REINVESTIGATION OF HETEROCYCLIC STRUCTURES: OXIDATION PRODUCTS FROM 1-SUBSTITUTED 2,4,6-TRIPHENYLPYRIDINIUM SALTS

Stanislav BÖHM[a], Richard KUBÍK[a], Jiří NOVOTNÝ[b], Jan ONDRÁČEK[b], Bohumil KRATOCHVÍL[b] and Josef KUTHAN[a]

[a] *Department of Organic Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6*
[b] *Department of Solid State Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6*

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Dedicated to Dr Miroslav Protiva on the occasion of his 70th birthday.

Ferricyanide oxidation of pyridinium salts *Ia, Ib* leads to mixture of isomeric heterocyclic ketones *IIa, IIb* and *IVa, IVb*, respectively. Crystal and molecular structures of the products *IIb* and *IVb* were determined by X-ray diffraction analysis. Formerly presumed formation of heterocyclic systems type of the *III* type has been corrected.

Oxidation of quaternary 2,4,6-triphenylpyridinium salts with potassium ferricyanide in strongly alkaline medium was found to be associated with a pyridine ring contraction into a pyrrole ring[1,2]. A different reaction course has been observed[3] with such substrates in which the 1-substituent is a 2-pyridyl-like heterocyclic residue. Thus, the quaternary salt *Ic* gave, instead of expected colorless pyrrole derivative *IIa*, another yellow compound for which the formula *IIIa* has been suggested on the basis of spectral data[3].

In fact, neither the structures similar to *III* nor those similar to *II* were able to be proved with certainty on the basis of molecular spectra only. Hence, in this paper we have attempted to furnish a definitive structure proof by X-ray diffraction analysis of suitable product crystals.

The ferricyanide oxidation of 1-(2-pyridyl)-2,4,6-triphenylpyridinium perchlorate (*Ia*) was carried out followed by a preparative column chromatography of reaction mixture. As expected, the yellow product of presumed formula *IIIa* was isolated in this way besides its minor colorless isomer exhibiting typical spectral properties of pyrrole derivative *IIa*. Analogous two products of presumed formulae *IIb* and *IIIb* but of better crystallisation properties were similarly obtained from 1-(2-pyrimidyl)-2,4,6-triphenylpyridiniumperchlorate (*Ib*).

Figures 1 and 2 show the results of X-ray diffraction analysis of the both mentioned colorless and yellow products from the quaternary salt *Ib*. It is evident that only in the first case (Fig. 1) the presumed[1] molecular structure *IIb* is present in the crystal. On the other hand, from Fig. 2 it follows that molecules of the yellow isomer contain, instead of formerly presumed[3] seven-membered heterocyclic ring (formula *IIIb*), another five-membered heterocycle connected to unsaturated ketonic side chain (formula *IVb*).

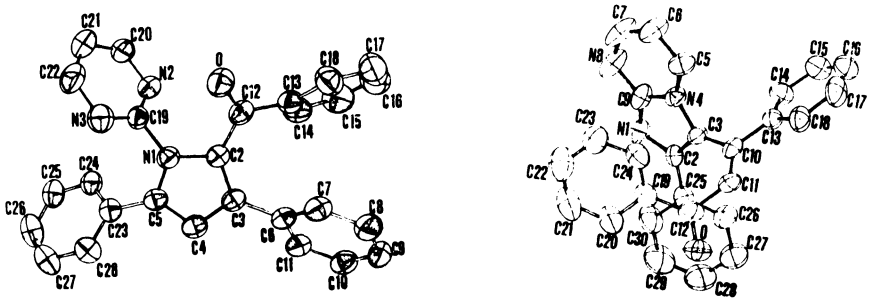


FIG. 1

Molecular structure of *IIb* (*a*) and *IVb* (*b*). Thermal ellipsoids are drawn at the 50% probability level

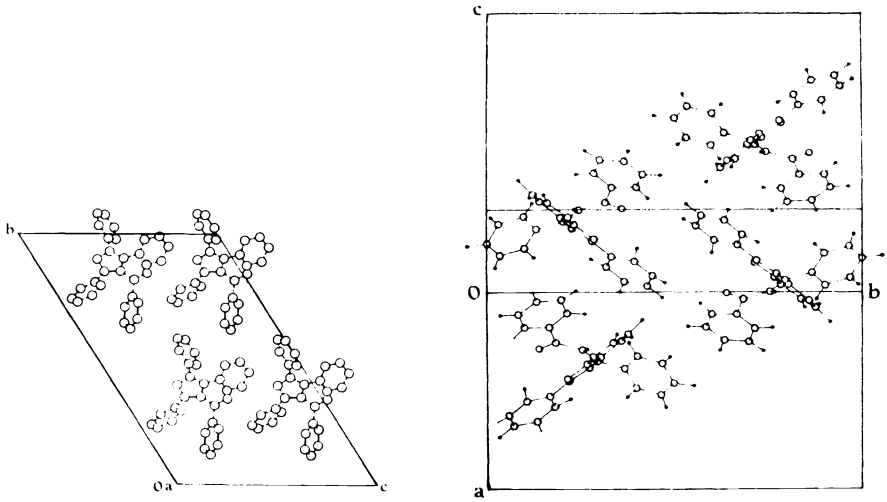
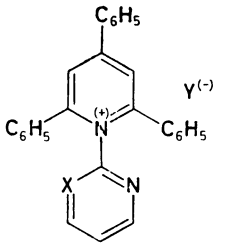


