Synthesis and Photochromic Behaviour of Novel 2*H*-1-Benzopyrans (=2*H*-Chromenes) Derived from Carbazololes

by **M. Manuel Oliveira***[a]), **Luis M. Carvalho**[a]), **Corinne Moustrou**[b]), **André Samat**[b]), **Robert Guglielmetti**[b]), and **Ana M. F. Oliveira-Campos**[c])

[a]) Dept. de Química, Universidade de Trás-os-Montes e Alto Douro, P-5000 Vila Real Phone 00351259350273; fax 00351259350480; e-mail moliveir@utad.pt

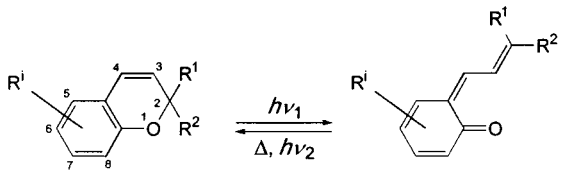
[b]) LCMOM, UMR 6114 CNRS, Université de la Mediterranée, F-13288 Marseille Cedex 9

[c]) Centro de Química, IBQF, Universidade do Minho, P-4710 Braga

The synthesis and photochromic properties of new 2,2-diphenyl-2*H*-1-benzopyrans, fused to an indole moiety, are described. All compounds exhibit photochromic behaviour in solution at room temperature. The heteroanellation effects are variable and depend on the position and geometry of the fused indole moiety. A general bathochromic shift in the spectra of the open forms is observed. The presence of a *N*-methyl group prevents the broadening of the absorption spectra and promotes the instability of some photoinduced forms of compounds with the indole moiety fused at the 5,6 positions of the 2*H*-1-benzopyran skeleton. The enhanced photocolouration efficiency in the near-UV and the kinetics of thermal bleaching indicate that the novel compounds with an indole moiety fused at the 6,7 positions, particularly those with a linked thiophene moiety, are very interesting molecules for applications in the field of variable optical absorption systems.

1. Introduction. – The 2*H*-chromenes (*i.e.* benzo- and naphthopyrans) constitute an important family of oxygenated heterocycles whose interesting photochromic properties only began to be systematically studied in the last decade. Analogously to the spiropyrans, the photochromism involves a photoinduced breaking of the $C(sp)^3-O$ bond of the pyran ring leading to an equilibrium between the closed form (CF) and a set of stereoisomers of the open form (OF) of variable stabilities, constituting a system with a distinct absorption spectrum, generally in the VIS range [1]. The system reverts through a thermal pathway to its original closed form (*Scheme*).

Scheme



Colourless closed form Coloured s-*trans* open form

In principle, the process can be repeated many times, but fatigue occurs as a result of irreversible side reactions leading to the photodegradation of the system. This constitutes the main limitation on the commercial applicability of these systems as variable-transmission materials, and important advances are appearing in the field of their stabilization.

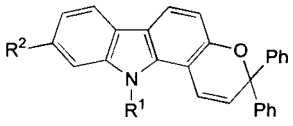
In the domain of materials that undergo variable optical absorption, intense research efforts are being made with the aim to design systems that are responsive to solar radiation at room temperature and exhibit interesting photochromic properties, such as a high efficiency for colouring covering an extended range of the VIS absorption spectrum, low quantum yield for bleaching with VIS light, fast thermal fading at room temperature, and an extended lifetime [2]. In the case of 2*H*-1-benzopyrans, the main strategies for structure modifications that allow an improvement the photochromic properties include heteroaromatic anellation with five or six-membered rings and appropriate substitution at the molecule [3]. The replacement of one or both alkyl groups at the tetrahedral sp^3 C-atom of the 2*H*-1-benzopyrans by aromatic substituents without an α-H-atom, such as phenyl or spirofluorene, seems to be indispensable for observing photochromism at room temperature. An extended conjugated π system is an important condition for the generation of stable open forms at room temperature [4][5].

As the photochromic parameters depend significantly on the anellated heteroaromatic moieties and on the relative positions of the heteroanellation at the 2*H*-1-benzopyran skeleton, we decided to study new 2*H*-1-benzopyrans containing a carbazole moiety [6] to investigate the photochromic behaviour of these systems. In this paper, we report the synthesis and the spectrokinetic properties in solution of further heteroanellated 2,2-diphenyl-2*H*-1-benzopyrans, obtained in continuation of our work in this field.

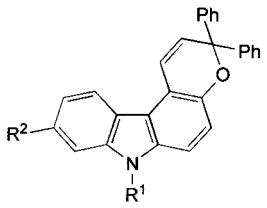
2. Results and Discussion. – 2.1 *Synthesis.* Among the several methods available to obtain heteroanellated 2,2-diaryl-2*H*-1-benzopyranes [7], two synthetic approaches were considered, both involving the transformation of the corresponding heterocyclic phenols in a 'one-pot reaction'. *Method A* is based on the organotitanium-mediated condensation of α,β-unsaturated aldehydes with phenols. It involves the reaction of an α,β-unsaturated aldehyde with a Ti^{IV} phenolate, obtained by adding $Ti(OEt)_4$ to the phenol and separating the EtOH formed by azeotropic distillation, leading to *C*-alkylation in *ortho*-position; subsequent electrocyclization yields the 2*H*-1-benzopyran moiety [8][9]. *Method B* is based on the thermal condensation of a suitable alkynol and the phenol in an apolar solvent under acid catalysis (*p*-toluenesulfonic acid or pyridinium *p*-toluenesulfonate). The reaction proceeds *via* a *Claisen*-like [3,3]-sigmatropic rearrangement of the obtained prop-2-ynyl aryl ether, and a subsequent [1,5]-sigmatropic shift and electrocyclization leads to the 2*H*-1-benzopyran [9–11]. According to these methodologies, the preparation of 2*H*-1-benzopyrans containing the carbazole ring system requires the availability of carbazolols as starting materials (see, *e.g.* **1a**, obtained from **1b** *via* **1c**). This was achieved as already described [6].

