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Received January 11, 1995

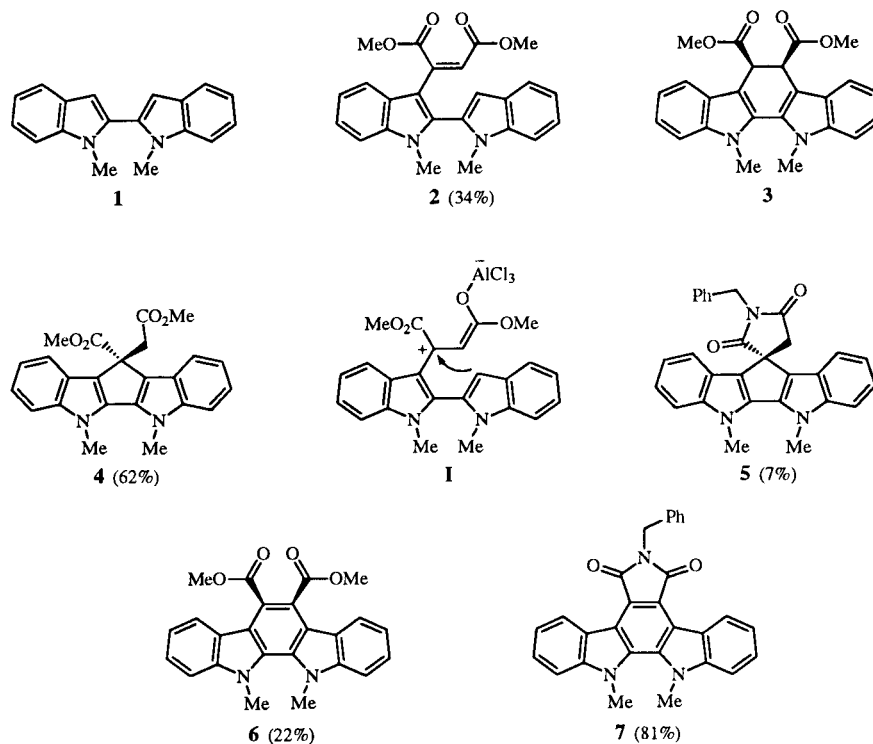
[a] Dedicated with best wishes to Professor Dr. H. Möhrle, Düsseldorf, on the occasion of his 65th birthday

2,2'-Bis(*N*-methylindolyl) **1** reacts with dimethyl acetylenedicarboxylate to furnish the 3-dimethyl maleoyl-substituted 2,2'-bisindolyl **2**. Compound **2** cyclizes under aluminum trichloride catalysis according to a polar process to give a cyclopenta[2,1-*b*:3,4-*b'*]diindole derivative **4**. Reaction of compound **4** with benzylamine yields the spiro derivative **5**. Photochemically-induced 1,6-electrocyclization of compound **2** gives rise to the indolo[2,3-*a*]carbazole **6** directly, which is readily transformed to the pyrrolo-annulated carbazole **7** by treatment with benzylamine.

J. Heterocyclic Chem., **32**, 1335 (1995).**Introduction.**

Electrophilic substitution and thermally-induced cyclization reactions of 2,2'-bis(*N*-methylindolyl) **1** have given rise to several potential protein kinase C inhibitors [1-3] possessing the substructure of the alkaloid staurosporine [4]. In continuation of our studies on the cyclization reactions of indole derivatives [5], we now report a further ring closure reaction of the bisindolyl **1**

with dimethyl acetylenedicarboxylate and subsequent cyclization reactions of the thus formed 3-dimethyl maleoyl-substituted 2,2'-bisindolyl **2**. In this context it should be mentioned that, besides the thermally-induced reactions, the photochemically-induced cyclization of a bisindolyl derivative is reported for the first time. Additionally, based on an X-ray analysis, we now revise the constitutions of two cyclization products previously reported from our laboratories.



Results and Discussion.

The 3-vinylindole derivative **2** is readily available by reaction of the bisindolyl **1** with dimethyl acetylenedicarboxylate [2]. This compound cyclizes thermally under the influence of a Lewis acid catalyst, for example in the presence of aluminum trichloride. However, the cyclization product does not have the dihydroindolo[2,3-*a*]carbazole structure **3** reported previously [2,3] on the basis of some unfortunate and misleading coincidences of nmr signals. According to the results of an X-ray analysis, the structure of the cyclization product must be revised and is now unambiguously demonstrated to have the constitution shown by formula **4**. The cyclization of **2** to a five-membered ring system is probably induced by formation of a polar complex intermediate **I** in the presence of aluminum trichloride. The cyclization reaction is fully compatible with the Baldwin ring closure rules and is characterized as an energetically favored, 5-*exo*-trig process [6].