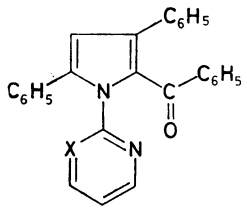
FIG. 2

Crystal packing of *IIb* (*a*) and *IVb* (*b*)

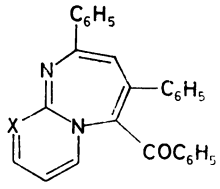
Some general conclusions may be drawn from the above mentioned structural evidence: (i) the formation of pyrrole derivatives *II* via the oxidative six-membered ring contraction seems to be of general validity; (ii) the ring-contraction leading to bicyclic arrangements like in compound *IV* is the correct reaction course contrary to the formerly presumed ring-expansion; (iii) a ring-opening evidently takes place during the chemical transformations of quaternary salts *I* in alkaline medium at least in the reaction sequence affording the products *IV*.



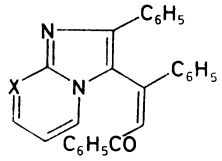
Ia, X = CH ; Y = ClO_4
Ib, X = N ; Y = ClO_4
Ic, X = CH ; Y = BF_4



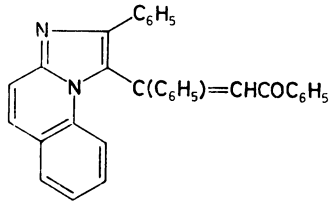
IIa, X = CH
IIb, X = N



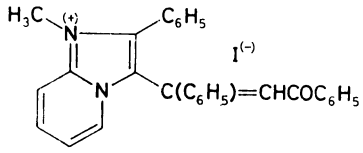
IIIa, X = CH
IIIb, X = N



IVa, X = CH
IVb, X = N



V



VI

In connection with the novel findings a new correct formula *V* can be assigned to the earlier described[3] oxidation product from 1-(2-quinolyl)-2,4,6-triphenylpyridinium tetrafluoroborate. Consequently, the formula *VI* may be valid for the corresponding product of quaternisation[3].

EXPERIMENTAL

The temperature data are uncorrected. Melting points were determined on a Boetius block, NMR spectra were taken on a BRUKER B25 400 MHz instrument and are given in δ ppm; J in Hz, $(CD_3)_2SO$ was used as a solvent unless stated otherwise. Mass spectra were recorded on a JMS-DX 303/DA 5000 apparatus.

In order to distinguish hydrogens and non-quaternary carbons in NMR spectra the labeling A, B, C and A, B, C, D was used for pyrimidine (compound *IVb*) and pyridine (compounds *Ia*, *IIa* and *IVa*) ring, respectively. Full assignment of heterocyclic hydrogens as well as phenyl rings was not possible and the abbreviations Ph1, Ph2 and Ph3 were used.

2,4,6-Triphenyl-1-(2-pyridyl)pyridinium Perchlorate (*Ia*)

Solution of 3 g 2,4,6-triphenylpyrylium perchlorate (0·00734 mol) and 1 g 2-aminopyridine (0·0106 mol) in 120 ml ethanol was refluxed 8 h. The white crystals precipitated on cooling were collected by suction. Yield 2·9 g (82%), m.p. (ethanol) 243—244°C (ref.[4] 238—240°C, ref.[5] 262°C). For $C_{28}H_{21}ClO_4N_2$ (484·9) calculated: 69·36% C, 4·37% H, 5·78% N; found: 69·57% C, 4·59% H, 5·65% N. ^{1}H NMR spectrum: 7·30—7·38 mt, 5 H (7·32 — B, 7·36 — *m*-Ph1); 7·38 to 7·45 mt, 6 H (*o*- and *p*-Ph1); 7·57—7·78 mt 5 H (7·59 — D, 7·65 — *m*- and *p*-Ph2, 7·72 — C); 8·25 mt, 2 H (*o*-Ph2); 8·30 mt, 1 H (hydrogen A in neighbourhood of nitrogen atom); 8·56 s, 2 H (two hydrogens on pyridinium ring). ^{13}C NMR spectrum: 124·99 CH (D), 125·77 2 CH (two CH atoms of pyridinium ring), 126·30 CH (B), 128·79 4 CH (*m*-Ph1), 129·33 2 CH (*o*-Ph2), 130·09 4 CH (*o*-Ph1), 130·20 2 CH (*m*-Ph2), 130·86 2 CH (*p*-Ph1), 132·69 2 C (Ph1), 133·20 CH (*p*-Ph2), 133·76 C (Ar2), 139·45 CH (C), 149·20 CH (carbon A in neighbourhood of nitrogen atom), 151·37 C (carbon on pyridinium ring), 155·93 2 C (two carbons on pyridinium ring), 157·13 C (carbon on pyridine ring).