2.2. *Photochromic Properties.* The compounds described belong to a series of 2,2-diphenyl-2*H*-1-benzopyrans fused to an indole moiety at different sites, namely at the 5,6-, 6,7-, or 7,8-positions of the 2*H*-1-benzopyran ring system (see **2**–**14**).

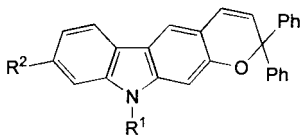
All of the compounds described exhibit photochromic behaviour at room temperature in toluene solutions. Their spectrokinetic parameters (λ_{max} of the coloured form, colourability, and rate constant of thermal bleaching) [12] are summarized in the *Table*, together with those of two corresponding naphthopyrans [13] for comparison, *i.e.*, 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (Ref 1) and 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran (Ref 2).



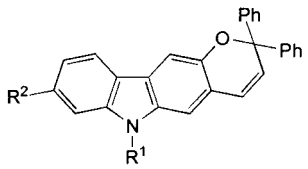
2 R^1 = H, R^2 = H
3 R^1 = Me, R^2 = H
4 R^1 = H, R^2 = Br
5 R^1 = Me, R^2 = Br



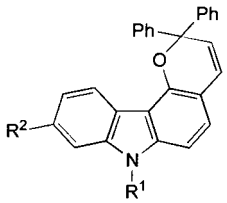
6 R^1 = H, R^2 = H



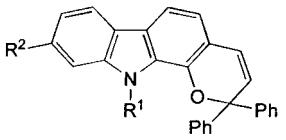
7 R^1 = Me, R^2 = H
8 R^1 = Me, R^2 = Br
9 R^1 = Me, R^2 = CN
10 R^1 = Me, R^2 = thienyl



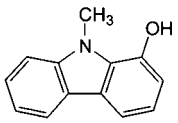
11 R^1 = Me, R^2 = H



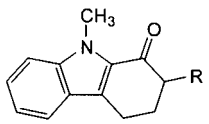
12 R^1 = H, R^2 = H
13 R^1 = Me, R^2 = H



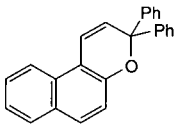
14 R^1 = Me, R^2 = H



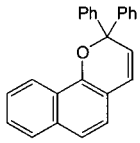
1a



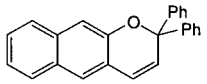
1b R = H
c R = Br



2,2-Diphenyl-2*H*-naphtho[1,2-*b*]pyran (Ref 2)



3,3-Diphenyl-3*H*-naphtho[2,1-*b*]pyran (Ref 1)



2,2-Diphenyl-2*H*-naphtho[2,3-*b*]pyran (Ref 3)

Table. *Maximum Wavelengths* (λ_{max}) *of the Coloured Forms* (λ_1(OF), λ_2(OF)), *Colourability* (A_{01}, A_{02}) *and Fading Rate* (k_Δ) *of the Described* 2H-*1-Benzopyrans and of Two Reference Compounds in Toluene Solutions* ($2.5 \cdot 10^{-5}$ M at 25°).

	Type of anellation (N position)[a])	λ_1(OF) [nm]	A_{01}	λ_2(OF) [nm]	A_{02}	k_Δ (amplitude) (s^{-1}) (%)
2 [8]	5,6 (N–C(5))	443	1.1	590	0.29	0.17 (94); 0.02 (6)
3	5,6 (N–C(5))	456	1.2	–	–	0.61 (93); 0.03 (7)
4	5,6 (N–C(5))	448	1.2	586	0.4	0.18
5	5,6 (N–C(5))	445	1.3	–	–	0.79 (95); 0.04 (5)
6 [6]	5,6 (N–C(6))	460	0.68	549	0.61	0.04
7 [6]	6,7 (N–C(7))	444	2.5	–	–	0.19 (48); 0.02 (52)
8	6,7 (N–C(7))	454	5.5	–	–	0.20 (81); 0.02 (19)
9	6,7 (N–C(7))	460	3.2	–	–	0.44 (34); 0.03 (66)
10	6,7 (N–C(7))	461	8.4	–	–	0.13 (84); 0.01 (16)
11	6,7 (N–C(6))	478	0.61	568	0.69	0.05
12 [6]	7,8 (N–C(7))	415	1.8	542	0.26	0.04
13	7,8 (N–C(7))	431	1.8	557	0.21	0.01 (65); <0.01 (35)
14	7,8 (N–C(8))	434	1.9	580	0.36	0.04 (90); <0.001 (10)
Ref 1[b])	5,6 (–)	432	0.84	–	–	0.09
Ref 2[c])	7,8 (–)	403	1.08	481	1.62	0.002

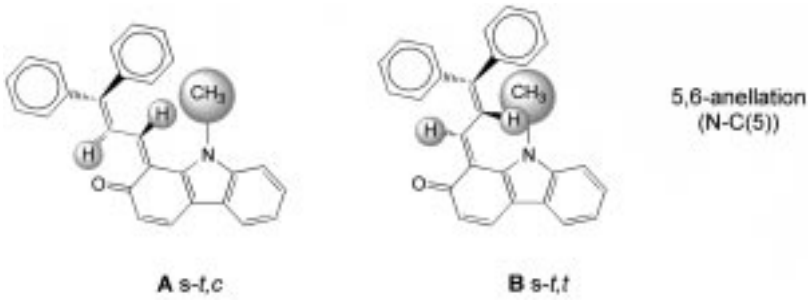
[a]) The *N* position is relative to the 2*H*-1-benzopyran moiety. [b]) Ref 1 = 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran. [c]) Ref 2 = 2,2-diphenyl-2*H*-naphtho[1,2-*b*]pyran (from [13]).

