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Fused *N*-(di)arylamino-pyrrol-2,3-diones **1** are reacted with diphenylketene, thiosemicarbazide or 1,2-diaminobenzene to afford the 3-diphenylmethylene pyrrolones **2**, the thiosemicarbazones **4** or the quinoxaline derivatives **5** as well as **6**, respectively. Thermolysis of **2b,c,e,f,6b** and the pyrrolo-quinoxaline **8** afford the corresponding *N*-deaminated products **3**, **7** and **9**. Rearrangements into diazapropellanes following a thermally initiated Fischer – indolization as originally expected do not occur.

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1-(Di)arylamino-pyrrol-2,3-diones were found to rearrange into the corresponding pyrrolo[2,3-*b*]indoles *via* a Fischer-indolization process by simple heating in the solid state or in inert solvents [2,3,4,5]. The rearrangement is nicely indicated by a change of colour from deep red into bright yellow. Consequently, applying 4,5-bridged pyrrol-2,3-diones a simple and versatile approach to diaza-[n.3.3]propellanes became feasible [6,7] (see Chart). The reaction mechanism of those conversions has been thoroughly investigated with aid of isotopic labeling, a) making evident an intramolecular course of these rearrangements [8], and b), from KIE-measurements a sigmatropic [3.3] shift as required for a true Fischer-indole synthesis could be established as the rate determining step [9].

In order to prove the scope and limitations of these indolization reactions we now wanted to investigate the influence of changes within the 2,3-dioxo moiety of the educts **1** on the overall outcome of the thermolysis reactions, in particular, if the ability to undergo the indolization process towards diazapropellanes was still alive.

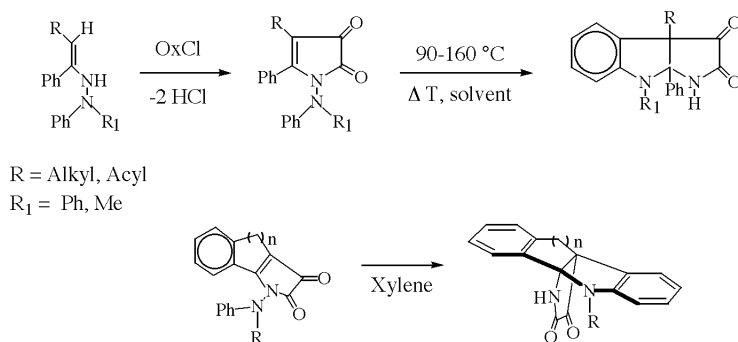
This should be achieved by converting one or both of the carbonyl groups into different functionalities: a) reacting the pyrroldiones **1**, easily prepared from cyclocondensation

reactions of the corresponding hydrazones and oxalylchloride [7], with diphenylketene [10,11] converted the carbonyl on C-3 into a (Ph)₂C=C - moiety thus affording the 3-diphenylmethylene- pyrrol-2-ones **2** (Scheme 1). b) Reaction of pyrroldiones **1** and thiosemicarbazide resulted in the introduction of a C=N-group at C-3 with formation of the thiosemicarbazones **4** (Scheme 2). c) 1,2-Diaminobenzene and **1** combined to give the 2-quinoxalinone derivatives **5** as well as the pyrrolo[2,3-*b*]quinoxalines **6** (Scheme 3). d) Attempts to convert the C=O groups of **1** into one or even two C=S moieties by treating with Lawesson reagent [12] did not follow the expected route, but from these novel experiments, deeply coloured dyes of the isoindigoide type were recently obtained [13].

Preparation of Functionalized Fused Pyrrol-2,3-diones **2**, **4**, **5** and **6**.

a) The fused 3-diphenylmethylene-pyrrol-2-ones **2** are obtained in 54-90% yield from heating diphenylketene and the corresponding pyrrol-2,3-diones **1** [7] to 60 - 110 °C without any solvent until the evolution of carbon dioxide is complete. The reaction proceeds *via* a

Chart



[2 + 2] cycloaddition/cycloreversion process as usually observed and expected from ketene-carbonyl interactions in general [14,15,16] and also found from the reaction of isatin and dichloroketene [17]. In particular, similar to **1**, monocyclic furan- as well as pyrrol-2,3-diones and diphenylketene also afford the corresponding 3-diphenylmethylene products, under both photochemical and thermal conditions [18]. Therefore, besides correct elemental analyses (see Experimental), structural confirmation of the fused pyrrolones **2** was easily obtained by comparison of their ir - as well as ^{13}C - nmr data (selected example **2d**) with those of very close related derivatives reported in reference [18]. Characteristic ir-absorptions at 1705-1715 (lactam carbonyls) and 1585-1590 cm^{-1} (C=C) and loss of absorptions at 1765 cm^{-1} (for educts **1** [7]) indicate a chemical transformation at C-3. The ^{13}C -nmr signals of **2d** appear at 168.5 (C-2) 117.5 (C-4) 148.0, 145.5 (C-5, C-6, interchangeable), the signal for C-3 in the educt **1d** (expected within 172-175 ppm, see [7,18]) is missing as with further compounds **2** (details see Experimental). The 3-methylene-pyrrol-2-one ring

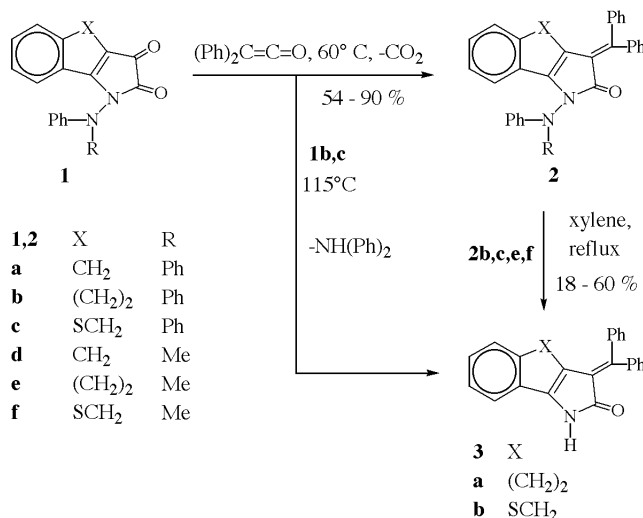
system represents the basic skeleton for several molecules with cytotoxic, antitumor and antiinflammatory [19-21] as well as antibiotic and antifungal activities [22,23].

b) The orange-red coloured thiosemicarbazone derivatives **4** are obtained in 52-81% yields from the H^+ (ether/hydrochloric acid) catalyzed reaction of the corresponding fused diones **1** and thiosemicarbazide in boiling ethanol as the result of a simple condensation of a carbonyl group and the NH_2 -functionality.

