Carbazole Synthesis *via* an *in situ* Trapping Strategy with Indolyl Enol Ethers

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Indolyl enol ethers, generated from the alkoxy(indolyl)carbenium tetrafluoroborates **1** by treatment with sodium hydride, can be trapped with dimethyl acetylenedicarboxylate or N-phenylmaleimide to furnish the selectively functionalized carbazoles **3, 4, 5, 9, 10**, and **13**. In addition, the biaryl derivatives **6** and **11** are produced by a ring-opening reaction of the primarily formed Diels-Alder adduct. In the case of the biaryl derivative **6**, an X-ray crystal structure analysis yields valuable information on constitutions and configurations in the biaryl series. The phenomenon of atropisomerism is discussed for this compound.

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Introduction.

In the last 15 years, Diels-Alder reactions of 2- and 3-vinylindoles were widely investigated and many efficient syntheses of selectively functionalized, [*b*]annelated indoles and/or carbazoles, including alkaloids, have now been developed by several groups [1-6] and in our laboratories [6-13]. However, only a few studies have been concerned with the synthetic potential of donor-activated vinylindoles, *i.e.* compounds bearing amino, alkoxy, or trialkylsiloxy groups, as building blocks for the preparation of oxo- or amino-functionalized carbazoles [11-15]. On the other hand, an interesting and flexible route to alkoxy-functionalized carbazoles has been introduced by Knölker and coworkers [16].

In continuation of our investigations on pericyclic reactions of indole derivatives [7,17] and as a supplement to our preliminary communication [18], we now report in detail on further novel trapping reactions of indolyl enol ethers and their anions, generated from the readily available alkoxy(indolyl)carbenium tetrafluoroborates **1** [19], with carbodienophiles.

Results and Discussion.

Synthetic Aspects.

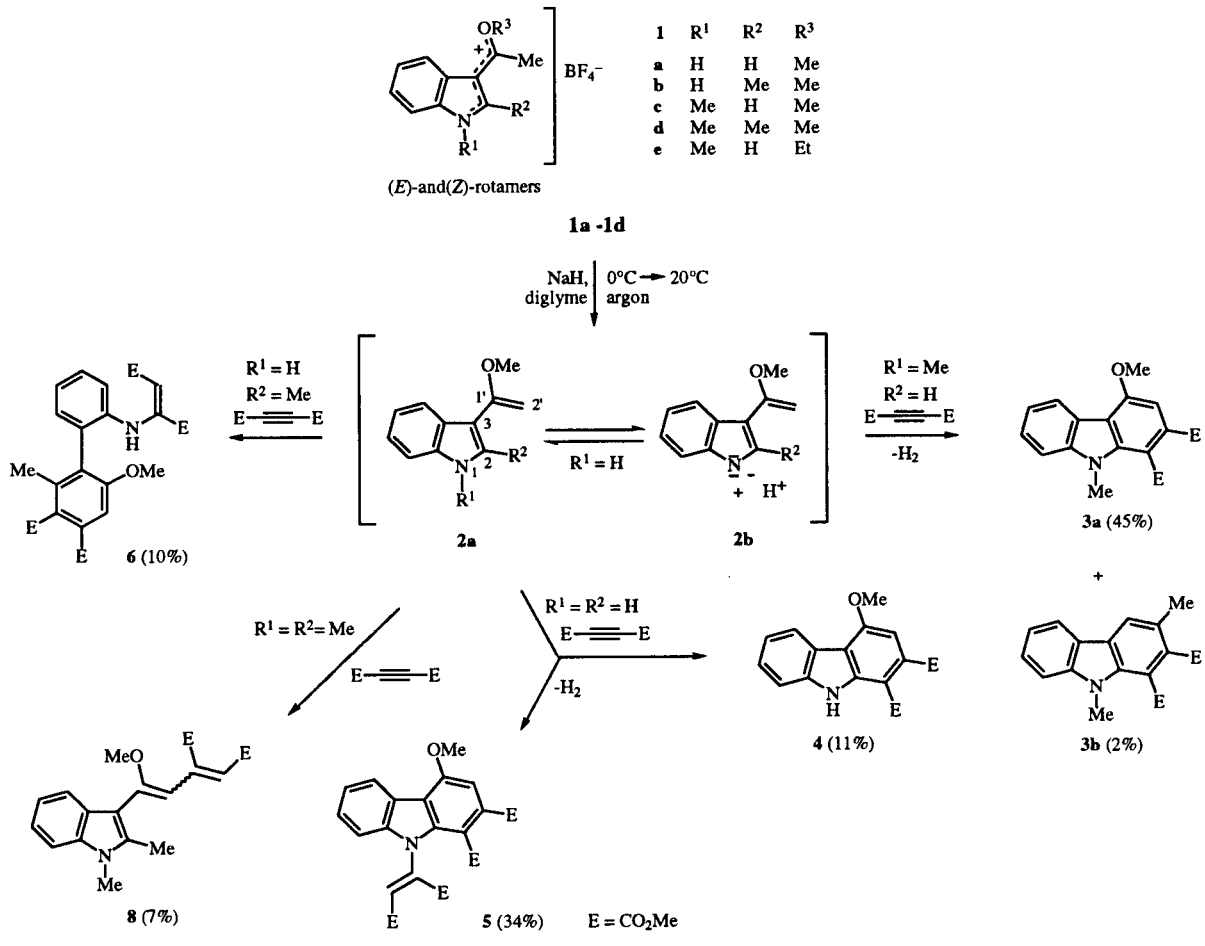
The ambident cations **1a-d**, readily accessible from the corresponding indoles and dimethoxy(methyl)carbenium tetrafluoroborate [19], were deprotonated by treatment with sodium hydride to generate 3-indolyl methyl enol ethers of the type **2a** (Scheme 1). In those cases where R^1 = H, the anion of the type **2b** also exists in the equilibrium mixture (detection by quenching the mixture with dideuteriosulfuric acid and subsequent ^{1}H nmr spectroscopy).