The effects of the heteroanellation and of some substituents at the molecule on the photoactivity of these compounds can be evaluated and discussed by comparison with values obtained for reference compounds [4][13]. All the closed forms of the 2*H*-1-benzopyrans synthesized that contain a carbazole moiety have absorption bands in the near-UV (see *Exper. Part*). This means that these compounds may be interesting for applications where the activation by sunlight (heliochromism) is desired.

2.3. *Anellation Effects.* From a general point of view, the introduction of a fused indole moiety, whatever the anellation site, led to a global bathochromic shift in the spectra of the open forms when compared to the spectra of the reference naphthopyrans.

5,6-Anellation. With respect to the 2*H*-1-benzopyran moiety, two different 5,6-anellation types may be considered: in one, the N(sp^2)-atom is bonded to C(5) (see **2**–**5**), and in the other, the N(sp^2)-atom is bonded to C(6) (see **6**). In both types the compounds containing a Me group at the N-atom show a more pronounced bathochromic shift. An important feature is that the VIS absorption spectra of the coloured forms of compounds **2** and **4** (NH–C(5)) display two bands at *ca.* 440 and 580 nm, whereas compounds **3** and **5** (MeN–C(5)) display one single band at *ca.* 450 nm. This markedly different behaviour can be explained by the strong steric hindrance induced by the Me group, which prevents, in the open form, the necessary planarity to allow the extension of the π-electron conjugation between the Ph groups at C(2) (tetrahedral C-atom in the closed form) and the remaining aromatic rings of the molecule. This effect, which causes the loss of the interesting broadening of the VIS absorption spectra of the open forms, is less important when the Me group is removed (see **2** and **4**) and disappears in compound **6**, where the geometry of the fused indole

moiety is reversed (see **A** and **B** where, for simplicity, only the *trans* quinoid open forms, believed to be more stable, are depicted) or when the trivalent N-atom is substituted with a bivalent N-atom as it can be seen from literature data [4].



A s-*t*,*c* **B** s-*t*,*t*

It is apparent that the observed splitting into two bands of the VIS absorption of the open forms of 2*H*-1-benzopyrans heteroanellated at the 5,6-positions, can be ascribed to an extension of the conjugated system involving the two parts of the molecule. This assumption is substantiated by the VIS absorption pattern of the open forms of **12**–**14**, which are devoid of the steric hindrance just described, and which also display two bands with similar λ_{max} as **2** and **4**. The effect of this steric destabilization of the open forms can also be seen in the k_{Δ} values for **2** and **3**: compound **3** with an *N*-Me group exhibits a fading rate almost 3 times greater than the corresponding compound **2** without the *N*-Me group (see also k_{Δ} of **4** and **5**).

6,7-Anellation. The corresponding reference naphthopyran is 2,2-diphenyl-2*H*-naphtho[2,3-*b*]pyran; its poor photochromicity (photochromic only at very low temperatures [1][14]) is the result of the loss of aromaticity of both rings in the naphthalene nucleus present in the open form. Compounds **7**–**10** should be considered substituted 2,2-diphenyl-2*H*-1-benzopyrans, and, as such, they exhibit a VIS absorption spectrum with a single band. Besides a small bathochromic shift, the enhanced colourability due to the groups introduced by the heteroanellation and subsequent modifications is noteworthy. As a group, the 2*H*-1-benzopyrans are less photochromic, less fatigue resistant, and less responsive to solar radiation than the corresponding photochromic naphthopyran due to their UV absorption at lower wavelengths [1][14]. However, compounds **7**–**10** exhibit a strong photocolouration efficiency and, for the closed forms, activation bands in the near-UV (see *Exper. Part*) and, in the cases of **7**, **8**, and **10**, interesting kinetics of thermal bleaching. All these characteristics indicate that the introduction of an indole moiety at the 6,7 position represents a structural modification that leads to an important improvement of the photochromic properties of 2*H*-1-benzopyrans, making them interesting for variable optical-transmission materials.

7,8-Anellation. Compounds **12**–**14** represent the 7,8 type of anellation. Compound **14** has the geometry of the fused indole moiety reversed relative to **13**. The open forms of these compounds exhibit a reasonably high stability (very slow thermal-bleaching rates) due to the less important nonbonding interactions between the ethylenic H-atom and a ring H-atom, as observed with naphthopyrans [9]. The same reason should explain the pattern of the VIS absorption spectra of the open form with two absorption bands covering a large wavelength range, like the reference naphthopyran (Ref 2) and

markedly different from Ref 1. The absence of important nonbonding interactions in the open forms allows for better planarity and, consequently, leads to extended delocalization of the π-electrons of the whole molecule. This situation is not much altered by reversing the geometry of the indole fusion site or by the presence of a *N*-Me group, as confirmed by the similar absorbance characteristics of the open forms of **12**–**14**. The observed slow fading rates discourage application of these compounds in optical-transmission materials.