Oxidation of the salt Ia: Solution of 10 g salt *Ia* (0·0206 mol) in 500 ml ethanol was refluxed and treated with solution of 20 g potassium ferricyanide (0·0607 mol) and 5 g potassium hydroxide (0·0890 mol) in water. After 5 min boiling, the mixture was diluted with 1 500 ml ice water and extracted with 4 × 200 ml chloroform. The collected organic extracts were dried with sodium sulfate, the solvent was evaporated and the residue was submitted to column chromatography (silica gel, chloroform–diethylether 9 : 1). Two individual substances were obtained: 0·1 g (1·2%) white crystals of 2-benzoyl-3,5-diphenyl-1-(2-pyridyl)pyrrole (*IIa*), m.p. 167—169°C (ethanol–water). ^{1}H NMR spectrum ($CDCl_3$): 6·59 s, 1 H; 7·03—7·10 mt, 5 H; 7·13—7·25 mt, 10 H (B and D); 7·61 ddd 1 H (C, J = 7·6, 7·6 and 1·9); 7·66 ddd, 1 H (A, J = 4·9, 1·9 and 0·9). ^{13}C NMR spectrum ($CDCl_3$): 111·80 CH, 112·28 CH, 123·00 CH, 126·52 CH, 127·58 2 CH, 127·63 2 CH, 127·77 2 CH, 128·17 2 CH, 128·85 2 CH, 129·32 2 CH, 129·91 2 CH, 129·99 C, 131·60 C, 131·92 CH, 133·26 C, 135·01 C, 137·48 CH (C), 138·31 C, 138·92 C, 148·86 CH (A), 151·83 C, 188·00 CO. Mass spectrum, m/z (% r.i.): (for $C_{28}H_{20}N_2O$ calculated mol. mass: 400·483) 400 (87), 372 (14), 371 (14), 323 (100), 307 (4), 306 (4), 295 (10), 267 (4), 217 (4), 191 (25), 189 (13), 165 (5), 105 (34), 89 (7), 83 (6), 78 (23), 77 (35).

The second substance obtained was 6 g (73%) yellow crystals of 2-phenyl-3-(1,3-diphenyl-3-oxopropenyl)imidazo[1,2-*a*]pyridine (*IVa*) m.p. 163—165°C (ethanol) identical with the authetical sample[3]. ^{1}H NMR spectrum ($CDCl_3$): 6·67 ddd, 1 H (B, J = 6·8, 6·8 and 1·3); 7·10—7·22 mt, 6 H (7·13 — *m*-Ph2, 7·13 — *p*-Ph1, 7·15 — C, 7·19 — *m*-Ph1); 7·28—7·40 mt, 4 H (7·30 — *p*-Ph2, 7·30 — *m*-Ph3, 7·37 — *p*-Ph3); 7·45—7·48 mt, 3 H (7·45 s, 7·46 — *o*-Ph3); 7·55—7·60 mt 4 H (7·56 — *o*-Ph2, 7·57 — A and D); 7·63—7·67 mt, 2 H (*o*-Ph1). ^{13}C NMR spectrum ($CDCl_3$): 112·24 CH (B), 117·27 CH (D), 117·40 C, 124·40 CH (A), 124·88 CH (C), 127·43 2 CH (*o*-Ph2), 127·45 2 CH (*o*-Ph3), 127·59 CH (*p*-Ph1), 127·79 2 CH (*m*-Ph2), 127·89 2 CH (*o*-Ph1), 127·97 CH,

128·00 2 CH (*m*-Ph1), 129·05 2 CH (*m*-Ph3), 130·23 CH (*p*-Ph3), 132·14 CH (*p*-Ph2), 133·33 C, 137·48 C, 137·73 C, 141·49 C, 145·51 C, 146·04 C, 190·89 CO. Mass spectrum, *m/z* (% r.i.): (for $C_{28}H_{20}N_2O$ calculated mol. mass: 400·483) 400 (24), 232 (14), 295 (100), 267 (4), 218 (11), 191 (11), 154 (4), 105 (57), 78 (74), 77 (56).

2,4,6-Triphenyl-1-(2-pyrimidyl)pyridinium Perchlorate (*Ib*)

2,4,6-Triphenylpyrylium perchlorate (8·8 g), 2-aminopyrimidine (3·1 g) and diethylene glycol (33 ml) were heated at 180°C for 1 h. The mixture was then added to boiling ethanol (400 ml) and the solution let to crystallize at room temperature. The product was isolated by suction,

TABLE I

Data collection and structure refinement parameters

Parameter	*IIb*	*IVb*
Crystal dimensions, mm	0·60 × 0·40 × 0·15	0·55 × 0·22 × 0·06
Diffractometer and radiation used	Enraf–Nonius CAD4 $\lambda(MoK_\alpha) = 0{\cdot}71073$ Å	
Scan technique	$\omega/2\theta$	
No. and θ range of reflections for lattice parameter refinement	21, 10 . 10° ≤ θ ≤ 18·93°	21, 11·85° ≤ θ ≤ 16·63°
Range of h, k and l	−7 → 7, −15 → 15, −17 → 17	−10 → 10, 0 → 23, −15 → 15
Standard reflections	12−2, 01−1	0−20, 0−23
Standard reflections monitored in interval, intensity fluctuation	120 min, 1·0%	120 min, −50·2%
Total number of reflections measured, 2θ range	6 010, $2\theta \leq 50$	7 376, $2\theta \leq 50$
Value of R_{int}	0·032	0·064
No. of observed reflections	4 795	1 729
Criterion for observed reflections	$I > 1{\cdot}96\sigma(I)$	$I > 3\sigma(I)$
Function minimized	$\sum w(\|F_o\| - \|F_c\|)^2$	
Weighting scheme	$w = 1{\cdot}3566/[\sigma^2(F_o) + 0{\cdot}0009F_o^2]$	$w = 4F_o^2/[\sigma(F_o)^2]^2$
Parameters refined	356	281
Value of R, wR and S	0·060, 0·063, 1·45	0·079, 0·082, 1·20
Ratio of max. least-squares shift to e.s.d. (Δ/σ) in the last cycle	0·019	0·03
Max. and min. heights in final $\Delta\varrho$ map	0·35, −0·35 eÅ^{-3}	0·30, −0·27 eÅ^{-3}
Source of atomic scattering factors	SHELX-76 program	SDP program
Program used	SHELXS-86[a], SHELX-76[b], SDP[c], PARST[d]	
Computer used	DEC PDP 11/73	