According to AM1 calculations [20] on **2a** and **2b**, a HOMO(diene)-LUMO(dienophile)-controlled Diels-Alder reaction with electron-poor dienophiles is predicted while, in the case of reactions of the anion **2b**, a polarity-controlled cyclization as a formal Diels-Alder reaction is also feasible. However, in our hands, the reactions of **1** with dimethyl acetylenedicarboxylate and *N*-phenylmaleimide gave rise to several functionalized indole and carbazole derivatives. Furthermore, some spontaneous dealkylation of compounds **1** to 3-acetylindoles [19] as well as uncontrollable polymerization processes in the reaction mixtures diminished the yields of the characterizable products in all cases.

Thus, for example, the cation **1c** reacted with dimethyl acetylenedicarboxylate *via* a [4 + 2] cycloaddition and elimination of hydrogen to furnish the carbazole **3a**, a precursor of the antibiotic 9-methyl-3-demethoxycarbazomycin [21], together with a small amount of the unexpected 3-methylated carbazole 36. We are not able to present a convincing mechanistic rationale for the formation of the latter product but suggest that methanol is eliminated for the primary cycloadduct and the thus formed species is methylated at the C3 position by the methoxycarbenium salt **1c**. The general alkylating ability of alkoxycarbenium salts is well known [19]. In an analogous process, **1a** reacted with the same dienophile to yield the carbazole **4**, a precursor of 3-demethoxycarbazomycin [21] together with the *N*-substituted carbazole **5**.

Interestingly, the reaction of **1b** with dimethyl acetylenedicarboxylate furnished the tri-*ortho*-substituted biaryl derivative **6** as the only characterizable reaction product apart from the 3-acetyl-2-methylindole. The constitution and preferred conformation of **6** in the solid state were clarified by an X-ray crystallographic analysis (see section on Structural Aspects). Our rationalization for the formation of **6** comprises the intermediate formation of the primary Diels-Alder adduct **7a** which undergoes equilibration with **7b** (Scheme 2). Subsequent ring opening of **7b** then gives rise to the more stable biaryl derivative **6**; the

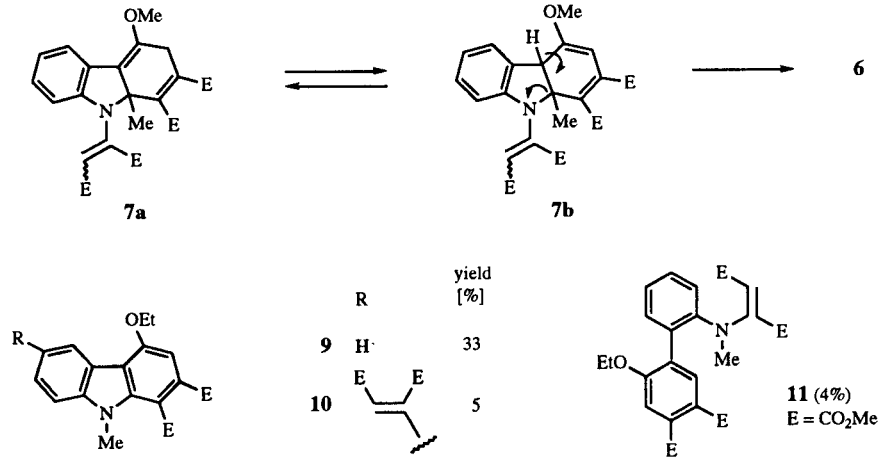
Scheme 1



putative driving force for this reaction is the primary loss of strain energy in the carbazole intermediates and the gain of aromatization energy.