2.4. *Substituent Effects.* In this series of compounds, the influence of a few electron-withdrawing substituents, all located at C(7) of the carbazole moiety, was tested. The introduction of the Br group is interesting as it allows further modifications of the molecule, but it does not lead to important modifications in the photochromic characteristics. The most significant effect promoted by this weak electron-withdrawing group (inductive effect) is observed for **8**, which exhibits an enhanced colourability and better fading kinetics (enlargement of the amplitude of the faster phase) compared to **7**. The CN group, a stronger electron-withdrawing group with π-electrons, induces a bathochromic shift and a faster fading rate for **9**, although smaller than that observed when CN is directly bonded to the conjugated system in naphthopyrans [15]. The introduction of a thienyl group leads to a compound **10** with very interesting photochromic properties, namely a substantial colourability increase compared to **7**, without significant modification of the thermal stability of the coloured form.

3. Conclusion. – The synthesis of indole-fused 2*H*-1-benzopyrans, with photochromic activity in solution at room temperature, was achieved by the usual methods. The observed spectrokinetic parameters are dependent on the relative position and geometry of anellation. The electronic absorption spectra of some photoinduced forms of molecules with the indole moiety fused at the 5,6 and 7,8 positions of the benzopyran moiety display an interesting splitting into two bands, covering a large wavelength range. However, the existence of important nonbonding interactions, preventing the necessary planarity to allow optimal delocalization of the π-electrons of the whole molecule, destroys this effect. The coloured forms of molecules with the indole moiety fused at the 6,7 positions exhibit VIS absorption spectra with a single band and should be considered substituted 2,2-diphenyl-2*H*-1-benzopyrans with enhanced photochromic properties. The observed intense photocolouration efficiencies (colourabilities) and kinetics of thermal bleaching of molecules with this 6,7-anellation pattern is remarkable, particularly when additional substitution with a thiophene moiety is present (see **10**); thus, these structures are specially interesting with respect to their application as variable optical transmission systems.

Experimental Part

1. *General.* Column chromatography (CC): silica gel *60* (70–230 mesh). M.p.: uncorrected. IR Spectra: *Perkin-Elmer FTIR-1600* spectrometer; KBr discs; wave numbers in cm^{-1}. UV/VIS Spectra: $1.0 \cdot 10^{-5}$ M toluene soln.; *Varian-Cary 50* spectrometer; λ_{max} in nm. Photochromic measurements: $2.5 \cdot 10^{-5}$ M toluene soln. at 25°; *Warner & Swasey* spectrometer; cell pathlength 10 cm; flash energy 60 J. ^{1}H- and ^{13}C-NMR Spectra: *Varian Unity Plus* (300 and 75.4 MHz, resp.), *Bruker BM-250* (250 and 62.9 MHz, resp.) or *Bruker AMX-400* (400 or 100.5 MHz, resp.); in $CDCl_3$ soln., unless stated otherwise; δ in ppm, J in Hz; assignments from irradiation experiments. MS: *AutoSpecE* spectrometer. Elemental analyses: *LECO-932-CNS* analyser.

2. *9-Methyl-9*H*-carbazol-1-ol* (**1a**) [7][16]. A mixture of copper(II) bromide (1.91 g, 8.56 mmol) and 2,3,4,9-tetrahydro-9-methyl-1*H*-carbazol-1-one (**1b**; 0.85 g, 4.28 mmol) in AcOEt (20 ml) was stirred under reflux and Ar for 2 h. From the hot soln., copper(I) bromide was filtered off. The mother liquor was diluted with CH_2Cl_2, washed with H_2O, dried ($MgSO_4$), and evaporated. The residue was purified by CC (silica gel; petroleum ether/Et_2O 7:3): *2-bromo-2,3,4,9-tetrahydro-9-methyl-1*H*-carbazol-1-one* (**1c**; 0.31 g, 26%). Off-white solid. M.p. 83–85°. ^{1}H-NMR ((D$_6$)acetone): 2.62 (*m*, 2 H–C(4)); 3.19 (*m*, 2 H–C(3)); 4.12 (*s*, MeN); 4.89 (*t*, H–C(2)); 7.23 (*dt*, *J* = 1.2, 7.5, H–C(6)); 7.52 (*dt*, *J* = 1, 7, H–C(7)); 7.58 (*dd*, *J* = 2, 8, H–C(8)); 7.80 (*dd*, *J* = 2, 8, H–C(5)).

A soln. of **1c** (0.31 g, 1.12 mmol) in DMF (20 ml) was heated in the presence of LiBr (0.103, 1.18 mmol) and Li_2CO_3 (0.087, 1.17 mmol) under Ar for 1 h at 150°. The mixture was poured into aq. NH_4Cl soln. and extracted with CH_2Cl_2. The org. layer was washed twice with H_2O, dried ($MgSO_4$), and evaporated: **1a** (0.219 g, 99%). Brown oil. ^{1}H-NMR ((D$_6$)acetone): 4.22 (*s*, MeN); 6.92 (*dd*, *J* = 2, 8, H–C(2)); 6.96 (*t*, *J* = 8, H–C(3)); 7.18 (*dt*, *J* = 2, 8, H–C(6)); 7.42–7.50 (*m*, H–C(7), H–C(8)); 7.64 (*dd*, *J* = 1, 8, H–C(4)); 8.07 (br. *d*, *J* = 8, H–C(5)); 8.90 (*s*, OH).