Reaction of **4** with refluxing benzylamine gave rise to the bisindolyl spiro-derivative **5**. A previously discussed dihydroindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazoledione structure [3] as a constitutional isomer of **5**, logically formed from **3**, has to be ruled out. Taken together, the X-ray crystal structure of **4** and some further detailed nmr spectroscopic studies (see Experimental) confirm the structures of the bisindolocyclopentadienes **4** and **5**.

However, the photochemically-induced 1,6-electrocyclization reaction of **2** yielded the indolo[2,3-*a*]carbazole **6** directly which, in turn, was readily transformed in refluxing benzylamine to the pyrrolo-annelated carbazole **7**. The product **7** was also obtained in 12% yield by a thermal, one-pot procedure directly from **2** in the presence of benzylamine. According to semiempirical quantum chemical AM1 calculations [7], the 1,3,5-hexatriene unit of **2** is involved in a LUMO-controlled, photochemically allowed conrotatory process (Figure 1) with subsequent hydrogen elimination.

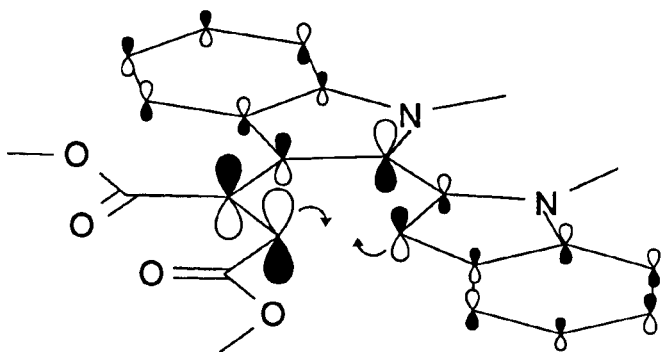


Figure 1. LUMO of the 3-vinylindole **2** (geometry optimized structure) according to AM1 calculations [7] for a conrotatory 6 π electrocyclization; $E_{\text{LUMO}} = -0.73$ eV.

X-Ray Crystallographic Data of Methyl 5,6-Dimethyl-11-methoxycarbonylmethyl-6,11-dihydro-5*H*-cyclopenta-

[2,1-*b*;3,4-*b'*]diindole-11-carboxylate (**4**) and its Structure Determination.

A single crystal of **4**, obtained from an ethyl acetate solution, with the approximate size 0.32 x 0.16 x 0.42 mm was employed for the X-ray analysis. The compound crystallized in the orthorhombic space group *Fddd* (No.70) with $a = 30.5890(9)$, $b = 33.323(4)$, and $c = 18.043(1)$ Å; $Z = 32$; $V = 18388(2)$ Å³; $D_c = 1.29$ g cm⁻³. The intensities were measured on an Enraf Nonius Turbo CAD 4 diffractometer in the $\omega/2\theta$ scan mode. The total of 14285 reflections (monoclinic measurement) in the range of $1.5 < \theta < 70^\circ$ utilizing CuK α radiation ($\lambda = 1.5418$ Å) and 4356 unique reflections were used for the structure determination. The structure was solved by direct methods using SIR92 [8] and refined by full matrix least squares (SHELXL 93) [9] with anisotropic displacement parameters for the non-hydrogen atoms. The positions of the hydrogen atoms were obtained from difference Fourier maps and refined isotropically. The final R1-value is 0.055 for 2816 reflections with $I \geq 2\sigma(I)$.

The atomic coordinates and displacement parameters are recorded in Table 1, the bond lengths and bond angles are given in Tables 2 and 3, while Figure 2 shows a view [10] of the molecule with the numbering system.