[a] Ref.[7]; [b] ref.[8]; [c] ref.[9]; [d] ref.[10].

washed with ethanol and diethyl ether and dried. Yield 8 g (77%), white crystals, m.p. (ethanol) 267–269°C (ref.[6] 258°C). For $C_{27}H_{20}ClO_4N_3$ (485·9) calculated: 66·74% C, 4·15% H, 8·65% N; found: 66·78% C, 4·48% H, 8·57% N. ^{1}H NMR spectrum: 7·39–7·5 m, 10 H; 7·58 t, 1 H (J = 4·9); 7·67–7·77 mt, 3 H; 8·39 d, 2 H (J = 7·2); 8·8 d, 4 H (J = 5·4). ^{13}C NMR spectrum: 126·83 CH, 129·46 2 CH, 132·45 4 CH, 133·12 2 CH, 133·32 4 CH, 133·48 2 CH, 134·57 2 CH, 135·69 2 C, 136·80 CH, 137·20 C, 158·53 2 C, 160·91 C, 161·24 C, 163·50 2 CH.

TABLE II

Final coordinates (.10^4) and thermal parameters for non-hydrogen atoms. The isotropic equivalent parameter is defined as $B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} a_i a_j$

Atom	x	y	z	B_{eq}, Å^2
		Molecule *IIb*		
O	3419[a]	6383(3)	5240[a]	4·53(8)
N1	4013(1)	3579(4)	4551(2)	3·45(8)
N2	3751(1)	1579(4)	5488(2)	3·76(9)
N3	4754(1)	3323(5)	6190(2)	4·9(1)
C2	3494(1)	4995(5)	3985(2)	3·27(9)
C3	3473(1)	5307(4)	3149(2)	3·4(1)
C4	3967(2)	4078(5)	3195(2)	3·9(1)
C5	4287(1)	3012(5)	4066(2)	3·5(1)
C6	3043(1)	6810(5)	2346(2)	3·4(1)
C7	2913(2)	8926(6)	2519(2)	3·8(1)
C8	2510(2)	10280(6)	1765(3)	4·4(1)
C9	2247(2)	9592(2)	835(3)	4·5(1)
C10	2382(2)	7536(6)	648(3)	4·3(1)
C11	2784(2)	6134(6)	1397(2)	3·8(1)
C12	3156(2)	5956(5)	4391(2)	3·7(1)
C13	2467(2)	6403(5)	3744(2)	3·7(1)
C14	2060(2)	4861(7)	3056(3)	5·0(1)
C15	1417(2)	5286(9)	2505(3)	6·6(2)
C16	1184(2)	7208(10)	2623(3)	7·1(2)
C17	1578(2)	8739(8)	3286(3)	6·6(2)
C18	2220(2)	8343(6)	3848(3)	5·0(1)
C19	4182(1)	2770(5)	5476(2)	3·4(1)
C20	3903(2)	876(6)	6353(2)	4·3(1)
C21	4486(2)	1383(7)	7161(3)	5·4(1)
C22	4890(2)	2565(8)	7044(3)	5·6(1)
C23	4809(1)	1397(5)	4420(2)	3·7(1)
C24	4771(2)	−667(5)	4773(2)	4·0(1)
C25	5248(2)	−2188(6)	5075(3)	4·8(1)
C26	5758(2)	−1699(7)	5015(3)	5·9(2)
C27	5809(2)	302(8)	4669(3)	5·8(1)
C28	5327(2)	1855(6)	4369(3)	4·6(1)

TABLE II
(*Continued*)