3. *Pyrano-carbazoles*. 3.1. *General Procedure: Method A*. A soln. of the carbazole (10 mmol) in anh. toluene (50 ml), under Ar, was stirred until all the carbazole was dissolved. A soln. of titanium(IV) ethoxide (10 mmol) in anh. toluene (40 ml) was added within 10 min. The mixture was refluxed for 30 min, and the EtOH formed was slowly distilled (up to 1/3 of the initial volume). The mixture was cooled to r.t., and a soln. of 3,3-diphenylprop-2-enal (10 mmol in 40 ml of anh. toluene; 7 mmol in 40 ml of anh. toluene for 9*H*-carbazol-4-ol) was added dropwise. The mixture was refluxed for 2–6 h, cooled to r.t., alkalinized with 2M NaOH, and extracted with CH_2Cl_2 (3 × 40 ml). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue purified by CC.

3.2. *General Procedure: Method B*. To a stirred mixture of the 9-methyl-9*H*-carbazole (10 mmol) and 1,1-diphenylprop-2-yn-1-ol (11 mmol) in dry CH_2Cl_2 (10–25 ml) under Ar, a cat. amount of pyridinium *p*-toluenesulfonate (PPTS) was added. The mixture was kept at r.t. or heated to reflux (TLC monitoring).

*3,11-Dihydro-11-methyl-3,3-diphenylpyrano[3,2-*a*]carbazole* (**3**). To a mixture of **2** (0.500 g, 1.34 mmol), 50% NaOH soln. (1 ml), benzene (5 ml), and benzyltriethylammonium chloride (0.092 g, 0.04 mmol), MeI (0.285 g, 2.01 mmol) was added dropwise under stirring and Ar [17]. The mixture was left for 2 h at r.t., poured into hot H_2O (10–20 ml), and stirred again for 4 h. The light yellow solid formed was filtered, washed with H_2O, and dissolved in CH_2Cl_2. The org. soln. was dried ($MgSO_4$) and evaporated and the residue purified by CC (silica gel, CH_2Cl_2/pentane 1:1): **3** (56%). White solid. M.p. 231–233°. IR: 3052, 1631, 1608, 1587, 1484, 1463, 1442, 1344, 1211, 1024, 964, 738, 696. UV/VIS (closed form): 294, 334 (sh), 346 (sh), 362. ^{1}H-NMR ((D$_6$)acetone): 4.10 (*s*, 3 H); 6.43 (*d*, *J* = 10, 1 H); 6.94 (*dd*, *J* = 7.5, 1, 1 H); 7.16 (*dt*, *J* = 7.5, 1, 1 H); 7.22–7.28 (*m*, 2 H); 7.32–7.40 (*m*, 5 H); 7.48 (*d*, *J* = 8.4, 1 H); 7.56–7.60 (*m*, 4 H); 7.66 (*d*, *J* = 10, 1 H); 7.94 (*d*, *J* = 8.4, 1 H); 7.98 (*dd*, *J* = 7.5, 1, 1 H). ^{13}C-NMR: 32.9 (*q*); 81.7 (*s*); 106.3 (*s*); 108.3 (*d*); 109.7 (*d*); 118.3 (*s*); 119.1 (*d*); 119.3 (*d*); 120.0 (*d*); 121.0 (*d*); 122.9 (*s*); 124.5 (*d*); 127.0 (*d*, 4 C); 127.2 (*d*); 127.4 (*d*, 2 C); 128.0 (*d*, 4 C); 137.3 (*s*); 141.6 (*s*); 144.8 (*s*, 2 C), 152.1 (*s*). MS: 387 (100, $M^{+\cdot}$), 372 (7), 310 (77), 295 (13), 267 (7), 220 (8), 191 (9), 165 (13), 155 (8). Anal. calc. for $C_{28}H_{21}NO$: C 86.79, H 5.46, N 3.62; found: C 86.99, H 5.42, N 3.68.

*9-Bromo-3,11-dihydro-3,3-diphenylpyrano-[3,2-*a*]carbazole* (**4**). According to *Method A* (reflux 3 h 30 min). The pink solid residue (1.187 g) was purified by CC (silica gel, CH_2Cl_2/pentane 2:3): **4** (65%). White solid. M.p. 221–223°. IR: 3434 (N–H), 1635, 1612, 1583, 1446, 1218, 1079, 1052, 798, 698. UV/VIS (closed form): 284, 294, 328 (sh), 338, 354. ^{1}H-NMR: 6.28 (*d*, *J* = 9.8, 1 H); 6.83 (*d*, *J* = 9.8, 1 H), 6.88 (*d*, *J* = 8.5, 1 H); 7.24 (*dd*, *J* = 7.7, 1.5, 1 H); 7.25–7.27 (*m*, 2 H); 7.33 (*t*, *J* = 7.7, 4 H); 7.40 (*d*, *J* = 1.6, 1 H); 7.48–7.50 (*m*, 4 H); 7.65 (*d*, *J* = 8.1, 1 H); 7.66 (*d*, *J* = 8.84, 1 H); 7.79 (*s*, 1 H). ^{13}C-NMR (62.9 MHz): 82.5 (*s*); 104.9 (*s*); 110.2 (*d*); 113.4 (*d*); 117.2 (*s*); 117.8 (*s*); 117.9 (*d*); 120.5 (*d*); 120.9 (*d*); 122.6 (*s*); 122.9 (*d*); 127.0 (*d*, 4 C); 127.6 (*d*, 2 C); 128.1 (*d*, 4 C); 128.2 (*d*); 136.1 (*s*); 140.1 (*s*); 146.6 (*s*, 2 C); 151.4 (*s*). FAB-MS (pos. mode): 453 (100, $[M+1]^+$), 374 (56), 295 (14), 191 (13), 165 (12), 77 (6). Anal. calc. for $C_{27}H_{18}BrNO$: C 71.69, H 4.09, N 3.08; found: C 71.59, H 4.17, N 3.08.