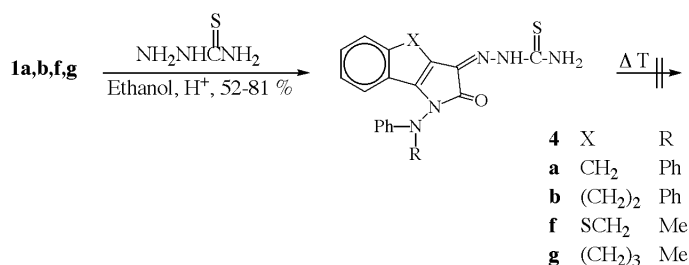
Structural analogues of **4** [4], in particular thiosemicarbazones of several isatins have found strong interest due to their distinct biological (antiviral, bacteriostatic) activities [24-29]. Comparison of the IR-data of **4** (C=O absorptions at 1695-1715 cm^{-1}) among themselves and with those of several analogues reported in [4,24,29], together with correct results of their elemental analyses (see Experimental), evidence their molecular skeleton. Further confirmation also came from ^1H - and ^{13}C nmr data (see Experimental).

c) Reaction of **1** and 1,2-diaminobenzene in general was expected to afford fused pyrrolo[2,3-*b*]quinoxaline derivatives as found with isatins [30] and analogues [31] as well

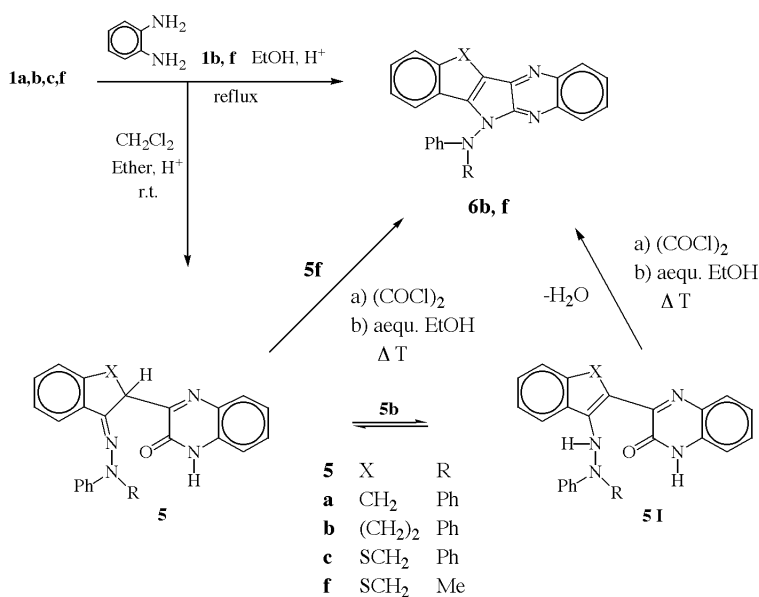
Scheme 1



Scheme 2



Scheme 3



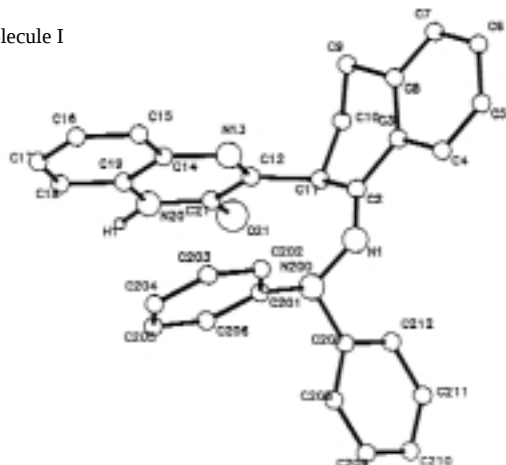
as monocyclic pyrrol-2,3-diones [32,33]. Actually, as examples, from **1b,f** the corresponding target molecules **6b,f** could be obtained in rather divergent yields of 60% (**6b**) and 21% (**6f**) by acid catalyzed heating of the reactants in boiling aqueous ethanol.

However, formation of **6** could also be achieved *via* quinoxalinone derivatives **5** following a similar procedure observed with non-fused pyrrol-2,3-diones [31] (see Scheme 3). The reactants **1** and 1,2-diaminobenzene (molar ratio 1:2) were dissolved in a suitable amount of dichloromethane, a few drops of ethereal hydrochloric acid were added and the reaction mixture stirred at room temperature for up to 48 hours. Evaporation and triturating with ether afforded **5a,b,c,f** in yields from 16-75%, depending on the specific nature of **1**. Quinoxalinones **5b,f** (**5b** *via* the tautomeric form **5I**) then were converted into the desired fused compounds **6b,f** by treating with oxalyl chloride and subsequent refluxing in aqueous ethanol. In case of **5b**, formation of an additional rather unstable intermediate was observed, that analytical and ir-spectroscopic data (see Experimental) indicate, should be the tautomeric form **5I**. It decomposes in solution, but by immediate heating in aqueous ethanol (80%) it is also converted into **6b**.

Elucidation of the molecular skeletons of the quinoxalinone derivatives **5** was based upon the X-ray crystal structure determination of **5b** (Figure 1):

5b crystallizes triclinic within the space group $P\bar{1}$ (Nr.2) and with $a = 1526.7(6)$, $b = 1548.2(6)$, $c = 1027.7(4)$ pm, $\alpha = 91.71(4)^\circ$, $\beta = 100.70(4)^\circ$ and $\gamma = 87.36(4)^\circ$. The unit cell contains $Z = 4$ molecules with $Z = 2$ asymmetric units (see Table 1). Table 2 shows bond lengths and angles, the numbering of atoms can be found from Figure 1. The cyclohexene ring represents the boat conformation while the