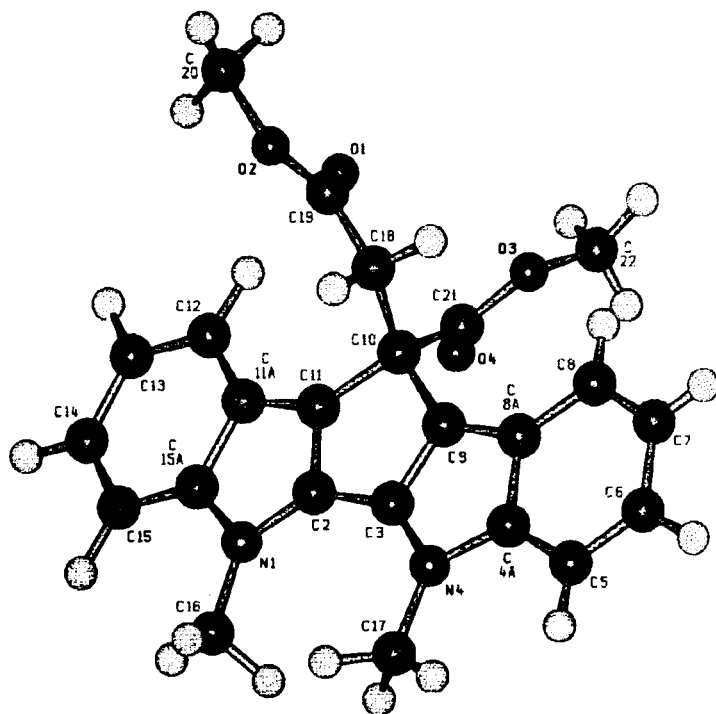


Figure 2. Molecular structure of compound **4** in the crystal state (SCHAKAL plot); space group: *Fddd*. For the sake of better clarity, the solvent molecule of ethyl acetate is omitted. The numbering scheme shown does not correspond to that of the IUPAC nomenclature.

Table 1

Positional Parameters and Equivalent Displacement Parameters (\AA^2)
with Estimated Standard Deviations in Parenthesis

$$U_{eq} = (1/3) * \sum \sum U_{ij} a_i^* a_j^* a_k^*$$

Atom	X	Y	Z	U_{eq}
N1	0.5116(1)	0.02440(7)	0.04930(6)	0.0479(7)
C2	0.4477(1)	0.04467(7)	0.03747(7)	0.0413(7)
C3	0.4229(1)	0.07766(7)	0.00932(7)	0.0423(7)
N4	0.4511(1)	0.10784(6)	-0.01748(6)	0.0463(6)
C4A	0.3905(1)	0.12953(8)	-0.03375(7)	0.0458(8)
C5	0.3906(2)	0.16228(8)	-0.06305(8)	0.0570(9)
C6	0.3233(2)	0.17882(9)	-0.07472(8)	0.0612(10)
C7	0.2573(2)	0.16381(9)	-0.05784(8)	0.0604(10)
C8	0.2564(2)	0.13134(8)	-0.02884(7)	0.0521(8)
C8A	0.3241(1)	0.11329(7)	-0.01642(7)	0.0437(7)
C9	0.3472(1)	0.08004(7)	0.01071(7)	0.0420(7)
C10	0.3161(1)	0.04933(7)	0.04279(7)	0.0413(7)
C11	0.3867(1)	0.02683(7)	0.05620(7)	0.0411(7)
C11A	0.4131(1)	-0.00717(7)	0.08181(7)	0.0438(7)
C12	0.3814(2)	-0.03759(8)	0.10830(8)	0.0541(9)
C13	0.4276(2)	-0.0661(1)	0.1287(1)	0.066(1)
C14	0.5046(2)	-0.0654(1)	0.1236(1)	0.070(1)
C15	0.5376(2)	-0.03647(9)	0.09747(9)	0.0599(10)
C15A	0.4915(1)	-0.00742(8)	0.07692(8)	0.0482(8)
C16	0.5872(1)	0.0344(1)	0.0376(1)	0.063(1)
C17	0.5281(2)	0.11779(9)	-0.02624(9)	0.0612(10)
C18	0.2812(1)	0.07711(7)	0.07647(7)	0.0459(8)
C19	0.2495(1)	0.05018(8)	0.10999(7)	0.0475(8)
O1	0.2233(1)	0.01460(6)	0.10693(6)	0.0660(7)
O2	0.2536(2)	0.07104(7)	0.14465(6)	0.0892(10)
C20	0.2235(3)	0.0487(1)	0.1795(1)	0.120(2)
C21	0.2605(1)	0.01830(8)	0.02354(7)	0.0432(7)
O3	0.19685(9)	0.03925(6)	0.01504(5)	0.0542(6)
O4	0.27191(9)	-0.01913(6)	0.01511(6)	0.0580(6)
C22	0.1424(2)	0.0143(1)	-0.00672(9)	0.067(1)
C1L	0.4566(3)	0.0711(1)	0.1744(1)	0.110(2)
C2LA	0.5070(10)	0.0912(4)	0.1434(5)	0.106(6)*
O1L	0.4653(2)	0.1250	0.1250	0.090(1)
C2LB	0.4980(7)	0.1054(4)	0.1575(4)	0.069(4)*
O2L	0.5539(3)	0.1186(2)	0.1710(2)	0.106(2)

* occupation factor 0.5.