*9-Bromo-3,11-dihydro-11-methyl-3,3-diphenylpyrano[3,2-*a*]carbazole* (**5**). To a mixture of **4** (1.091 g; 2.41 mmol), 50% NaOH soln. (2 ml), benzene (18 ml), and benzyltriethylammonium chloride (0.016 g, 0.072 mmol), MeI was added (1.028 g, 7.24 mmol) dropwise under stirring and Ar [17]. The mixture was left at r.t. for 2 h and then poured into hot H_2O (30 ml) and left under stirring for 3 h. Et_2O was added. After separation, the org. phase was dried ($MgSO_4$) and the solvent evaporated. The residue was purified by CC (silica gel, CH_2Cl_2/pentane 30:70 → 35:65): **5** (64%). Light yellow crystalline solid. M.p. 177–178°. IR: 2933, 1598, 1577, 1436, 1218, 1056, 1020, 798, 694. UV/VIS (closed form): 300, 330, 346, 362. ^{1}H-NMR: 3.97 (*s*, 3 H); 6.25 (*d*, *J* = 10, 1 H); 6.93 (*d*, *J* = 8.6, 1 H); 7.25–7.35 (*m*, 7 H); 7.40 (*d*, *J* = 10, 1 H); 7.44 (*d*, *J* = 1.5, 1 H); 7.48–7.52 (*m*,

4 H); 7.73 (*d*, *J* = 8.2, 1 H); 7.78 (*d*, *J* = 8.2, 1 H). ^{13}C-NMR (62.9 MHz): 29.7 (*q*); 81.8 (*s*); 106.5 (*s*); 110.3 (*c*); 111.5 (*d*); 117.7 (*s*); 118.0 (*s*); 119.6 (*d*); 120.2 (*d*); 121.0 (*d*); 121.9 (*s*); 122.4 (*d*); 127.0 (*d*, 4 C); 127.5 (*d*, 2 C); 127.6 (*d*); 128.1 (*d*, 4 C); 137.4 (*s*); 142.4 (*s*); 144.6 (*s*, 2 C); 152.3 (*s*). MS: 467 (5, $[M+1]^+$), 388 (2), 281 (6), 221 (7), 123 (20), 109 (32), 95 (51), 83 (61), 69 (87), 57 (100). Anal. calc. for $C_{28}H_{20}BrNO$: C 72.11, H 4.32, N 3.00; found: C 72.15, H 4.32, N 3.08.

*8-Bromo-2,10-dihydro-10-methyl-2,2-diphenylpyrano[2,3-*b*]carbazole* (**8**). According to *Method A* (reflux for 2 h 30 min). The residue was submitted to CC (silica gel, CH_2Cl_2/pentane 35 : 65 → 45 : 55): **8** (36%). White solid. M.p. 241 – 244°. IR: 3058, 1631, 1596, 1484, 1446, 1236, 1199, 1060, 1000, 941, 881, 811, 759, 698. UV/VIS (closed form): 288, 304, 344, 362. ^{1}H-NMR: 3.70 (*s*, 3 H); 6.17 (*d*, *J* = 9.9, 1 H); 6.83 (*d*, *J* = 9.6, 1 H); 6.92 (*s*, 1 H); 7.26 – 7.31 (*m*, 3 H); 7.36 (*t*, *J* = 7.8, 4 H); 7.44 (*d*, *J* = 1.5, 1 H); 7.50 – 7.53 (*m*, 4 H); 7.63 (*s*, 1 H); 7.74 (br. *d*, *J* = 8.1, 1 H). ^{13}C-NMR (62.9 MHz): 29.2 (*q*); 83.0 (*s*); 96.5 (*d*); 111.4 (*d*); 114.9 (*s*); 116.5 (*s*); 118.0 (*s*); 118.1 (*d*); 120.4 (*d*); 122.0 (*s*); 122.1 (*d*); 124.2 (*d*); 126.8 (*d*); 127.1 (*d*, 4 C); 127.5 (*d*, 2 C); 128.1 (*d*, 4 C); 141.9 (*s*); 142.4 (*s*); 145.0 (*s*, 2 C); 152.5 (s). FAB-MS (pos. mode): 467 (100, $[M+1]^+$), 388 (44), 338 (37), 289 (23), 191 (22), 180 (15), 165 (19), 77 (41). Anal. calc. for $C_{28}H_{20}BrNO$: C 72.11, H 4.32, N 3.00; found: C 72.36, H 4.32, N 2.87.