Molecule I



Molecule II

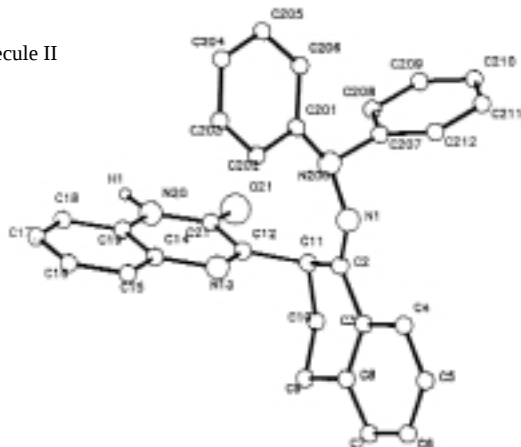


Figure 1

Table 1

Atom	x	y	z	Molecule I			Molecule II			z	x	y	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
N(1)	4234(2)	1294(2)	2349(3)	64(2)	56(2)	54(2)	58(2)	40(2)	50(2)	4738(3)	9904(2)	2199(2)	58(2)	40(2)	50(2)	-5(1)	10(1)	-2(2)
C(2)	4532(2)	1902(2)	1749(3)	53(2)	51(2)	38(2)	52(2)	50(2)	34(2)	4420(3)	9058(2)	2100(2)	52(2)	50(2)	37(2)	1(2)	8(2)	-1(2)
C(3)	5297(3)	1665(3)	1116(4)	53(3)	49(3)	40(2)	61(2)	47(2)	39(3)	3999(3)	8769(2)	1221(2)	61(2)	47(2)	34(2)	-1(2)	7(2)	-4(2)
C(4)	5566(3)	792(3)	977(4)	69(3)	61(3)	67(3)	63(3)	55(3)	66(3)	3690(4)	9393(3)	596(3)	63(3)	55(3)	66(3)	-8(2)	12(2)	-3(2)
C(5)	6276(3)	573(3)	361(4)	76(3)	69(3)	91(3)	83(3)	54(3)	82(3)	3335(4)	9136(3)	-237(3)	83(3)	54(3)	82(3)	-12(3)	14(2)	-2(2)
C(6)	6737(3)	1201(3)	-101(4)	62(3)	102(4)	82(3)	99(3)	53(2)	68(3)	3257(4)	8267(3)	-450(2)	99(3)	53(2)	68(3)	-8(2)	18(2)	-17(2)
C(7)	6494(3)	2055(3)	63(4)	61(3)	83(3)	67(3)	76(3)	70(3)	52(2)	3529(4)	7644(3)	164(3)	76(3)	70(3)	52(2)	-5(2)	12(2)	-22(2)
C(8)	5774(3)	2302(3)	665(4)	51(3)	66(3)	41(2)	61(3)	63(3)	42(2)	3910(3)	7879(3)	1007(3)	61(3)	63(3)	42(2)	1(2)	6(2)	-8(2)
C(9)	5503(3)	3243(2)	827(3)	77(3)	65(3)	51(2)	54(3)	79(3)	60(3)	4198(4)	7198(3)	1684(3)	54(3)	79(3)	60(3)	-8(2)	10(2)	-11(2)
C(10)	4492(3)	3345(2)	612(3)	79(3)	53(2)	49(2)	59(2)	68(3)	50(2)	3766(3)	7421(2)	2564(2)	59(2)	68(3)	50(2)	-4(2)	8(2)	7(2)
C(11)	4132(2)	2825(2)	1633(3)	52(2)	60(2)	40(2)	50(2)	46(2)	42(2)	4462(3)	8357(2)	2827(2)	50(2)	46(2)	42(2)	3(2)	12(2)	5(2)
C(12)	4252(2)	3299(2)	2961(3)	50(2)	42(2)	48(2)	46(2)	50(2)	44(2)	5880(3)	8339(2)	3107(2)	46(2)	50(2)	44(2)	-1(2)	8(2)	0(2)
N(13)	4935(2)	3123(2)	3870(3)	52(2)	53(2)	48(2)	58(2)	54(2)	44(2)	6835(3)	8588(2)	2570(2)	58(2)	54(2)	44(2)	6(1)	10(1)	4(1)
C(14)	4994(3)	3555(3)	5097(4)	47(3)	49(3)	47(2)	54(3)	68(3)	42(2)	8129(4)	8542(3)	2848(3)	54(3)	68(3)	42(2)	4(2)	8(2)	-11(2)
C(15)	5716(3)	3369(3)	6105(4)	54(3)	68(3)	50(3)	77(3)	78(3)	50(3)	9170(4)	8830(3)	2279(3)	77(3)	78(3)	50(3)	17(2)	8(2)	-3(2)
C(16)	5775(3)	3772(3)	7328(4)	67(3)	84(3)	47(3)	86(4)	106(4)	46(3)	4411(4)	8790(3)	2549(4)	86(4)	106(4)	46(3)	19(3)	9(2)	-19(3)
C(17)	5112(3)	4363(3)	7554(4)	87(3)	70(3)	46(2)	81(4)	121(4)	46(3)	703(4)	8475(3)	3372(4)	81(4)	121(4)	46(3)	-10(3)	13(2)	-38(3)
C(18)	4393(3)	4563(3)	6589(4)	74(3)	53(3)	48(3)	71(3)	82(3)	50(3)	9698(4)	8191(3)	3945(3)	71(3)	82(3)	50(3)	-14(2)	16(2)	-24(2)
C(19)	4328(2)	4148(2)	5353(3)	50(2)	47(2)	45(2)	47(2)	63(3)	42(2)	8400(3)	8233(2)	3681(3)	47(2)	63(3)	42(2)	-5(2)	9(2)	-14(2)
N(20)	3616(2)	4324(2)	4341(3)	60(2)	53(2)	48(2)	62(2)	51(2)	43(2)	7358(3)	7965(2)	4236(2)	62(2)	51(2)	43(2)	-6(1)	11(1)	-0(2)
C(21)	3546(3)	3960(3)	3112(4)	56(3)	49(3)	52(3)	45(2)	52(2)	49(2)	6083(4)	7989(2)	4001(2)	45(2)	52(2)	49(2)	-3(2)	11(2)	-1(2)
O(21)	2934(2)	4177(2)	2188(2)	62(2)	69(2)	56(2)	76(2)	53(2)	52(2)	5152(2)	7726(2)	4497(2)	76(2)	53(2)	52(2)	7(1)	14(1)	16(1)
N(200)	3497(2)	1574(2)	3002(3)	54(2)	62(2)	52(2)	56(2)	48(2)	41(2)	5003(3)	135(2)	3098(2)	56(2)	48(2)	41(2)	2(1)	9(1)	-3(2)
C(201)	3784(3)	1567(3)	4427(4)	66(3)	50(3)	48(2)	49(2)	47(2)	46(2)	6159(3)	792(2)	3203(2)	49(2)	47(2)	46(2)	-4(2)	8(2)	4(2)
C(202)	4554(3)	1136(3)	5029(4)	76(3)	65(3)	64(3)	67(3)	50(2)	51(2)	7256(4)	760(3)	2708(2)	67(3)	50(2)	51(2)	1(2)	8(2)	2(2)
C(203)	4796(3)	1183(3)	6404(4)	91(4)	92(4)	62(3)	80(3)	64(3)	52(2)	8443(4)	1342(3)	2861(3)	80(3)	64(3)	52(2)	7(2)	6(2)	12(2)
C(204)	4275(3)	1647(3)	7150(4)	124(4)	82(3)	57(3)	70(3)	81(3)	53(2)	8560(4)	1957(3)	3495(3)	70(3)	81(3)	53(2)	-10(2)	-3(2)	6(2)
C(205)	3510(3)	2081(3)	6536(4)	105(4)	72(3)	76(3)	63(3)	75(3)	68(3)	7464(4)	2003(3)	3974(3)	63(3)	75(3)	68(3)	-13(2)	7(2)	-9(2)
C(206)	3263(3)	2045(3)	5173(4)	80(3)	69(3)	55(3)	55(2)	60(2)	50(2)	6264(4)	1430(2)	3827(2)	55(2)	60(2)	50(2)	-3(2)	2(2)	-3(2)
C(207)	2726(3)	1093(3)	2469(4)	55(3)	55(3)	53(2)	46(2)	54(2)	42(2)	3802(3)	307(2)	3469(2)	46(2)	54(2)	42(2)	-4(2)	2(2)	-3(2)
C(208)	2323(3)	562(3)	3213(4)	76(3)	99(4)	57(3)	67(3)	51(2)	51(2)	3461(3)	9963(2)	4288(2)	67(3)	51(2)	51(2)	0(2)	3(2)	-2(2)
C(209)	1563(3)	133(3)	2651(5)	74(3)	109(4)	83(4)	83(3)	63(3)	63(3)	2323(4)	124(3)	4658(3)	83(3)	63(3)	63(3)	13(2)	-2(2)	-12(2)
C(210)	1200(3)	222(3)	1345(5)	68(3)	81(4)	94(4)	89(4)	99(4)	53(3)	1533(4)	625(3)	4212(3)	89(4)	99(4)	53(3)	7(3)	10(2)	-29(3)
C(211)	1597(3)	731(3)	580(4)	91(4)	84(3)	69(3)	76(3)	99(3)	60(2)	1872(4)	977(3)	3397(3)	76(3)	99(3)	60(2)	-10(2)	24(2)	-17(2)
C(212)	2359(3)	1163(3)	1125(4)	79(3)	74(3)	61(2)	60(2)	66(3)	59(2)	3013(4)	821(2)	3015(2)	60(2)	66(3)	59(2)	-3(2)	16(2)	1(2)
H	3112(22)	4741(21)	4527(32)							7594(34)	7734(23)	4835(23)						

Table 2

Distances (pm)

	I	II		I	II		I	II
N(1)-C(2)	128.5(5)	128.4(4)	C(12)-N(13)	129.0(4)	129.6(4)	N(200)-C(201)	144.9(5)	141.6(4)
N(1)-N(200)	145.7(4)	145.6(4)	C(12)-C(21)	147.7(5)	148.4(5)	N(200)-C(207)	143.4(5)	145.0(4)
C(2)-C(3)	146.7(5)	147.7(5)	N(13)-C(14)	140.0(5)	139.8(5)	C(201)-C(202)	137.6(6)	139.1(5)
C(2)-C(11)	152.6(5)	152.1(5)	C(14)-C(15)	139.1(5)	140.0(5)	C(201)-C(206)	138.0(6)	139.2(5)
C(3)-C(4)	140.5(6)	139.8(5)	C(14)-C(19)	139.4(5)	139.1(6)	C(202)-C(203)	139.3(6)	139.0(5)
C(3)-C(8)	139.1(6)	139.9(5)	C(16)-(17)	137.7(6)	137.2(6)	C(203)-C(204)	137.1(7)	137.7(6)
C(4)-C(5)	137.9(7)	138.4(6)	C(16)-C(17)	138.1(6)	137.7(8)	C(204)-C(205)	137.5(6)	138.2(6)
C(5)-C(6)	137.1(7)	136.9(6)	C(17)-C(18)	136.6(5)	137.6(6)	C(205)-C(206)	138.1(6)	139.2(5)
C(6)-C(7)	137.0(7)	137.3(6)	C(18)-C(19)	139.4(5)	139.5(5)	C(207)-C(208)	137.8(6)	138.0(5)
C(7)-C(8)	139.3(6)	139.4(6)	C(19)-N(20)	138.1(4)	138.4(4)	C(208)-C(209)	138.7(6)	138.3(6)
C(8)-C(9)	150.8(6)	150.4(6)	N(20)-C(21)	135.5(5)	135.6(4)	C(209)-C(210)	136.2(7)	136.8(6)
C(9)-C(10)	152.0(6)	151.7(6)	N(20)-H	102(3)	102(4)	C(210)-C(211)	136.6(7)	137.6(6)
C(10)-C(11)	153.6(5)	154.2(5)	C(21)-O(21)	124.4(4)	124.0(4)	C(211)-C(212)	138.7(6)	139.2(6)
C(11)-C(12)	151.5(4)	151.3(5)						