Atom	*x*	*y*	*z*	B_{eq}, Å^2
		Molecule *IVb*		
O	782(4)	3607(2)	3528(3)	6·7(1)
N1	7049(3)	2855(2)	6863(3)	4·0(1)
N4	5994(3)	1956(2)	6896(3)	3·5(1)
N8	9224(4)	2163(3)	9185(3)	6·0(2)
C2	5201(4)	2812(2)	5484(3)	3·1(1)
C3	4483(4)	2272(2)	5449(3)	3·2(1)
C5	6131(5)	1409(3)	7569(4)	4·9(2)
C6	7891(5)	1233(3)	9056(4)	6·2(2)
C7	9341(5)	1627(3)	9778(4)	6·8(2)
C9	7496(4)	2333(3)	7701(3)	4·1(1)
C10	2602(4)	2045(2)	4364(3)	3·1(1)
C11	1430(4)	2453(2)	3939(4)	4·1(2)
C12	1800(4)	3165(3)	4514(4)	4·3(2)
C13	2146(4)	1325(2)	3770(3)	3·4(1)
C14	3110(5)	1010(2)	3758(4)	4·4(2)
C15	2637(6)	351(3)	3171(4)	5·8(2)
C16	1244(5)	9(3)	2615(4)	5·9(2)
C17	338(5)	320(3)	2677(4)	6·2(2)
C18	721(5)	988(3)	3217(4)	4·7(2)
C19	3505(5)	3336(2)	6212(4)	4·2(1)
C20	4431(4)	2858(3)	7374(3)	4·6(2)
C21	6033(5)	3017(3)	8983(4)	5·5(2)
C22	6715(5)	3671(3)	9401(4)	7·1(2)
C23	5757(6)	4159(3)	8265(4)	7·0(2)
C24	4149(5)	3995(3)	6668(4)	5·7(2)
C25	4199(4)	3320(2)	4224(3)	3·7(1)
C26	5006(5)	3940(3)	4622(4)	6·0(2)
C27	4066(6)	4422(3)	3445(5)	7·6(2)
C28	2369(6)	4286(3)	1887(5)	7·1(2)
C29	1555(5)	3666(3)	1472(4)	5·9(2)
C30	2457(5)	3190(3)	2634(4)	4·4(2)

[a] The origin fixed.

Oxidation of the salt Ib: Suspension of 7 g salt *Ib* in 500 ml ethanol was refluxed and treated with solution of 16 g potassium ferricyanide and 4 g potassium hydroxide in 100 ml water. After 15 min boiling, the mixture was diluted with 1 000 ml ice water and extracted with 4 × 160 ml chloroform. The organic extract was washed with 100 ml water, dried with sodium sulfate and evaporated. The residue was submitted to column chromatography (silica gel, chloroform–

–diethylether 10 : 1) and afforded two individual substances: 1 g (17%) white crystals of 2-benzoyl-3,5-diphenyl-1-(2-pyrimidyl)pyrrole (*IIb*), m.p. 181–183°C (ethanol–chloroform). For $C_{27}H_{19}N_3O$ (401·5) calculated: 80·78% C, 4·77% H, 10·47% N; found: 80·56% C, 5·03% H, 10·37% N. ^{1}H NMR spectrum ($CDCl_3$): 6·6 s, 1 H; 7·05–7·11 mt, 5 H; 7·16 t, 1 H (J = 4·9); 7·19–7·27 mt, 8 H; 7·64 dd, 2 H (J = 1·3 and 8·2); 8·63 d 2 H (J = 4·9). ^{13}C NMR spectrum ($CDCl_3$): 112·71 CH, 119·53 CH, 126·76 CH, 127·69 2 CH, 127·78 2 CH, 127·84 2 CH, 128·83 2 CH, 128·74 2 CH, 129·51 2 CH, 129·81 2 CH, 130·05 C, 131·86 C, 131·93 CH, 133·77 C, 134·90 C, 138·27 C, 139·27 C, 158·30 CH, 187·68 CO. Mass spectrum, m/z (% r.i.): 401 (100), 373 (5), 324 (69), 296 (9), 191 (11), 182 (6), 105 (13), 97 (9), 85 (11), 83 (10), 81 (8), 77 (21).

The other substance was 2·35 g (41%) yellow crystals of 2-phenyl-3-(1,3-diphenyl-3-oxopropenyl) imidazo[1,2-a]pyrimidine (*IVb*), m.p. 207–209°C (ethanol), for $C_{27}H_{19}N_3O$ (401·5) calculated: 80·78% C, 4·77% H, 10·47% N; found: 81·22% C, 5·09% H, 10·46% N. ^{1}H NMR spectrum ($CDCl_3$): 6·73 dd, 1 H (B, J = 6·8 and 4·1); 7·10 dddd, 1 H (*p*-Ph1, J = 7·1, 7·1, 1·4 and 1·4), 7·16 dddd, 2 H (*m*-Ph1, J = 7·4, 7·1, 1·4 and 1·4); 7·24 dddd, 2 H (*m*-Ph3, J = 7·4, 7·4, 1·3 and; 1·3); 7·30 dddd, 2 H (*m*-Ph2, J = 7·4, 7·1, 1·3 and 1·3); 7·31 dddd, 1 H (*p*-Ph3, J = 7·1, 7·1, 1·3 and 1·3); 7·38 dddd, 1 H (*p*-Ph2, J = 7·1, 7·1, 1·3 and 1·3); 7·41 ddd, 2 H (*o*-Ph3, J = 7·1, 1·3 and 1·3); 7·65 s, 1 H; 7·68 ddd, 2 H (*o*-Ph2, J = 7·1, 1·3 and 1·3); 7·73 ddd, 2 H (*o*-Ph1, J = 6·9, 1·5 and 1·5); 7·90 dd, 1 H (A, J = 6·8 and 2·0); 8·46 dd, 1 H (C, J = 4·1 and 2·0). ^{13}C NMR spectrum ($CDCl_3$): 108·42 CH (B), 116·01 C, 127·35 CH (CH=), 127·45 2 CH (*o*-Ph3), 127·59

TABLE III

The interatomic distances (in Å), angles (in °) and selected torsion angles (in °)