Table 2

Bond Lengths (\AA) with Estimated Standard Deviations in Parenthesis

N1	-C2	1.366(3)	C11A	-C12	1.405(3)
N1	-C15A	1.387(3)	C11A	-C15A	1.424(3)
N1	-C16	1.453(3)	C12	-C13	1.384(4)
C2	-C3	1.448(3)	C13	-C14	1.400(4)
C2	-C11	1.378(3)	C14	-C15	1.378(4)
C3	-N4	1.381(3)	C15	-C15A	1.397(4)
C3	-C9	1.369(3)	C18	-C19	1.501(3)
N4	-C4A	1.388(3)	C19	-O1	1.191(3)
N4	-C17	1.452(3)	C19	-O2	1.322(3)
C4A	-C5	1.399(4)	O2	-C20	1.452(4)
C4A	-C8A	1.420(3)	C21	-O3	1.345(3)
C5	-C6	1.371(4)	C21	-O4	1.197(3)
C6	-C7	1.395(4)	O3	-C22	1.441(3)
C7	-C8	1.386(4)	C1L	-C2LA	1.51(2)
C8	-C8A	1.402(4)	C1L	-C2LB	1.41(1)
C8A	-C9	1.423(3)	C2LA	-O1L	1.42(2)
C9	-C10	1.530(3)	C2LA	-O2L	1.50(2)
C10	-C11	1.516(3)	O1L	-C2LB	1.37(1)
C10	-C18	1.542(3)	O1L	-C2LB	1.37(1)
C10	-C21	1.523(3)	C2LB	-O2L	1.17(1)
C11	-C11A	1.427(3)			

Table 3

Bond Angles ($^\circ$) with Estimated Standard Deviations in Parenthesis

C15A	-N1	-C2	106.9(2)	C12	-C11A	-C11	136.3(2)
C16	-N1	-C2	128.3(2)	C15A	-C11A	-C11	105.5(2)
C16	-N1	-C15A	124.8(2)	C15A	-C11A	-C12	118.3(2)
C3	-C2	-N1	139.8(2)	C13	-C12	-C11A	118.7(2)
C11	-C2	-N1	111.3(2)	C14	-C13	-C12	122.0(3)
C11	-C2	-C3	108.8(2)	C15	-C14	-C13	121.0(3)
N4	-C3	-C2	140.4(2)	C15A	-C15	-C14	117.4(2)
C9	-C3	-C2	108.9(2)	C11A	-C15A	-N1	109.3(2)
C9	-C3	-N4	110.7(2)	C15	-C15A	-N1	128.0(2)
C4A	-N4	-C3	106.4(2)	C15	-C15A	-C11A	122.6(2)
C17	-N4	-C3	128.4(2)	C19	-C18	-C10	113.3(2)
C17	-N4	-C4A	125.1(2)	O1	-C19	-C18	126.1(2)
C5	-C4A	-N4	127.9(2)	O2	-C19	-C18	111.4(2)
C8A	-C4A	-N4	109.8(2)	O2	-C19	-O1	122.6(2)
C8A	-C4A	-C5	122.3(2)	C20	-O2	-C19	116.8(2)
C6	-C5	-C4A	117.5(2)	O3	-C21	-C10	110.8(2)
C7	-C6	-C5	121.3(2)	O4	-C21	-C10	125.5(2)
C8	-C7	-C6	121.8(2)	O4	-C21	-O3	123.6(2)
C8A	-C8	-C7	118.6(2)	C22	-O3	-C21	115.8(2)
C8	-C8A	-C4A	118.5(2)	O1L	-C2LA	-C1L	105.9(9)
C9	-C8A	-C4A	105.1(2)	C2LB	-C2LA	-C1L	68. (2)
C9	-C8A	-C8	136.4(2)	C2LB	-C2LA	-O1L	73. (2)
C8A	-C9	-C3	108.0(2)	O2L	-C2LA	-C1L	98.5(9)
C10	-C9	-C3	110.9(2)	O2L	-C2LA	-O1L	99.0(9)
C10	-C9	-C8A	140.8(2)	C2LA	-O1L	-C2LA	115.8(9)
C11	-C10	-C9	100.2(2)	C2LB	-O1L	-C2LA	115.6(8)
C18	-C10	-C9	108.7(2)	C2LB	-O1L	-C2LA	115.6(8)
C18	-C10	-C11	112.3(2)	C2LB	-O1L	-C2LB	129.1(7)
C21	-C10	-C9	109.3(2)	C2LA	-C2LB	-C1L	86. (2)
C21	-C10	-C11	113.3(2)	O1L	-C2LB	-C1L	114.5(8)
C21	-C10	-C18	112.4(2)	O1L	-C2LB	-C2LA	80. (2)
C10	-C11	-C2	111.0(2)	O2L	-C2LB	-C1L	124.1(8)
C11A	-C11	-C2	107.0(2)	O2L	-C2LB	-C2LA	107. (2)
C11A	-C11	-C10	142.0(2)	O2L	-C2LB	-O1L	121.2(9)