Angles (°)

	I	II		I	II		I	II
C(2)-N(1)-N(200)	113.7(3)	113.3(3)	C(11)-C(12)-N(13)	120.5(3)	120.5(3)	N(1)-N(200)-C(201)	110.2(3)	112.6(2)
N(1)-C(2)-C(3)	116.1(3)	116.8(3)	C(11)-C(12)-C(21)	115.4(3)	116.1(3)	N(1)-N(200)-C(207)	109.7(3)	109.3(2)
N(1)-C(2)-C(11)	124.6(3)	123.9(3)	N(13)-C(12)-C(21)	124.0(3)	123.3(3)	C(201)-N(200)-C(207)	116.5(3)	116.7(3)
C(3)-C(2)-C(11)	119.3(3)	119.3(3)	C(12)-N(13)-C(14)	118.1(3)	118.7(3)	N(200)-C(201)-C(202)	122.5(4)	118.9(3)
C(2)-C(3)-C(4)	120.3(4)	119.6(3)	N(13)-C(14)-C(15)	119.5(4)	119.1(3)	N(200)-C(201)-C(206)	119.6(3)	122.1(3)
C(2)-C(3)-C(8)	120.4(3)	120.8(3)	N(13)-C(14)-C(19)	121.6(3)	121.3(3)	C(202)-C(201)-C(206)	120.5(4)	118.9(3)
C(4)-C(3)-C(8)	119.2(4)	119.6(3)	C(15)-C(14)-C(19)	118.9(3)	119.6(3)	C(201)-C(202)-C(203)	119.0(4)	119.9(3)
C(3)-C(4)-C(5)	120.1(4)	120.1(4)	C(14)-C(15)-C(16)	120.4(4)	119.3(4)	C(202)-C(203)-C(204)	120.7(4)	121.3(4)
C(4)-C(5)-C(6)	120.6(4)	120.3(4)	C(15)-C(16)-C(17)	119.7(4)	120.8(4)	C(203)-C(204)-C(205)	119.7(4)	118.9(3)
C(5)-C(6)-C(7)	119.7(4)	120.0(4)	C(16)-C(17)-C(18)	121.6(4)	121.0(4)	C(204)-C(205)-C(206)	120.3(4)	120.7(4)
C(6)-C(7)-C(8)	121.4(4)	120.0(4)	C(17)-C(18)-C(19)	118.8(4)	118.4(4)	C(201)-C(206)-C(205)	119.8(4)	120.3(3)
C(3)-C(7)-C(7)	118.9(4)	118.5(4)	C(14)-C(19)-C(18)	120.7(3)	120.4(3)	N(200)-C(207)-C(208)	123.5(3)	119.2(3)
C(3)-C(8)-C(9)	119.9(4)	119.9(3)	C(14)-C(19)-N(20)	118.0(3)	118.6(3)	N(200)-C(207)-C(212)	118.7(4)	120.2(3)
C(7)-C(8)-C(9)	121.2(4)	121.6(4)	C(18)-C(19)-N(20)	121.3(3)	121.0(3)	C(208)-C(207)-C(212)	117.8(4)	120.2(3)
C(8)-C(9)-C(10)	109.5(3)	110.3(3)	C(19)-N(20)-C(21)	123.0(3)	122.7(3)	C(207)-C(208)-C(209)	120.9(4)	120.2(3)
C(9)-C(10)-C(11)	110.3(3)	111.8(3)	C(21)-N(20)-H	119(2)	116(2)	C(208)-C(209)-C(210)	120.7(5)	120.0(4)
C(2)-C(11)-C(10)	112.4(3)	112.1(3)	C(21)-N(20)-H	118(2)	121(2)	C(209)-C(210)-C(211)	119.6(4)	120.2(4)
C(2)-C(11)-C(12)	112.1(2)	110.2(3)	C(12)-C(21)-N(20)	114.9(3)	115.3(3)	C(210)-C(211)-C(212)	120.5(4)	120.6(4)
C(10)-C(11)-C(12)	110.8(3)	110.0(3)	C(12)-C(21)-O(21)	123.2(3)	122.5(3)	C(207)-C(212)-C(211)	120.5(4)	118.9(3)
			N(20)-C(21)-O(21)	121.9(4)	122.2(3)			

quinoxalinone ring is planar within standard deviations. From the packing plot of **5b** (Figure 2) "stacking" of two quinoxalinones with one phenyl group of the diphenylhydrazone unit each becomes evident, as well as the association of two molecules of **5b** via hydrogen bridges N(20) - H(1)O(21).

From the ir spectra of **5** lactam carbonyl absorptions are observed in the 1650-1665 cm⁻¹ region as expected [31], while from the ¹H nmr spectra of **5a,b,f** characteristic signals for the C-H's are found at δ 4.2, 4.8, and 5.1 ppm, respectively. The ¹³C nmr data also agree well with the established molecular skeleton of **5b**. The assignment was achieved from coupling as well as comparison with structural analogues, *e.g.*, 3-methylquinoxalin-2-one [34] and 2-(3-oxo-quinoxaliny)-acetophenon-*N,N*-diphenylhydrazone [32]. The signals of the C=O at 155.3 (q, ³J = 2 Hz), 155.5 (**5b**, d, ³J = 2 Hz) and 155.4 (t, ³J = 3.5 Hz), of

Scheme 4

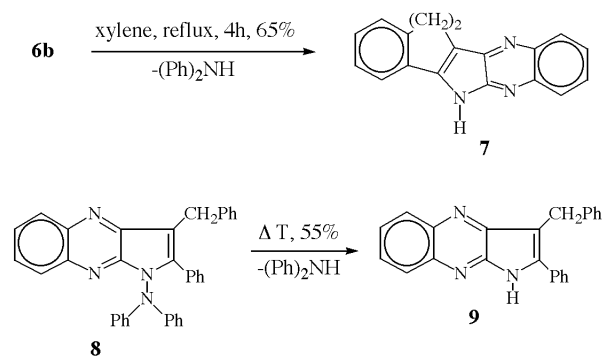


Table 3
X-Ray Structure Analysis of **5b** - Experimental Details

Yellow crystal	
Empirical formula	C ₃₀ H ₂₄ N ₄ O
Crystal size	0.2 x 0.8 x 0.05
Crystal system	triclinic
Space group	P $\bar{1}$ (2)
Unit cell dimensions (standard deviations)	a = 1526.7(6) pm α = 91.71 (4) $^\circ$ b = 1548.2(6) pm β = 100.70 (4) $^\circ$ c = 1027.7(4) pm γ = 87.36 (4) $^\circ$
Z	4
d _{calc} [g.cm ⁻³]	1.272
Syntex-P3 four circle diffractometer	
Measurement of intensities	ω -scan, MoK α - radiation scan width 1 $^\circ$, $2\theta_{\max}$ = 55 $^\circ$
Reflections collected	3146
Reflections observed (F > 3 σ)	3111
Refinement method	Full-matrix least-squares on F ²
R _{anis}	0.034

the C=N at 161.8 (m) and 166.8 (5b, m) as well as of the C-3 of the quinoxalinone moiety at 159.7 (q, 2J = 7.5 Hz), 158.8 (5b, m) and 161.8 (m) correspond well among each other.