Molecule *IIb*

Bond	Distance	Bond	Distance
O—C12	1·217(3)	C9—C10	1·365(6)
N1—C2	1·412(3)	C10—C11	1·388(5)
N1—C5	1·349(5)	C12—C13	1·488(6)
N1—C19	1·437(4)	C13—C14	1·399(5)
N2—C19	1·306(4)	C13—C18	1·378(6)
N2—C20	1·337(5)	C14—C15	1·384(6)
N3—C19	1·321(3)	C15—C16	1·360(8)
N3—C22	1·343(6)	C16—C17	1·368(6)
C2—C3	1·368(5)	C17—C18	1·380(6)
C2—C12	1·454(6)	C20—C21	1·385(5)
C3—C4	1·409(6)	C21—C22	1·334(8)
C3—C6	1·488(3)	C23—C24	1·401(5)
C4—C5	1·376(4)	C23—C28	1·372(6)
C5—C23	1·477(4)	C24—C25	1·371(6)
C6—C7	1·386(5)	C25—C26	1·365(8)
C6—C11	1·400(4)	C26—C27	1·372(7)
C7—C8	1·376(4)	C27—C28	1·393(6)
C8—C9	1·373(6)		

TABLE III
(*Continued*)

Atoms	Angle	Atoms	Angle
C5—N1—C19	126·4(3)	C2—C12—C13	118·6(3)
C2—N1—C19	123·6(3)	O—C12—C13	119·5(3)
C2—N1—C5	109·9(3)	C12—C13—C18	119·3(3)
C19—N2—C20	115·3(3)	C12—C13—C14	121·5(3)
C19—N3—C22	113·3(3)	C14—C13—C18	119·2(4)
N1—C2—C12	119·5(3)	C13—C14—C15	119·7(4)
N1—C2—C3	106·1(3)	C14—C15—C16	120·1(4)
C3—C2—C12	134·0(3)	C15—C16—C17	120·8(5)
C2—C3—C6	127·1(3)	C16—C17—C18	120·1(4)
C2—C3—C4	108·4(3)	C13—C18—C17	120·1(4)
C4—C3—C6	124·3(3)	N2—C19—N3	129·4(3)
C3—C4—C5	107·7(3)	N1—C19—N3	115·2(3)
N1—C5—C4	107·9(3)	N1—C19—N2	115·4(3)
C4—C5—C23	128·2(3)	N2—C20—C21	120·7(4)
N1—C5—C23	123·8(3)	C20—C21—C22	117·9(4)
C3—C6—C11	120·1(3)	N3—C22—C21	123·4(4)
C3—C6—C7	121·1(3)	C5—C23—C28	120·5(3)
C7—C6—C11	118·8(3)	C5—C23—C24	120·6(3)
C6—C7—C8	120·0(3)	C24—C23—C28	118·8(3)
C7—C8—C9	120·9(3)	C23—C24—C25	120·5(4)
C8—C9—C10	120·0(4)	C24—C25—C26	119·6(4)
C9—C10—C11	120·1(4)	C25—C26—C27	121·4(5)
C6—C11—C10	120·1(3)	C26—C27—C28	119·0(5)
O—C12—C2	121·9(3)	C23—C28—C27	120·6(4)
N1—C2—C3—C4	0·7(3)	C14—C15—C16—C17	−0·3(8)
C2—C3—C4—C5	0·2(4)	C15—C16—C17—C18	−0·2(8)
N1—C2—C3—C6	−174·8(3)	C19—N1—C2—C3	−177·3(3)
C2—C3—C6—C7	42·1(5)	C5—N1—C19—N2	−114·5(4)
C3—C6—C7—C8	−179·5(3)	C20—N2—C19—N1	−178·3(3)
C6—C7—C8—C9	−2·0(6)	C19—N2—C20—C21	−0·9(5)
C7—C8—C9—C10	0·3(7)	N2—C20—C21—C22	−0·8(7)
C8—C9—C10—C11	0·2(7)	C20—C21—C22—N3	1·6(7)
C5—N1—C2—C12	−175·3(3)	C3—C4—C5—C23	174·9(4)
N1—C2—C12—O	30·9(5)	C4—C5—C23—C24	−126·9(4)
N1—C2—C12—C13	−148·5(3)	C5—C23—C24—C25	178·1(4)
C2—C12—C13—C14	43·8(5)	C23—C24—C25—C26	−1·2(6)
C12—C13—C14—C15	176·4(4)	C24—C25—C26—C27	0·9(7)
C13—C14—C15—C16	1·0(7)	C25—C26—C27—C28	−0·4(7)

TABLE III
(*Continued*)

Molecule *IVb*

Bond	Distance	Bond	Distance
O—C12	1·221(5)	C13—C18	1·399(9)
N1—C2	1·353(3)	C14—C15	1·397(7)
N1—C9	1·327(7)	C15—C16	1·37(1)
N4—C3	1·384(4)	C16—C17	1·37(1)
N4—C5	1·375(7)	C17—C18	1·405(7)
N4—C9	1·374(7)	C19—C20	1·380(6)
N8—C7	1·300(9)	C19—C24	1·384(7)
N8—C9	1·360(3)	C20—C21	1·398(4)
C2—C3	1·375(7)	C21—C22	1·386(8)
C2—C25	1·483(6)	C22—C23	1·369(8)
C3—C10	1·484(6)	C23—C24	1·392(5)
C5—C6	1·377(4)	C25—C26	1·382(8)
C6—C7	1·384(9)	C25—C30	1·399(3)
C10—C11	1·314(7)	C26—C27	1·394(7)
C10—C13	1·514(6)	C27—C28	1·371(5)
C11—C12	1·494(7)	C28—C29	1·381(8)
C12—C19	1·475(4)	C29—C30	1·382(7)
C13—C14	1·383(9)		