Structure Determination Summary

Crystal Data

Empirical Formula	$C_{24}H_{22}N_2O_4 \cdot 1/2 C_4H_8O_2$ (1/2 Ethyl acetate)
Formula Weight	462 g mol ⁻¹
Crystal Size (mm)	0.32 x 0.16 x 0.42 mm ³
Crystal System	Orthorhombic
Space Group	F ddd
Unit Cell Dimensions	a = 30.5830 (9) \AA b = 33.323 (4) \AA c = 18.043 (1) \AA V = 18388 (2) \AA^3 Z = 32 F(000) = 7552
Density	1.290 g cm ⁻³
Temperature	300 K
Data Collection	
Diffraction	Turbo-CAD4 (Enraf-Nonius)
Radiation	CuK α , graphite monochromator
Scan Type	$\omega/2\theta$
Scan Range	0.7 + 0.14*tan (θ) and 25% right and left for Background Measurement
Measuring Range	1.5° < θ < 70.0° 0 ≤ h ≤ 22, -27 ≤ k ≤ 37 -27 ≤ l ≤ 40
Reflections Collected	14285 (Monoclinic measured and transformed later to orthorhombic space group)
Independent Reflections	4356 ($R_{int} = 0.0533\%$)
Observed Reflections	2816 ($I/F/\sigma(F) > 4.0$)

Structure Determination Summary (continued)

Data Correction, Solution and Refinement

Correction	Lorentz- and polarisation correction Variation of standard reflections corrected with a Cubic Spline Function
Solution	Program: SIR92-92 (Direct methods)
Refinement	Program: SHEL X-93 (Full-Matrix Least-Squares) 327 refined parameters, weights scheme: $w = 1/[\sigma^2(F_o^2) + (0.0818 * P)^2 + 7.81 * P]$ Hydrogens atoms were located in Difference Fourier Calculations (except methyl-H) and refined as riding atoms with isotropic thermal parameters. Non-hydrogen atoms were anisotropically refined.
Extinction parameter	$g = 0.00012 (1)$
Final R-Value	$wR2 = 0.1639 (R1 = 0.0550)$ for observed reflections and 0.0876 for all reflections)
Goodness-of-Fit	$S = 1.020$
Maximal deviation of Parameters in last Cycle	0.000 * e.s.d.
Maximal Peak in Difference Fourier Map	0.22, -0.21 eÅ ⁻³
Remark	The solvent molecule ethyl acetate cocrystallizes in a disordered manner.

EXPERIMENTAL

Materials and Techniques.

All reactions were carried out in highly pure and strictly anhydrous solvents under an argon atmosphere. Flash chromatography was performed with silica gel 60 (Merck, 0.040-0.063 mm particle size). The petroleum ether used had the boiling range 40-60°. Melting points were determined on Büchi SMP-20 and Electrothermal IA 920 instruments and are not corrected. Elemental analyses were performed with a Carlo Erba Strumentazione 1106 apparatus. The infrared spectra were recorded on a Beckmann IR 4220 spectrophotometer. The electron impact (70 eV) mass spectra were obtained using a Varian MAT CH 7A spectrometer. The ¹H nmr spectra at 400 MHz and ¹³C nmr spectra at 100.6 MHz were recorded on a Bruker AM 400 spectrometer. The photochemical reactions were carried out using a Normag Photoreactor with fluid circulation. The UV-lamp TQ 150 from Heraeus was used (radiation pathlengths: 44 mm, radiation power: 150 W, emitted radiation in the range of 200-600 nm).

2,2'-Bis(*N*-methylindolyl) (1).