The molecular scaffold of the pyrrolo[2,3-*b*]quinoxaline derivatives **6b,f** was characterized by their molecular formula deduced from the results of elemental analysis, as well as the lack of any carbonyl and NH absorption bands in the IR-spectrum. The uv spectra of the yellow coloured and fluorescent

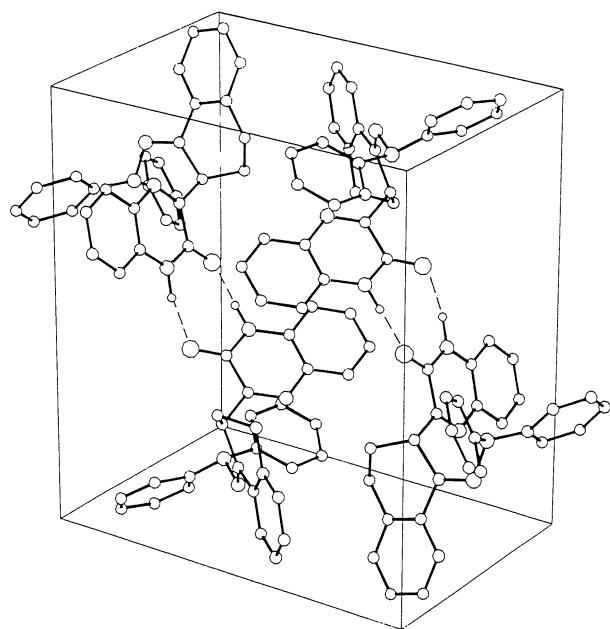


Figure 2

compounds exhibit $\lambda_{\max}$ values at 370 (ϵ = 19100), 420 nm (ϵ = 10770) for **6b**, and 352 (ϵ = 12100), 370 nm (ϵ = 10500) for **6f**, respectively.

Thermolysis of Compounds **2**, **4** and **6**.

Heating of fused pyrrolones **2b,c,e,f** in boiling xylene did not afford the corresponding rearranged diazapropellanes as expected and outlined in the Chart, but instead the N-unsubstituted pyrrolones **3** were obtained as a result of loss of diphenylamine or methylphenylamine, respectively (see Scheme 1). From thermolysis of thiosemicarbazone derivatives **4** no distinct reaction product could be isolated out of the complex reaction mixture. Finally, pyrrolo[2,3-*b*]quinoxaline **6b**, when refluxed in xylene for 4 hours, again gave the deaminated derivative **7** as the only isolable reaction product, similarly to the formation of compounds **3** starting with **2**. In addition, the pyrrolo-quinoxaline **8**, related to **6b** and obtained according to a known procedure [32], revealed a quite similar behaviour during thermolysis leading to compound **9**.

EXPERIMENTAL

Melting points were acquired on a Tottoli Apparatus and are uncorrected. IR-spectra (potassium bromide pellets) were recorded on a Perkin Elmer Model 298. The ^1H and ^{13}C nmr spectra were obtained with a Varian XL 200 operating at 200 MHz and 50 MHz respectively, a Bruker AMX 360 operating at 360 MHz and 90 MHz, respectively, a Bruker DMX Avance operating at 500 and 125 MHz, respectively, and TMS as internal standard. The ms measurements were performed on a Varian MAT 111 spectrometer and elemental analyses were obtained using a Carlo Erba Elemental Analyzer 1106.

Synthesis of 3-Diphenylmethylene-pyrrol-2-ones **2**.

General Procedure.

The respective pyrrol-2-one derivative **1** (1 mmole) [7] as a solid was mixed with an slight excess (1.5 mmoles) of diphenylketene [11] and heated to 60 $^\circ\text{C}$ (**1a-c**) or 110 $^\circ\text{C}$ (**1d-f**) under dry nitrogen until the evolution of carbon dioxide ceased. Cooling to room temperature and triturating of the crude residue with dry ether afforded the compounds **2** as red/orange products which were recrystallized from ethanol (**2a-c**) or *n*-butanol (**2d-f**).

1-Diphenylamino-3-diphenylmethylene-3,4-dihydro-indeno-[1,2-*b*]pyrrol-2(1*H*)-one **2a**.

This compound was obtained by the general procedure as red crystals, mp 167 $^\circ\text{C}$, yield 88%; ir (potassium bromide): 1710 (C=O), 1585 cm^{-1} (C=C); ^1H nmr (CDCl₃): δ 3.06 (s, 2H), 7.16-7.47 (m, 24H) ppm; ^{13}C nmr (CDCl₃): δ 169.2 (C=O), 149.5, 148.5, 145.8, 145.2, 141.7, 138.8, 133.5, 118.5 (quaternary carbons), 131.0-119.2 (aromatic carbons), 34.5 (CH₂) ppm.

Anal. Calcd. for C₃₆H₂₆N₂O: C, 86.02; H, 5.22; N, 5.58. Found: C, 86.05; H, 5.35; N, 5.57.

1-Diphenylamino-3-diphenylmethylene-3*H*-4,5-dihydrobenz[*g*]indol-2(1*H*)-one (**2b**).

This compound was obtained by the general procedure as red crystals, mp 163 °C, yield 90%; ir (potassium bromide): 1715 (C=O), 1585 cm⁻¹ (C=C); ¹H nmr (CDCl₃): δ 1.85 (t, *J* = 7.5 Hz, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 7.01-7.4 (m, 24 H) ppm; ¹³C nmr (CDCl₃): δ 168.0 (C=O), 151.9, 145.2, 141.9, 139.6, 137.5, 129.9, 126.3, 113.2 (quaternary carbons), 131.6-119.5 (aromatic carbons), 29.9 (t, *J* = 142.5 Hz, CH₂), 21.85 (t, *J* = 142.5 Hz, CH₂) ppm; ms: *m/z* 516 (M⁺), 347 (M⁺ - (Ph)₂N), 270, 215.

Anal. Calcd for C₃₇H₂₈N₂O: C, 86.01; H, 5.46; N, 5.42. Found: C, 86.08; H, 5.44; N, 5.37.

1-Diphenylamino-3-diphenylmethylene-3,4-dihydro-1-benzothiopyrano[4,3-*b*]pyrrol-2(1*H*)-one (**2c**).

This compound was obtained by the general procedure as red crystals, mp 150 °C, yield 76%; ir (potassium bromide): 1715 (C=O), 1585 cm⁻¹ (C=C); ¹H nmr (CDCl₃): δ 2.89 (s, 2H), 6.15-7.6 (m, 24H) ppm.

Anal. Calcd for C₃₆H₂₆N₂OS: C, 80.87; H, 4.91; N, 5.24; S, 6.00. Found: C, 80.75; H, 5.02; N, 5.14; S, 6.04.

3-Diphenylmethylene-1-(*N*-methyl-*N*-phenylamino)-3,4-dihydro-indeno[1,2-*b*]pyrrol-2(1*H*)-one (**2d**).

This compound was obtained by the general procedure as orange crystals, mp 110 °C, yield 60%; ir (potassium bromide): 1715 (C=O), 1595 cm⁻¹ (C=C); ¹H nmr (CDCl₃): δ 3.06, 3.08 (AB-system, *J* = 14.2 Hz, 2H), 3.45 (s, 3H), 6.88-7.48 (m, 19H) ppm; ¹³C nmr (CDCl₃): δ 168.5 (C=O) 149.1, 148.0, 141.5, 138.0, 133.2, 117.8 (quaternary carbons), 132-119.0 (aromat), 39.1 (CH₃), 34.0 (CH₂) ppm.

