.23 CH, 128.59 CH, 128.94 4 × CH (*m*-Ph2′ and *m*-Ph6′), 129.22 2 × CH (*o*-Ph4′), 129.60 CH, 130.11 CH, 130.39 2 × CH (*m*-Ph4′), 130.46 4 × CH (*o*-Ph2′ and *o*-Ph6′), 131.47 C (C-10a), 132.79 CH (*p*-Ph4′), 133.29 2 × C (*i*-Ph2′ and *i*-Ph6′), 134.31 C (C-6a), 135.41 C (*i*-Ph4′), 144.57 C (C-10b), 149.27 C (C-4), 149.87 C (C-4′), 156.85 2 × C (C-2′ and C-6′), 158.80 C (C-2).

1-(1,10-Phenanthrolin-2-yl)-2,4,6-triphenylpyridinium Perchlorate (**16**)

The reaction of 2,4,6-triphenylpyrylium perchlorate[15] (1.33 g, 3.26 mmol) and amine **11** (0.7 g, 3.586 mmol) in boiling ethanol (40 ml) was carried out by the standard procedure. After 8 h the hot reaction mixture was treated with charcoal, filtered and, after addition of twenty drops of 70% $HClO_4$, cooled. The originally separated oily product solidified and was recrystallized from ethanol–nitromethane (4 : 1) (see Table I). ^{1}H NMR spectrum: 7.09–7.18 m, 6 H (*m*,*p*-Ph2′ and *m*,*p*-Ph6′); 7.56–7.67 m, 7 H (*o*-Ph2′, *o*-Ph6′ and *m*,*p*-Ph4′); 7.69 d, 1 H, *J* = 9.0 (H-5); 7.71 dd, 1 H, *J* = 8.0 and 4.5 (H-8); 7.86 d, 1 H, *J* = 9.0 (H-6); 7.92 dd, 2 H, *J* = 7.5 and 2.5 (*o*-Ph4′); 8.01 d, 1 H, *J* = 8.5 (H-3); 8.09 d, 1 H, *J* = 8.5 (H-4); 8.16 s, 2 H (H-3′ and H-5′); 8.29 dd, 1 H, *J* = 8.0 and 1.5 (H-7); 9.20 dd, 1 H, *J* = 4.5 and 1.5 (H-9). ^{13}C NMR spectrum: 124.25 CH, 124.55 CH, 126.49 CH, 127.31 2 × CH (C-3′ and C-5′), 129.00 4 CH (*m*-Ph2′ and *m*-Ph6′), 129.24 2 × CH (*o*-Ph4′), 129.41 C, 129.55 CH, 130.10 C, 130.45 2 × CH (*m*-Ph4′), 130.91 6 × CH (*o*,*p*-Ph2′ and *o*,*p*-Ph6′), 132.76 CH (*p*-Ph4′), 133.13 2 × C (*i*-Ph2′ and *i*-Ph6′), 135.68 C (*i*-Ph4), 137.03 CH (C-7), 140.19 CH (C-4), 144.74 C (C-10a), 145.85 C (C-10b), 151.47 CH (C-9), 151.54 C (C-4′), 157.05 2 × C (C-2′ and C-6′), 159.28 C (C-2).

Calculations

Various MO models of molecules of **4** and **6** were calculated by the semiempirical PM3 method[16] for given torsion angles Φ (Figs 1 and 2) using a full optimization procedure with respect to all other geometric degrees of freedom including the torsion angle Ψ (formulae **22** and **23**). The data for conformers **4a–4d** and **6a–6d** are collected in Table V.

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