*2,10-Dihydro-10-methyl-2,2-diphenylpyrano[2,3-*b*]carbazole-8-carbonitrile* (**9**). To a soln. of **8** (0.500 g, 1.07 mmol) in DMF (10 ml), 1,1′-bis(diphenylphosphino)ferrocene (0.119 g, 0.215 mmol) and $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone; 0.050 g, 0.054 mmol) were added. When the mixture reached 90°, $Zn(CN)_2$ (0.151 g, 1.29 mmol) was added within 2 h, and heating was continued for 3 h [18]. The mixture was cooled to r.t., filtered through *Celite 545*, the latter washed with CH_2Cl_2, and the filtrate evaporated. The residue was poured into H_2O and extracted with sat. NaCl soln. The org. layer was dried ($MgSO_4$) and evaporated and the residue purified by CC (silica gel, CH_2Cl_2/pentane 4 : 1): **9** (30%). White solid. M.p. 187 – 189°. IR: 3056, 2925, 2219 (CN), 1633, 1486, 1448, 1236, 1201, 1160, 1000, 698. UV/VIS (closed form): 286, 306 (sh), 318 (sh), 334 (sh), 364, 382. ^{1}H-NMR ((D$_6$)acetone): 3.86 (*s*, 3 H); 6.39 (*d*, *J* = 9.9, 1 H); 6.92 (*d*, *J* = 10, 1 H); 7.16 (*s*, 1 H); 7.28 – 7.30 (*m*, 2 H); 7.37 (*t*, *J* = 8, 4 H); 7.45 (*dd*, *J* = 8, 1.5, 1 H); 7.54 – 7.57 (*m*, 4 H); 7.85 (*d*, *J* = 1, 1 H); 7.87 (*s*, 1 H); 8.08 (br. *d*, *J* = 7.8, 1 H). ^{13}C-NMR ((D$_6$)acetone, 62.9 MHz): 29.8 (*q*); 83.8 (*s*); 97.7 (*d*); 107.6 (*s*); 113.7 (*d*); 116.6 (*s*); 116.8 (*s*); 119.9 (*d*); 120.8 (*d*); 123.0 (*d*); 124.9 (*d*); 127.6 (*d*, 4 C); 128.2 (*d*, 2 C); 128.4 (*d*); 129.0 (*d*, 4 C); 133.2 (*s*); 141.1 (*s*); 144.5 (*s*); 146.1 (*s*, 2 C); 154.6 (*s*). MS: 412 (100, $M^{+\cdot}$), 335 (99), 320 (12), 291 (7), 206 (11), 191 (17), 165 (9), 146 (19), 77 (6). Anal. calc. for $C_{29}H_{20}N_2O$: C 84.44; H 4.89; N 6.79; found: C 84.15, H 4.90, N 6.45.

*2,10-Dihydro-10-methyl-2,2-diphenyl-8-(2-thienyl)pyrano[2,3-*b*]carbazole* (**10**). To a soln. of **8** (0.200 g, 0.430 mmol) in dry DMF (9 ml) under Ar, 5,5-dimethyl-2-thienyl[1,3,2]dioxoborinane (0.109 g, 0.515 mmol), anh. K_3PO_4 (0.137 g, 0.644 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.010 g, $8.59 \cdot 10^{-3}$ mmol) were added [19][20][21]. The mixture was left at r.t. for 24 h and then filtered through *Celite 545* and washed with benzene (250 ml). The org. phase was washed with sat. NaCl soln. (4 × 250 ml), dried ($MgSO_4$), and evaporated and the residue submitted to CC (silica gel, CH_2Cl_2/pentane 1 : 1): **10** (99%). White solid. M.p. 278 – 279°. IR: 3058, 2923, 1631, 1606, 1484, 1446, 1234, 1002, 819, 754, 696. UV/VIS (closed form): 280, 300, 344, 362. ^{1}H-NMR ((D$_5$)pyridine, 400 MHz): 3.59 (*s*, 3 H); 6.39 (*d*, *J* = 10, 1 H); 7.00 (*d*, *J* = 10, 1 H); 7.20 (*dd*, *J* = 5, 4, 1 H); 7.22 (*s*, 1 H); 7.31 (*t*, *J* = 7, 2 H); 7.42 (*t*, *J* = 8, 4 H); 7.47 (*d*, *J* = 5, 1 H); 7.62 (*d*, *J* = 4, 1 H); 7.70 (*dd*, *J* = 8, 1, 1 H); 7.76 – 7.79 (*m*, 5 H); 7.83 (*s*, 1 H); 8.10 (*d*, *J* = 8, 1 H). ^{13}C-NMR ((D$_5$)pyridine, 100.5 MHz): 29.4 (*q*); 83.8 (*s*); 97.7 (*d*); 106.7 (*d*); 115.8 (*s*); 117.9 (*s*); 118.7 (*d*); 119.2 (*d*); 120.8 (*d*); 123.7 (*s*); 124.0 (*d*); 125.3 (*d*); 125.6 (*d*); 127.6 (*d*); 127.9 (*d*, 4 C); 128.3 (*d*, 2 C); 129.0 (*d*, 4 C); 129.1 (*d*); 132.1 (*s*); 142.6 (*s*); 143.9 (*s*); 146.4 (*s*, 2 C); 146.6 (*s*); 153.4 (*s*). MS: 469 (100, $M^{+\cdot}$), 392 (57), 377 (6), 235 (8), 196 (10). Anal. calc. for $C_{32}H_{23}SNO$: C 81.36, H 4.94, S 6.83, N 2.98; found: C 81.36, H 5.14, S 6.65, N 2.80.

*2,6-Dihydro-6-methyl-2,2-diphenylpyrano[3,2-*b*]carbazole* (**11**). According to *Method B* (reflux for 88 h). CC (silica gel, Et_2O/pentane 35 : 65) gave **11** (13%). Yellow crystalline solid. M.p, 229 – 230°. IR: 2921, 2852, 1587, 1484, 1463, 1444, 1322, 1278, 1193, 1081, 989, 950, 802, 759, 692. UV/VIS (closed form): 316, 328, 386, 402. ^{1}H-NMR (400 MHz): 3.73 (*s*, 3 H); 6.38 (*d*, *J* = 9.8, 1 H); 7.13 (*s*, 1 H); 7.14 (*s*, 1 H); 7.18 (*dt*, *J* = 7.6, 1, 1 H); 7.20 – 7.24 (*m*, 2 H); 7.27 – 7.30 (*m*, 4 H); 7.32 (br. *d*, *J* = 7.5, 1 H), 7.42 (*dt*, *J* = 7.7, 1, 1 H), 7.50 – 7.53 (*m*, 4 H); 7.58 (*d*, *J* = 9.8, 1 H); 8.16 (br. *d*, *J* = 7.6, 1 H). ^{13}C-NMR (100.5 MHz): 29.0 (*q*); 82.0 (*s*); 108.6 (*d*); 108.8 (*d*); 115.5 (*d*); 115.8 (*s*); 118.1 (*s*); 118.7 (*d*); 121.6 (*d*); 122.4 (*d*); 125.5 (*d*); 125.8 (*s*); 127.2 (*d*, 4 C), 127.5 (*d*, 2 C); 128.1 (*d*, 4 C); 130.1 (*d*); 136.6 (*s*); 141.7 (*s*); 145.0 (*s*, 2 C); 146.1 (*s*). MS: 387 (100, $M^{+\cdot}$), 310 (63), 295 (6), 196 (10), 165 (8). Anal. calc. for $C_{28}H_{21}NO$: C 86.79, H 5.46, N 3.62, found: C 86.84, H 5.42, N 3.63.