Anal. Calcd for C₃₁H₂₄N₂O: C, 84.51; H, 5.49; N, 6.36. Found: C, 84.66; H, 5.69; N, 6.18.

3-Diphenylmethylene-1-(*N*-methyl-*N*-phenylamino)-3*H*-4,5-dihydrobenz[*g*]indol-2(1*H*)-one (**2e**).

This compound was obtained by the general procedure as orange crystals, mp 162 °C, yield 54%; ir (potassium bromide): 1705 (C=O), 1595 cm⁻¹ (C=C); ¹H nmr (CDCl₃): δ 1.80 (m, 1H), 1.91 (m, 1H), 2.74 (t, *J* = 7.2 Hz, 2H), 3.37 (s, 3H), 6.85-7.64 (m, 19H) ppm; ¹³C nmr (CDCl₃): δ 167.9 (C=O), 151.5, 149.2, 141.8, 139.8, 138.2, 137.5, 127.0, 126.6, 112.4 (quaternary carbons), 131.4-112.7 (aromatic carbons), 38.9 (CH₃), 29.8 (CH₂), 21.9 (CH₂) ppm.

Anal. Calcd for C₃₂H₂₆N₂O: C, 84.54; H, 5.77; N, 6.16. Found: C, 84.67; H, 5.83; N, 5.98.

3-Diphenylmethylene-1-(*N*-methyl-*N*-phenylamino)-3,4-dihydro-1-benzothiopyrano[4,3-*b*]pyrrole-2(1*H*)-one (**2f**).

This compound was obtained by the general procedure as orange crystals, mp 165 °C, yield 67%; ir (potassium bromide): 1705 (C=O), 1590 cm⁻¹ (C=C); ¹H nmr (CDCl₃): δ 2.73, 3.145 (AB-system, *J* = 15.1 Hz, 2H), 3.29 (s, 3H), 6.84-7.43 (m, 19H) ppm; ¹³C nmr (CDCl₃): δ 166.85 (C=O), 152.9, 148.9, 141.7, 139.3, 138.7, 133.9, 126.1, 108.6 (quaternary carbons), 38.9 (CH₃), 24.1(CH₂) ppm.

Anal. Calcd for C₃₁H₂₄N₂OS: C, 78.78; H, 5.13; N, 5.93; S, 6.78. Found: C, 78.93; H, 5.15; N, 5.61; S, 6.90.

3-Diphenylmethylene-3*H*-4,5-dihydrobenz[*g*]indole-2(1*H*)-one (**3a**).

a) Diphenylketene 0.5 ml (2.85 mmoles) and 0.75 g (2 mmoles) of **1b** were heated to 115 °C under dry nitrogen until the evolution of carbon dioxide is over. After cooling to room temperature and treating with dry ether, the crude product was recrystallized from *n*-butanol affording orange crystals (0.42 g, 60%), mp 287-290 °C.

b) Dry xylene (10 ml) and 0.3 g (0.58 mmole) of **2b** were heated at 140 °C for 1 hour. Then the solvent was evaporated and the crude residue recrystallized from *n*-butanol to give 0.1 g (46%) of **3a**.

c) During reflux of 0.3 g (0.66 mmole) of **2e** in dry xylene (10 ml) for 20 min the orange coloured product started to precipitate. After removing most of the solvent and cooling to room temperature, **3a** (0.13 g, 56%) was obtained, mp 291°C; ir (potassium bromide) : 1685 (C=O), 1610 cm⁻¹ (C=C); ¹H nmr (d₆-DMSO): δ 1.66 (t, *J* = 7.9 Hz, 2H), 2.63 (t, *J* = 7.9 Hz, 2H), 7.11- 7.52 (m, 14H), 10.33 (s, 1H) ppm; ¹³C nmr (d₆-DMSO): δ 169.3 (C=O), 148.4, 142.0, 141.0, 139.0, 137.0, 133.8, 111.0 (quaternary carbons), 28.7 (CH₂), 21.6 (CH₂) ppm; ms (70 eV): *m/z* 349 (M⁺), 180 (M⁺ - (Ph)₂C).

Anal. Calcd for C₂₅H₁₉NO: C, 85.92; H, 5.49; N, 4.01. Found: C, 85.72; H, 5.39; N, 3.93.

3-Diphenylmethylene-3,4-dihydro-1-benzothiopyrano[4,3-*b*]pyrrole-2(1*H*)-one (**3b**).

a) A mixture of 0.4 g (1.5 mmoles) of **1c** and 0.4 ml (2.3 mmoles) of diphenylketene was heated to 115 °C until the evolution of carbon dioxide ceased. Dark red crystals of **3b** (0.1 g, 26%) were obtained after cooling the reaction mixture to room temperature, triturating with ether and recrystallization from *n*-butanol; mp 220 °C.

b) A suspension of 0.2 g (0.37 mmole) of **2c** in dry xylene (10 ml) was refluxed for 1 hour. Then the solvent was removed *in vacuo* and the crude residue treated with ether and recrystallized from *n*-butanol to afford 0.025 g (18%) of dark red **3b**.

c) Compound **2f** 0.3 g (0.64 mmole) were treated under identical reaction conditions and work-up as described with b) to give 0.05 g (22%) of **3b** mp. 221 °C; ir (potassium bromide): 1685 (C=O), 1610 cm⁻¹ (C=C); ¹H nmr (CDCl₃): δ 2.97 (s, 2H), 7.07-7.48 (m, 14H), 8.5 (br s, 1H).

Anal. Calcd for C₂₄H₁₇NOS: C, 78.44; H, 4.67; N, 3.81; S, 8.72. Found: C, 78.32; H, 4.84; N, 3.64; S, 8.61.

Synthesis of Pyrrole-2,3-dione-3-thiosemicarbazones **4**.

General Procedure.

The pyrrole-2,3-dione derivatives **1a,b,f,g**, together with a slight excess of thiosemicarbazide and catalytic amounts of ethereal hydrogen chloride, were refluxed in ethanol for 1 hour. During cooling to room temperature an orange product precipitated which could be recrystallized from ethyl acetate.

1-Diphenylamino-3-thiosemicarbazono-3,4,-dihydro-indeno[1,2-*b*]pyrrol-2-one (**4a**).

This compound was obtained by the general procedure as orange crystals, mp 190 °C, yield 66%; ir (potassium bromide): 3400, 3200, 3120 (NH, NH₂), 1715 (C=O), 1590 cm⁻¹ (C=C); ¹H nmr (d₆-DMSO): δ 3.74 (s, 2H), 7.07-7.63 (m, 14H), 8.57

(s, 1H), 9.03 (s, 1H), 12.15 (s, 1H) ppm; ^{13}C nmr (d_6 -DMSO): δ 178.6 (C=S), 163.3 (C=O), 152.5, 146.9, 144.0, 132.8, 130.7, 115.3 (quarternary carbons), 31.5 (CH_2) ppm.

Anal. Calcd for $\text{C}_{24}\text{H}_{19}\text{N}_5\text{OS}$: C, 67.74; H, 4.51; N, 16.47; S, 7.53. Found: C, 67.94; H, 4.62; N, 16.42; S, 7.25.

1-Diphenylamino-3-thiosemicarbazono-3,4-dihydrobenz-[g]indol-2-one (**4b**).