To a solution of 6 g (0.046 mole) of *N*-methylindole in anhydrous diethyl ether (70 ml), 36 ml of a 1.6 *M* solution of *n*-butyllithium in *n*-hexane were slowly added dropwise during 20 minutes. The reaction mixture was heated at reflux under an inert gas atmosphere for 4 hours and then allowed to cool to room temperature. Anhydrous copper(II) chloride (3.18 g, 0.024 mole) was then added in three portions and the mixture was again refluxed for 2 hours. After being allowed to cool to room temperature, the mixture was poured into ice/water. The dirty brown-green precipitate was filtered off, the organic layer was separated, and the aqueous phase was extracted twice with

dichloromethane. The combined organic phases were dried with sodium sulfate, concentrated, and the residue was recrystallized from dichloromethane/ethyl acetate. The product **1** was obtained as light yellow crystals in 41% yield (2.42 g), mp 173-174° (dichloromethane/ethyl acetate); ir (potassium bromide): ν 3200, 1460, 1445, 1415, 1370, 1350, 1320, 1300, 1235, 1175, 1160, 1130, 1100, 1050, 920, 810, 790, 745, 735, 675, 655 cm⁻¹; ms: m/z (%) 261 ($M^+ + 1$, 19), 260 (M^+ , 100), 259 (39), 244 (10), 130 ($M^+ - N$ -methylindole, 21); ¹H nmr (400 MHz, deuteriochloroform): δ 3.73 (s, 6H, N-CH₃, N'-CH₃), 6.69 (s, 2H, C3-H, C3'-H), 7.20-7.24 (m, 2H, C6-H, C6'-H), 7.33 (mc, 2H, C5-H, C5'-H), 7.43 (d, ³J = 8.2 Hz, 2H, C7-H, C7'-H), 7.72 (d, ³J = 7.8 Hz, 2H, C4-H, C4'-H); ¹³C nmr (100.6 MHz, deuteriochloroform): δ 30.6 (N-CH₃, N'-CH₃), 104.3 (C3, C3'), 109.5 (C7, C7'), 119.9 (C4, C4'), 120.6 (C5, C5'), 122.1 (C6, C6'), 127.5 (C3a, C3a'), 131.4 (C2, C2'), 137.8 (C7a, C7a').

Anal. Calcd. for C₁₈H₁₆N₂ (260.34): C, 83.04; H, 6.19; N, 10.76. Found: C, 82.75; H, 6.23; N, 10.78.

3-(2-Dimethyl Maleoyl)-1-methyl-2-(1-methylindol-2-yl)indole (2).

The 2,2'-bisindolyl **8** (400 mg, 1.8 mmoles) was dissolved in 40 ml of dry bromobenzene and the solution was stirred for 5 minutes before the dropwise addition of 240 μ l (284 mg, 2.0 mmoles) of dimethyl acetylenedicarboxylate followed by 400 mg of aluminum trichloride. The resultant mixture was stirred for 2 hours at room temperature, kept for 2 hours at room temperature, and then poured into ice/water. The organic layer was separated, the aqueous layer was washed with dichloromethane, and the combined organic phases were dried with sodium sulfate. After concentration of the mixture, the residue was purified by column chromatography (petroleum ether/ethyl acetate, 3/1). The product was obtained as yellow crystals in 34% yield (210 mg), mp 159-161° (petroleum ether/ethyl acetate); uv-vis (ethanol): λ max nm (ϵ) 262 (19416); ms: m/z (%) 403 ($M^+ + 1$, 12), 402 (M^+ , 44), 343 (33), 342 (16), 312 (23), 311 (100), 285 (12), 284 (51), 283 (17), 269 (26), 268 (17), 171 (11); ¹H nmr (400 MHz, dideuteriodichloromethane): δ 3.12 (s, 3H, NCH₃ or OCH₃), 3.52 (s, 3H, NCH₃ or OCH₃), 3.55 (s, 3H, NCH₃ or OCH₃), 3.68 (s, 3H, NCH₃ or OCH₃), 6.32 (s, 1H, vinyl-H), 6.68 (s, 1H, C3'-H), 7.16-7.21 (m, 1H, aromatic H), 7.26-7.44 (m, 5H, aromatic H), 7.67 (d, ³J = 7.8 Hz, 1H, aromatic H), 7.88 (d, ³J = 7.4 Hz, 1H, aromatic H).

Anal. Calcd. for C₂₄H₂₂N₂O₄ (402.45): C, 71.63; H, 5.51; N, 6.96. Found: C, 71.60; H, 5.56; N, 6.96.

Methyl 5,6-Dimethyl-11-methoxycarbonylmethyl-6,11-dihydro-5H-cyclopenta[2,1-*b*:3,4-*b'*]diindole-11-carboxylate (4).