Atoms	Angle	Atoms	Angle
N1—C2—C3	112·8(3)	C3—C10—C11	121·4(4)
N4—C3—C2	104·5(3)	C10—C11—C12	124·1(4)
C3—N4—C9	106·2(4)	O—C12—C11	117·8(3)
N1—C9—N4	112·5(2)	C11—C12—C19	121·9(3)
C3—N4—C5	131·4(4)	C12—C19—C20	122·1(4)
N4—C5—C6	115·4(5)	C19—C20—C21	121·9(5)
C5—C6—C7	118·9(6)	C20—C21—C22	118·3(4)
N8—C7—C6	126·3(3)	C21—C22—C23	120·3(3)
C7—N8—C9	115·3(4)	C22—C23—C24	120·5(6)
C2—C3—C10	135·0(4)	C19—C24—C23	120·3(4)
C3—C10—C13	115·1(4)	N1—C2—C25	119·5(4)
C10—C13—C14	120·4(5)	C2—C25—C26	119·4(3)
C13—C14—C15	119·4(6)	C25—C26—C27	119·6(4)
C14—C15—C16	121·2(8)	C26—C27—C28	121·3(5)
C15—C16—C17	118·7(5)	C27—C28—C29	119·7(5)
C16—C17—C18	122·5(6)	C28—C29—C30	119·6(4)
C13—C18—C17	117·4(6)	C25—C30—C29	121·3(5)

TABLE III
(*Continued*)

Atoms	Torsion angle	Atoms	Torsion angle
N1—C2—C3—N4	−0·9(6)	N4—C3—C10—C11	118·3(5)
C9—N1—C2—C3	0·3(6)	C3—C10—C11—C12	−1·6(7)
C9—N4—C3—C2	1·1(6)	C10—C11—C12—O	130·4(6)
C5—N4—C3—C2	176·6(5)	C10—C11—C12—C19	−50·9(9)
C3—N4—C5—C6	−179·9(6)	C11—C12—C19—C20	−19·8(11)
N4—C5—C6—C7	3·3(9)	C12—C19—C20—C21	177·3(7)
C5—C6—C7—N8	−0·4(11)	C19—C20—C21—C22	−1·5(11)
C9—N8—C7—C6	−1·2(10)	C20—C21—C22—C23	5·1(12)
N1—C2—C3—C10	170·7(5)	C21—C22—C23—C24	−4·3(13)
N4—C3—C10—C13	−63·1(6)	C9—N1—C2—C25	−179·5(5)
C3—C10—C13—C14	−22·6(5)	N1—C2—C25—C26	−21·7(9)
C10—C13—C14—C15	−178·5(3)	C2—C25—C26—C27	−179·6(7)
C13—C14—C15—C16	−0·3(6)	C25—C26—C27—C28	−1·6(13)
C14—C15—C16—C17	−1·5(6)	C26—C27—C28—C29	1·1(14)
C15—C16—C17—C18	3·2(6)	C27—C28—C29—C30	0·4(12)

2 CH (*o*-Ph2), 127·89 2 CH (*m*-Ph1), 127·93 CH (*p*-Ph1), 127·99 2 CH (*o*-Ph1), 128·05 2 CH (*m*-Ph2), 128·95 2 CH (*m*-Ph3), 130·40 CH (*p*-Ph_3), 132·05 CH (A), 132·58 CH (*p*-Ph2), 132·69 C, 137·06 C, 137·47 C, 140·86 C, 146·78 C, 148·43 C, 149·82 C, 189·83 CO. Mass spectrum, *m/z* (% r.i.): 401 (33), 324 (18), 322 (34), 296 (100), 200 (8), 105 (30), 79 (11), 77 (14).

Structure Analysis

IIb: Monoclinic, space group *Cc*, $a = 25·037(3)$, $b = 6·041(4)$, $c = 16·536(4)$ Å, $\beta = 122·41(3)°$, $V = 2\,111·4(5)$ Å^3, $Z = 4$, $D_o = 1·28(2)$, $D_c = 1·26$ g cm^{-3}, $\mu = 0·73$ cm^{-1}, $F(000) = 840$.

IVb: Monoclinic, space group $P2_1/c$, $a = 12·662(2)$, $b = 19·739(4)$, $c = 14·694(4)$ Å, $\beta = 144·89(4)°$, $V = 2\,112·4(6)$ Å^3, $Z = 4$, $D_o = 1·28(2)$, $D_c = 1·26$ g cm^{-3}, $\mu = 0·73$ cm^{-1}, $F(000) = 840$.

The both structures were solved by direct methods and anisotropically refined by full-matrix least-squares. As concerned the structure of *IIb*, the hydrogen atom positions were found from difference Fourier synthesis and isotropically refined. Intensity data for the structure of *IVb* were corrected for the decay of the crystal (see Table I). The hydrogen atoms of *IVb* were fixed in positions found from difference Fourier synthesis and their thermal displacement parameters were refined isotropically. Absorption and extinction effects were neglected for the both structures. Data collection and structure refinement parameters are listed in Table I. In Table II are given the final atomic parameters and Table III summarizes geometrical characteristics of studied molecules. Figure 1 shows drawings of molecules and Fig. 2 depicts molecular packing.