This compound was obtained by the general procedure as orange crystals, mp 167 °C, yield 86%; ir (potassium bromide): 3480, 3360, 3215 (NH, NH_2), 1695 (C=O), 1575 (C=C); ^1H nmr (CDCl_3): δ 2.66 (t, $J = 8.2$ Hz, 2H), 3.01 (t, $J = 8.2$ Hz, 2H), 6.48 (s, 1H), 7.44 (s, 1H), 7.1-7.77 (m, 14H), 12.5 (s, 1H) ppm; ^{13}C nmr (CDCl_3): δ 179.7 (C=S), 162.0 (C=O), 144.7, 142.9, 138.3, 132.4, 125.5, 109.8 (quarternary carbons), 28.6 (CH_2), 17.6 (CH_2) ppm.

Anal. Calcd for $\text{C}_{25}\text{H}_{21}\text{N}_5\text{OS}$: C, 68.31; H, 4.83; N, 15.94, S, 7.29. Found: C, 68.34; H, 4.78; N, 15.95; S, 7.11.

1-(*N*-Methyl-*N*-phenylamino)-3-thiosemicarbazono-4*H*-1-benzothiopyrano[4,3-*b*]pyrrol-2-one (**4f**).

This compound was obtained by the general procedure as orange crystals, mp 196 °C, yield 52%; ir (potassium bromide): 3400, 3230, 3140 (NH, NH_2), 1705 (C=O), 1600 cm^{-1} (C=C); ^1H nmr (CDCl_3): δ 3.32 (s, 3H), 3.735, 3.855 (AB-system, $J = 14.5$ Hz, 2H), 6.43 (s, 1H), 7.38 (s, 1H), 6.84-7.73 (m, 9H), 12.49 (s, 1H) ppm.

Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{N}_5\text{OS}_2$: C, 57.69; H, 4.34; N, 17.71; S, 16.21. Found: C, 57.85; H, 4.20; N, 17.51; S, 15.78.

1-(*N*-Methyl-*N*-phenylamino)-3-thiosemicarbazono-3,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-*b*]pyrrol-2-one (**4g**).

This compound was obtained by the general procedure as orange crystals, mp 183 °C, yield 81%; ir (potassium bromide): 3400, 3230, 3140 (NH, NH_2), 1700 (C=O), 1595 cm^{-1} (C=C); ^1H nmr (CDCl_3): δ 2.17 (m, 1 H_{ax}), 2.255 (m, 1 H_{eq}), 2.41 (m, 1 H_{ax}), 2.55 (m, 1 H_{eq}), 2.80 (m, 2H), 3.22 (s, 3H), 6.48 (s, 1H), 7.45 (s, 1H), 6.79-7.32 (m, 9H) ppm.

Anal. Calcd for $\text{C}_{21}\text{H}_{21}\text{N}_5\text{OS}$: C, 64.45; H, 5.37; N, 17.90. Found: C, 64.12; H, 5.36; N, 17.51.

Synthesis of the Quinoxaline-2-ones 5.

General Procedure.

The fused pyrrolediones **1a,b,c,e,f,g** and 1,2-diaminobenzene (molar ratio 1:2) were dissolved in dichloromethane and catalytic amounts of etheral HCl were added. Then the solution was stirred for 48 hours at room temperature and the corresponding reaction products **5** either precipitated or were obtained after evaporation of the solvent and triturating with ether and recrystallized from the proper solvent (ethanol, *n*-butanol or toluene).

3-(1-Diphenylhydrazonoindan-2-yl)-quinoxalin-2(1*H*)-one (**5a**).

This compound was obtained by the general procedure as orange-yellow solid, mp 175-177 °C, yield 53% (from toluene); ir (potassium bromide): 3450 (b, NH), 1665 (C=O), 1595, 1490 cm^{-1} ; UV-VIS (methanol): λ_{max} 467 nm (ϵ 7984); ^1H nmr (d_6 -DMSO): δ 2.35 (s, CH_2), 4.2 (s, CH), 6.7-8.2 (aromat), 12.3 (NH) ppm.

Anal. Calcd for $\text{C}_{29}\text{H}_{22}\text{N}_4\text{O}$: C, 78.70; H, 5.02; N, 12.66. Found: C, 78.53; H, 4.97; N, 12.86.

3-(1-Diphenylhydrazono-1,2,3,4-tetrahydronaphthalin-2-yl)-quinoxalin-2(1*H*)-one (**5b**).

In slightly changing the general procedure, this reaction was performed in ethanol adding catalytic amounts of *p*-toluene sulfonic acid and stirring for 120 hours at room temperature. The product was obtained as yellow crystals, mp 194 °C, yield 48% (from ethanol); ir (potassium bromide): 3450 (b, NH), 1665 (C=O), 1590, 1490 cm^{-1} ; UV-VIS (methanol): λ_{max} 345 nm (ϵ 10380); ^1H nmr (CDCl_3): δ 2.2 (b, CH_2), 2.7 (b, CH_2), 4.8 (s, CH), 6.6-8.7 (m, aromat), 12.2 (s, NH) ppm; ^{13}C nmr (CDCl_3): δ 166.8 (m, C=N-N), 158.8 (m, C=N), 155.5 (d, $^3J = 2\text{Hz}$, C=O), 148.0 (t, $^3J = 8.5\text{Hz}$, N-C(phenyl)), 140.2, 133.5, 130.8, 129.9 (quarternary aryl-C), 41.7 (d, $J_{\text{CH}} = 140$ Hz, CH), 27.1, 26.7 (t, $J_{\text{CH}} = 130$ Hz, 2 CH_2) ppm.

Anal. Calcd for $\text{C}_{30}\text{H}_{24}\text{N}_4\text{O}$: C, 78.91; H, 5.31; N, 12.27. Found: C, 79.15; H, 5.30; N, 12.22.

3-(1-Diphenylhydrazonothiochroman-2-yl)-quinoxalin-2(1*H*)-one (**5c**).

This compound was obtained by the general procedure as pale yellow solid, mp 260 °C, yield 30% (from *n*-butanol); ir (potassium bromide): 3400-3100 (b, NH), 1655 (C=O), 1595, 1480 cm^{-1} ; UV-VIS (methanol): λ_{max} 340 nm (ϵ 10260). ^1H nmr (d_6 -DMSO): δ 3.42 (m, CH_2), 5.1 (m, CH), 6.3-8.7 (m, aromat), 12.20 (br s, NH) ppm.

Anal. Calcd for $\text{C}_{29}\text{H}_{22}\text{N}_4\text{OS}$: C, 73.39; H, 4.68; N, 11.81; S, 6.76. Found: C, 73.57; H, 4.40; N, 11.70; S, 6.74.

3-(1-*N*-Methyl-*N*-phenylhydrazonothiochroman-2-yl)quinoxalin-2(1*H*)-one (**5f**).

This compound was obtained by the general procedure as yellow solid, mp 195 °C, yield 78% (from ethanol); ir (potassium bromide): 3400-3000 (b, NH), 1660 (C=O), 1595, 1480 cm^{-1} ; UV-VIS (methanol): λ_{max} 350 nm (ϵ 12010); ^1H nmr (d_6 -DMSO): δ 2.84 (s, CH_3), 3.38, 3.45 (m, CH_2), 5.1 (m, CH), 6.5-8.5 (m, aromat), 12.17 (br s, NH); ^{13}C nmr (d_6 -DMSO): δ 167.3 (C=O), 158.4, 153.8, 149.7, 136.7, 131.7, 131.4, 129.4 (quarternary carbons), 42.2 (d, $J_{\text{CH}} = 139$ Hz, CH) 29.7 (t, $J_{\text{CH}} = 131$ Hz, CH_2) ppm.

Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{N}_4\text{OS}$: C, 69.87; H, 4.90; N, 13.58; S, 7.76. Found: C, 70.11; H, 5.01; N, 13.56; S, 7.90.

3-[1-(*N,N*-Diphenylhydrazino)-3,4-dihydro-2-naphthyl]-quinoxaline-2(1*H*)-one (**5i**).