Compound **2** (140 mg) was dissolved in anhydrous dichloromethane (40 ml) and aluminum trichloride (100 mg) was added. The resultant mixture was stirred for 2 hours, water was then added, the organic phase was separated, and the aqueous phase was washed twice with dichloromethane. The combined organic phase and washings were dried with sodium sulfate and then concentrated on a rotary evaporator. The residue was purified by flash chromatography with petroleum ether/ethyl acetate (2/1) as eluent. The product **4** was obtained as colorless crystals in 62% yield (87 mg), mp 187-189° (petroleum ether/ethyl acetate). From the X-ray and nmr structural analyses it is apparent that the solvent ethyl acetate has cocrystallized with compound **4** in the ratio 2:1; ms: m/z (%) 403 ($M^+ + 1$, 26), 402 (M^+ , 100), 344 (15), 343 (63), 330 (13),

329 (54), 285 (15), 284 (66), 269 (22), 268 (14); ^1H nmr (400 MHz, dideuteriodichloromethane): δ 3.16 (s, 2H $-\text{CH}_2-$), 3.71 (s, 6H 2 x NCH_3), 4.06 (s, 6H, 2 x OCH_3), 7.15-7.22 (m, 4H, aromatic H), 7.38-7.40 (m, 2H aromatic H), 7.71-7.73 (m, 2H, aromatic H); ^{13}C nmr (100.6 MHz, dideuteriodichloromethane): δ 33.5 (2 x NCH_3), 42.1 ($-\text{CH}_2-$), 51.3 (C_q), 52.1 (OCH_3), 52.9 (OCH_3), 110.6 (2 x C_1), 119.5 (2 x C_1), 121.0 (2 x C_1), 121.5 (2 x C_1), 124.5 (2 x C_q), 126.7 (2 x C_q), 138.2 (2 x C_q), 141.4 (2 x C_q), 172.5 (CO), 173.4 (CO).

Anal. Calcd. for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_4 \cdot 1/2 \text{C}_4\text{H}_8\text{O}_2$ (446.50): C, 69.94; H, 5.87; N, 6.27. Found: C, 70.31; H, 5.64; N, 6.87.

5,6-Dimethyl-6,11-dihydro-5*H*-cyclopenta[2,1-*b*:3,4-*b'*]diindole-11-spiro-3'-1'-benzyl-2',5'-dione (5).

Compound 4 (210 mg) was dissolved in 6 ml of benzylamine and the solution was then heated under reflux for 19 hours. The reaction mixture was allowed to cool to room temperature and then concentrated. The residue was dried over silica gel and then separated by flash chromatography (toluene/acetone, 9:1). The compound 5 was obtained as colorless crystals in 7% yield (17 mg), mp $>300^\circ$ (petroleum ether/ethyl acetate); ms: m/z (%) 445 (M^+ , 25), 421 (32), 420 (100), 286 (22), 285 (71), 284 (39), 272 (10), 271 (44), 270 (19), 269 (21), 268 (11), 256 (28), 255 (18); ^1H nmr (400 MHz, dideuteriodichloromethane): δ 3.33 (s, 2H, $-\text{CH}_2-\text{CO}-$), 4.12 (s, 6H, 2 x NCH_3), 4.87 (s, 2H, benzyl-H), 6.95-7.02 (m, 4H, aromatic H), 7.15-7.19 (m, 2H, aromatic H), 7.33-7.35 (m, 3H, aromatic H), 7.41 (d, $^3\text{J} = 8.4$ Hz, 2H, aromatic H), 7.44-7.47 (m, 2H, aromatic H); ^{13}C nmr (100.6 MHz, dideuteriodichloromethane): δ 33.6 (2 x NCH_3), 38.1 (C_s , $-\text{CH}_2-\text{CO}-$), 43.7 (C_s , benzyl-C), one C_q signal overlaps with a solvent peak, 111.0 (2 x C_1), 117.1 (2 x C_1), 121.2 (2 x C_1), 121.7 (2 x C_1), 123.0 (2 x C_q), 126.5 (C_q), 128.5 (C_1), 129.2 (2 x C_1), 129.4 (2 x C_1), 136.7 (2 x C_q), 139.4 (2 x C_q), 141.3 (2 x C_q), 176.0 (2 x CO).

Anal. Calcd. for $\text{C}_{29}\text{H}_{23}\text{N}_3\text{O}_2$ (445.52): C, 78.18; H, 5.20; N, 9.43. Found: C, 78.15; H, 5.59; N, 9.63.