*2,7-Dihydro-7-methyl-2,2-diphenylpyrano[3,2-*c*]carbazole* (**13**). To a mixture of **12** (0.356 g, 0.954 mmol), 50% NaOH soln. (0.7 ml), benzene (5 ml) and benzyltriethylammonium chloride (0.007 g, 0.029 mmol), MeI (0.203 g, 1.43 mmol) was added dropwise with stirring and under Ar [17]. The mixture was left at r.t. for 3 h

30 min and then poured into hot H_2O (10–20 ml) and left stirring for 4 h. A light yellow solid was filtered off, washed with H_2O and dissolved in CH_2Cl_2. The org. soln. was dried ($MgSO_4$) and evaporated and the residual light yellow solid (430 mg) purified by CC (silica gel, CH_2Cl_2/pentane 2:3): **13** (50%). White crystalline solid. M.p. 144–146°. IR: 3056, 3025, 1619, 1602, 1488, 1467, 1390, 1332, 1286, 1226, 1112, 1002, 752, 698. UV/VIS (closed form): 288, 324, 342, 360. ^{1}H-NMR: 3.76 (*s*, 3 H); 6.08 (*d*, *J* = 9.8, 1 H); 6.76 (*d*, *J* = 9.8, 1 H); 6.85 (*d*, *J* = 8.2, 1 H); 7.11 (*d*, *J* = 8.2, 1 H); 7.20–7.22 (*m*, 2 H); 7.23–7.28 (*m*, 5 H); 7.34 (br. *d*, *J* = 7.6, 1 H); 7.45 (*dt*, *J* = 8.3, 1, 1 H); 7.57–7.61 (*m*, 4 H); 8.45 (br. *d*, *J* = 7.7, 1 H). ^{13}C-NMR (62.9 MHz): 29.2 (*q*); 83.2 (*s*); 101.0 (*d*); 108.0 (*d*); 111.3 (*s*); 111.9 (*s*); 119.4 (*d*); 121.9 (*s*); 123.1 (*d*); 124.1 (*d*); 124.3 (*d*); 124.6 (*d*); 125.0 (*d*); 126.1 (*d*, 4 C); 127.3 (*d*, 2 C); 128.1 (*d*, 4 C); 140.8 (*s*); 142.9 (*s*); 145.6 (*s*, 2 C); 148.7 (*s*). MS: 387 (84, $M^{+\cdot}$), 310 (100), 295 (7), 194 (8), 165 (6), 91 (12). Anal. calc. for $C_{28}H_{21}NO$: C 86.79, H 5.46, N 3.62; found: C 86.50, H 5.46, N 3.46.

2,11-Dihydro-11-methyl-2,2-diphenylpyrano[2,3-a]carbazole (**14**). According to *Method A* (reflux for 2 h 50 min). The residue was purified by CC (silica gel, CH_2Cl_2/pentane 2:3): **14** (42%). Greenish solid. M.p. 136–138°. IR: 3054, 3021, 1617, 1488, 1467, 1444, 1284, 1224, 973, 815, 740, 698. UV/VIS (closed form): 314, 326, 349 (sh), 367, 387. ^{1}H-NMR: 4.21 (*s*, 3 H); 6.06 (*d*, *J* = 9.8, 1 H); 6.80 (*d*, *J* = 9.8, 1 H); 6.89 (*d*, *J* = 7.9, 1 H); 7.18 (*dt*, *J* = 7.9, 1, 1 H); 7.25–7.28 (*m*, 2 H); 7.30–7.35 (*m*, 5 H); 7.43 (*dt*, *J* = 7, 1.1, 1 H); 7.49–7.53 (*m*, 4 H); 7.56 (*d*, *J* = 7.9, 1 H); 7.97 (br. *d*, *J* = 7.7, 1 H). ^{13}C-NMR: 32.1 (*q*); 83.2 (*s*); 108.5 (*d*); 112.7 (*d*); 118.0 (*s*); 118.1 (*d*); 118.8 (*d*); 120.0 (*d*); 122.8 (*s*); 124.7 (*d*); 125.5 (*d*); 125.7 (*d*); 126.4 (*d*); 127.1 (*d*, 4 C); 127.4 (*d*, 2 C); 128.1 (*d*, 4 C); 129.3 (*s*); 141.8 (*s*); 144.7 (*s*, 2 C); 151.9 (*s*). MS: 387 (100, $M^{+\cdot}$), 370 (5), 310 (26), 295 (5), 196 (9), 165 (6). Anal. calc. for $C_{28}H_{21}NO$: C 86.79, H 5.46, N 3.62; found: C 86.84, H 5.37, N 3.47.

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