Compound **5b** (0.25 g) were reacted with 5 ml of oxalic acid dichloride at 25 °C for 3 hours. The reaction mixture is diluted by adding 5 ml of anhydrous ether. After suction filtration the crude product is carefully washed with anhydrous ether and dried to afford 0.2 g (80%) of colourless **5i**, mp 180 °C; ir (potassium bromide): 3450-3300 (b, NH), 1640 (w, C=O), 1590, 1490 cm^{-1} .

Anal. Calcd for $\text{C}_{30}\text{H}_{24}\text{N}_4\text{O}$: C, 78.91; H, 5.31; N, 12.27. Found: 78.71; H, 4.97; N, 12.06.

13-Diphenylamino-5,6-dihydronaphtho[2,1:4,5]pyrrolo[2,3-*b*]-quinoxaline (**6b**).

a) Compound **5i** 0.2 g (0.44 mmol) were heated under reflux in 20 ml of aqueous ethanol (80%) for 30 minutes to afford bright yellow fluorescent needles, mp 178 °C (from *n*-butanol), yield 0.1 g (52%).

b) Compound **1b** 0.35 g (0.96 mmol), 0.2 g (1.85 mmol) of 1,2-diaminobenzene and 0.01 ml of concentrated hydrochloric acid were refluxed in 20 ml of ethanol for 48 hours. Evaporation

of the solvent and triturating with ether afforded yellow fluorescent crystals, mp 177 °C (from *n*-butanol), yield 0.25 g (60%); ir (potassium chloride): 1590, 1490 cm⁻¹, no carbonyl absorption; uv-vis (methanol): λ_{max} 370 (ϵ 19100), 420 nm (ϵ 10770); fluorescence spectrum (methanol): λ_{excit} 420 nm, λ_{emiss} 518 nm; ¹H nmr (CDCl₃): δ 3.16, 3.27 (A₂B₂-system, $J \approx 8$ Hz, 4H), 7.01-8.17 (m, 18H) ppm; ¹³C nmr (CDCl₃): δ 145.3, 143.9, 143.4, 141.6, 139.8, 139.2, 126.8, 110.5 (quaternary-C), 129.5, 129.3, 129.02, 128.8, 127.5, 127.1, 124.3, 123.5, 119.77 (aryl-CH), 29.6, 18.4 (CH₂) ppm.

Anal. Calcd for C₃₀H₂₂N₄: C, 82.15; H, 5.07; N, 12.78. Found: C, 82.31; H, 5.00; N, 12.54.

13-*N*-Methyl-*N*-phenylamino-6*H*-thiochromeno[3,4:4,5]pyrrolo[2,3-*b*]quinoxaline (**6f**).

a) Compound **1f** 0.25 g (0.78 mmol), 0.27 g (2.5 mmol) of 1,2-diaminobenzene together with 0.1 ml of concentrated hydrochloric acid were dissolved in 20 ml of ethanol and refluxed for 72 hours. After cooling and evaporation of the solvent an oily residue by triturating with ether afforded yellow fluorescent crystals, mp 175 °C (from *n*-butanol), yield 0.05 g (16%).

b) Oxalic acid dichloride (5 ml) were added to 0.5 g (1.05 mmol) of **5f** at room temperature thus forming a pulp. After 30 minutes 5 ml of anhydrous ether were added and the solid residue was refluxed in aqueous ethanol (80%) for additional 30 minutes. After cooling to room temperature 0.09 g (21%) of yellow fluorescent crystals separated, mp. 177 °C; ir (potassium bromide): 1590, 1490, 1440 cm⁻¹, no carbonyl absorption; uv-vis (methanol): λ_{max} 352 (ϵ 12100), 370 nm (ϵ 10500); fluorescence spectrum (methanol): λ_{excit} 430 nm, λ_{emiss} 535 nm; ¹H nmr (CDCl₃): complete assignment by HMBC/HMQC: δ 3.579 (s, 3H), 4.420 (s, 2H), 6.738 (d, $J = 8$ Hz, 2H), 6.911 (t, $J = 4.5$ Hz, 1H), 7.142 (t, $J = 4.5$ Hz, H-2), 7.249 (t, $J = 4.5$ Hz, H-3), 7.263 (t, $J = 4.5$ Hz, 2H), 7.493 (d, $J = 7.5$ Hz, H-4), 7.630 (t, $J = 6.5$ Hz, H-9), 7.645 (t, $J = 6.5$ Hz, H-10), 7.953 (d, $J = 8$ Hz, H-1), 7.990 (d, $J = 7.5$ Hz, H-8), 8.171 (d, $J = 8$ Hz, H-11); ¹³C nmr (CDCl₃): δ 148.9 (N-Ph), 143.2 (C-4a), 139.6 (C-7a, C-11a), 137.6 (C-6b), 136.0 (C-13a), 129.4 (C-3), 129.3 (N-Ph,m), 128.8 (C-8), 128.5 (C-11), 128.1 (C-4), 127.8 (C-9), 127.3 (C-10), 126.5 (C-2), 125.8 (C-1), 125.4 (C-13b), 119.9 (N-Ph,p), 112.6 (N-Ph,o), 105.1 (C-6a), 40.1 (CH₃), 21.3 (CH₂) ppm.

Anal. Calcd for C₂₄H₁₈N₄S: C, 73.06; H, 4.61; N, 14.21. Found: C, 73.15; H, 4.75; N, 13.99.

5,6-Dihydronaphtho[2,1:4,5]pyrrolo[2,3-*b*]quinoxaline (**7**).

Compound **6b** 0.3 g (0.68 mmol) were heated in 10 ml of dry xylene under reflux for 2 hours. After cooling to room temperature fine yellow needles precipitate, mp 350 °C <, yield 0.12 g (55%); ir (potassium bromide): 3250-3050 (b, NH), 1625(w), 1590(w), 1490 cm⁻¹; uv-vis (methanol): λ_{max} 368 (ϵ 67250), 418 nm (ϵ 9770); fluorescence spectrum: λ_{excit} 423 nm, λ_{emiss} 513 nm; ¹H nmr (d₆-DMSO): δ 3.08, 3.11 (A₂B₂-system, $J \approx 6$ Hz, 4H), 7.38-8.69 (m, 8H), 13.03 (s, 1H); ¹³C nmr (d₆-DMSO): δ 145.7 (C-12a), 142.35 (C-6b), 140.10 (C-7a), 139.89 (C-13a), 139.58 (C-11a), 134.9 (C-4a), 129.95 (C-13b), 129.41, 128.95, 128.66, 127.67, 126.24, 123.82, 120.96, 118.84 (aryl-CH), 114.01 (C-6a), 28.50 (CH₂), 18.54 (CH₂) ppm.

Anal. Calcd for C₁₈H₁₃N₃: C, 79.67; H, 4.83; N, 15.49. Found: C, 79.43; H, 4.65; N, 15.31.

3-Benzyl-2-phenylpyrrolo[2,3-*b*]quinoxaline (**9**).

Compound **8** 0.15 g (0.30 mmol) [32] was suspended in 10 ml of dry xylene and refluxed for 4 hours. The solvent was evaporated and the oily residue crystallized upon triturating with ether (10 ml) to afford 0.055 g (55%) of yellow needles, mp 210 °C; ir (potassium bromide): 3200-3000 (b, NH), 1460(w), 1410(w) cm⁻¹; uv-vis (methanol): λ_{max} 352 nm (ϵ 9200); fluorescence spectrum (methanol): λ_{excit} 352 nm, λ_{emiss} 505 nm; ¹H nmr (CDCl₃): δ 4.47 (s, 2H), 7.17-8.24 (m, 14H), 10.48 (s, 1H) ppm.

Anal. Calcd for C₂₃H₁₇N₃: C, 82.35; H, 5.12; N, 12.53. Found: C, 82.16; H, 5.11; N, 12.34.

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