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APPENDIX

The optimal least-squares planes fitted through the atoms in molecule *IIb*. Each plane is defined as $A * X + B * Y + C * Z - D = 0$.

Atoms	Deviation, Å	Atoms	Deviation, Å	Atoms	Deviation, Å
Plane α[a]		Plane β[b]		Plane γ[c]	
N1	−0·007(3)	C6	0·008(3)	C13	−0·004(4)
C2	0·007(3)	C7	−0·018(5)	C14	0·006(5)
C3	−0·002(3)	C8	0·003(5)	C15	−0·003(5)
C4	−0·004(4)	C9	0·008(5)	C16	−0·002(5)
C5	0·007(3)	C10	−0·002(5)	C17	0·002(5)
		C11	−0·014(5)	C18	0·002(5)

Atoms	Deviation, Å	Atoms	Deviation, Å
Plane δ[d]		Plane ε[e]	
C19	−0·011(3)	C23	−0·003(3)
N2	0·007(3)	C24	0·004(3)
C20	−0·003(4)	C25	−0·006(4)
C21	−0·010(5)	C26	0·001(4)
C22	0·009(5)	C27	0·001(4)
N3	0·005(3)	C28	0·001(4)

Dihedral angles between planes

Plane–plane		Angle, °	Plane–plane		Angle, °
α	β	43·2(1)	β	δ	100·8(1)
α	γ	110·4(1)	β	ε	83·4(2)
α	δ	62·6(1)	γ	δ	88·3(1)
α	ε	49·3(1)	γ	ε	61·1(1)
β	γ	134·2(1)	δ	ε	62·8(1)

The optimal least-squares planes fitted through the atoms in molecule *IVb*. Each plane is defined as $A * X + B * Y + C * Z - D = 0$.

Atoms	Deviation, Å	Atoms	Deviation, Å	Atoms	Deviation, Å
Plane α[f]		Plane β[g]		Plane γ[h]	
N1	0·000(5)	N4	0·023(4)	C13	0·003(3)
C2	0·004(5)	C5	−0·023(6)	C14	−0·008(4)
C3	−0·006(5)	C6	0·008(7)	C15	0·000(4)
N4	0·006(4)	C7	0·009(7)	C16	0·012(4)
C9	−0·004(6)	N8	−0·009(6)	C17	−0·017(4)
		C9	−0·007(6)	C18	0·009(4)
Plane δ[i]		Plane ε[j]		Plane ζ[k]	
C19	0·026(7)	C25	0·000(6)	C10	0
C20	−0·007(7)	C26	0·008(8)	C11	0
C21	−0·021(7)	C27	−0·009(9)	C12	0
C22	0·031(8)	C28	0·002(9)	Other atom	
C23	−0·011(9)	C29	0·006(8)	O	0·823(4)
C24	−0·017(8)	C30	−0·007(7)		

Dihedral angles between planes

Plane–plane		Angle, °	Plane–plane		Angle, °
α	β	0·9(6·9)	β	ζ	59·7(4)
α	γ	74·4(2)	γ	δ	84·1(2)
α	δ	32·4(3)	γ	ε	82·2(2)
α	ε	22·1(5)	γ	ζ	24·1(8)
α	ζ	59·2(4)	δ	ε	10·5(6)
β	γ	74·6(2)	δ	ζ	61·0(4)
β	δ	33·2(3)	ε	ζ	60·9(4)
β	ε	22·8(4)			

[a] $A = -0·470(1)$, $B = -0·7885(9)$, $C = -0·397(1)$, $D = -7·045(7)$, $\chi^2 = 20$; [b] $A = -0·9298(7)$, $B = -0·368(2)$, $C = -0·005(2)$, $D = -6·689(8)$, $\chi^2 = 30$; [c] $A = 0·579(2)$, $B = 0·441(2)$, $C = -0·685(1)$, $D = -0·22(1)$, $\chi^2 = 4$; [d] $A = 0·533(1)$, $B = -0·836(1)$, $C = -0·131(2)$, $D = 0·60(1)$, $\chi^2 = 31$; [e] $A = 0·032(2)$, $B = -0·381(1)$, $C = -0·9241(6)$, $D = -5·76(1)$, $\chi^2 = 5$; [f] $A = 0·7249$, $B = -0·5709$, $C = -0·3854$, $D = -4·9630$, $\chi^2 = 4$; [g] $A = 0·7145$, $B = -0·5823$, $C = -0·3879$, $D = -5·0311$, $\chi^2 = 49$; [h] $A = 0·1636$, $B = 0·3580$, $C = -0·9193$, $D = -2·2935$, $\chi^2 = 38$; [i] $A = 0·9740$, $B = -0·2249$, $C = -0·0266$; $D = -4·5966$, $\chi^2 = 43$; [j] $A = 0·9212$, $B = -0·3680$, $C = -0·1268$, $D = -2·6432$, $\chi^2 = 4$. [k] $A = 0·5518$, $B = 0·3233$, $C = -0·7688$, $D = -2·6073$, $\chi^2 = 0$.

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