4,5-Bis(methoxycarbonyl)-10,11-dimethyl-10,11-dihydroindolo[2,3-*a*]carbazole (6).

Compound 2 (295 mg, 0.73 mmole) was dissolved in ethanol (250 ml) and irradiated at $17-20^\circ$. After completion of the reaction, the solvent was evaporated under reduced pressure and the residue recrystallized from ethanol. The product 6 was obtained as light yellow crystals in 22% yield (65 mg), mp $213-214^\circ$ (ethanol); ir (potassium bromide): ν 1710, 1580, 1545, 1475, 1435, 1390, 1355, 1325, 1285, 1250, 1230, 1175, 1130, 1070, 985, 940, 830, 780, 740, 690 cm^{-1} ; ms: m/z (%) 401 ($\text{M}^+ + 1$, 28), 400 (M^+ , 100), 369 (15), 200 (11); ^1H nmr (400 MHz, dideuteriodichloromethane): δ 4.07 (s, 6H, 2 x NCH_3 or 2 x OCH_3), 4.18 (s, 6H, 2 x NCH_3 or 2 x OCH_3), 7.30-7.34 (m, 2H, aromatic H), 7.57-7.58 (m, 4H, aromatic H), 8.17 (d, $^3\text{J} = 8.0$ Hz, 2H, aromatic H); ^{13}C nmr (100.6 MHz, dideuteriodichloromethane): δ 37.1 (2 x NCH_3), 53.0 (2 x OCH_3), 111.0 (2 x C_1), 120.0 (4 x C_q), 121.2 (2 x C_1), 122.7 (2 x C_1), 123.5 (2 x C_q), 126.9 (2 x C_1), 131.5 (2 x C_q), 145.2 (2 x C_q), 169.5 (2 x CO).

Anal. Calcd. for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_4$ (400.43): C, 71.99; H, 5.03; N, 7.00. Found: C, 71.38; H, 5.05; N, 6.91.

6-Benzyl-12,13-dimethyl-5,7,12,13-tetrahydroindolo[2,3-*a*]pyrrolo[3,4-*c*]carbazole-5,7-dione (7).

Compound 2 (100 mg) was dissolved in benzylamine (35 ml) and the solution heated under reflux for 3 days. The resultant mixture was concentrated on a rotary evaporator and the residue dried with silica gel. Purification by flash chromatography with petroleum ether/ethyl acetate (5/4) gave the product 7 as yellow-orange crystals in 81% yield (90 mg), mp $238-240^\circ$ (petroleum ether/ethyl acetate); ir (potassium bromide): ν 3300, 1685, 1655, 1575, 1470, 1430, 1410, 1350, 1320, 1240, 1125, 1070, 1020, 740, 710, 700 cm^{-1} ; ms: m/z (%) 445 ($\text{M}^+ + 1$, 42), 444 (M^+ , 33), 443 (100), 430 (10), 429 (35), 428 (18), 285 (24), 269 (10), 268 (14), 267 (11), 97 (19), 95 (11), 91 (36); ^1H nmr (400 MHz, dideuteriodichloromethane): δ 4.20 (s, 6H, 2 x NCH_3), 4.89 (s, 2H, benzyl-H), 7.24-7.28 (m, 1H, aromatic H), 7.32-7.36 (m, 2H, aromatic H), 7.39-7.43 (m, 2H, aromatic H), 7.48-7.50 (m, 2H, aromatic H), 7.56-7.58 (m, 2H, aromatic H), 7.61-7.65 (m, 2H, aromatic H), 9.21 (d, $^3\text{J} = 7.9$ Hz, 2H, aromatic H); ^{13}C nmr (100.6 MHz, dideuteriodichloromethane): δ 37.5 (2 x NCH_3), 41.8 (benzyl-C), 110.7 (2 x aromatic C), 120.2 (1 x aromatic C), 120.3 (2 x aromatic C), 121.8 (2 x aromatic C), 123.2 (2 x aromatic C), 125.8 (2 x aromatic C), 127.9 (1 x aromatic C), 128.0 (2 x aromatic C), 128.6 (2 x aromatic C), 129.0 (2 x aromatic C), 133.5 (2 x aromatic C), 138.2 (2 x aromatic C), 145.6 (2 x aromatic C), 170.1 (2 x CO).

Anal. Calcd. for $\text{C}_{29}\text{H}_{21}\text{N}_3\text{O}_2$ (443.50): C, 78.54; H, 4.77; N, 9.47. Found: C, 78.38; H, 4.79; N, 9.52.

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