The salt **1d** reacted with the acetylene derivative to furnish an inseparable mixture of the Michael-type adducts **8** [(*Z*/*E*) and (*Z*/*Z*) in a ratio of 1:2]. The configuration (*E* or *Z*) of the methoxyethene moiety of **8** has not yet been clarified unequivocally.

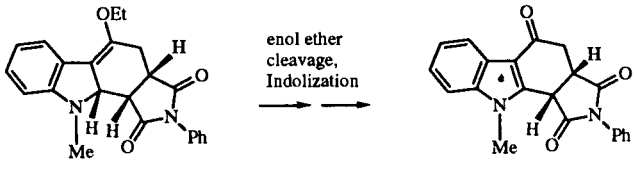
Scheme 2



In addition, we have investigated the reactivity of the ethoxy derivative **1e**, readily available from 1-methylindole and diethoxy(methyl)carbenium tetrafluoroborate [19], towards dimethyl acetylenedicarboxylate. Under the same reaction conditions as mentioned above, the dehydrogenated Diels-Alder product **9** and the pentasubstituted product **10** were obtained together with the biaryl derivative **11** in complete analogy to the formation of **6**.

The ethoxy(indolyl)carbenium salt **1e** reacted with *N*-phenylmaleimide in the presence of sodium hydride to furnish the trioxopyrrolo[3,4-*a*]carbazole **13** (Scheme 3). According to frontier molecular orbital (FMO) considerations and in accord with our previous results from cycloaddition reactions of vinylindoles with cyclic dienophiles [7], the *endo*-adduct **12** should be formed primarily. Enol ether cleavage and indolization processes involving the less stable **12** should then give rise to the [*a*]annelated trioxocarbazole **13**.

Scheme 3



12 **13** (18%)

We assume that the transformation of **12** to **13** occurs spontaneously in the absolute (water-free) reaction medium under an inert gas atmosphere.

Structural Aspects.

The constitutions and configurations of the products were established by routine high resolution nmr spectroscopy with the exception of the mixture of π-diastereomeric compounds **8** in which the vinyl configuration at the indole 3-position is still unknown. In the case of the biaryl derivative **6**, an X-ray crystallographic structural analysis substantiated the nmr data and provided valuable, basic geometrical information for the probable existence of atropisomers [23].

The X-ray crystallographic structural analysis of **6** (Figure 1) revealed the centrosymmetric space group $P\bar{1}$, thus both enantiomers of the chiral molecule are present. The central biphenyl moiety has a C11-C21 bond distance of 1.497(3) Å, a value in the upper quarter of all 212 hitherto known and well defined crystal structures of substituted biphenyls [24] with an average bond distance of 1.490(10) Å. Both phenyl rings are approximately planar [maximum deviation from the best planes 0.01(1) Å]; the dihedral angle between these planes is 69.7(1)°, indicating the strong steric interaction between the substituents at C12 and C26. This is comparable with the tilting angle of 79° in 6,6'-dinitro-2,2'-dicarboxybiphenyl [25] which also exhibits a large C11-C21 bond distance of 1.506 Å. In unsubstituted biphenyl in contrast (C11-C21 = 1.493 Å), the rings are coplanar in the crystal but with an anomalously high libration about the C11-C21 axis [26].

The geometry at the aniline N1 atom with an N1-C12 bond length of 1.420(2) Å is as expected for a system with a pyramidal N atom {average bond length 1.419(19) Å [24]}. Furthermore, although the sum of the angles at N1 amounts to only 356.4°, the deviation from 360° may not be significant due to the low accuracy of the hydrogen positions. The N1-C2 bond [1.362(2) Å] is rotated about the C12-N1 axis [torsion angle C11–C12–N1-C2 = 143.9(2)°], probably to avoid steric interactions between the ester group at C1 and the phenyl ring. The atoms N1, C2, C3, C4, and O2 including the double bond between C2 and C3 [1.350(2) Å], are approximately planar (maximum deviation of 0.12 Å for O2) and the interplanar angle with the phenyl ring is 57.4°.

The formation of intramolecular hydrogen bonds is suggested by the geometrical features: N1···O6 = 2.726(2) Å, angle N1–H1···O6 = 135°. There are no anomalous short intermolecular contacts.

On the basis of these X-ray crystallographic atomic coordinates, a conformational analysis of **6** was performed using the MAXIMIN2 molecular mechanics method from the SYBYL 5.5 program packet [28] [28a]. The energy profile by rotation about the central biaryl σ-bond revealed two

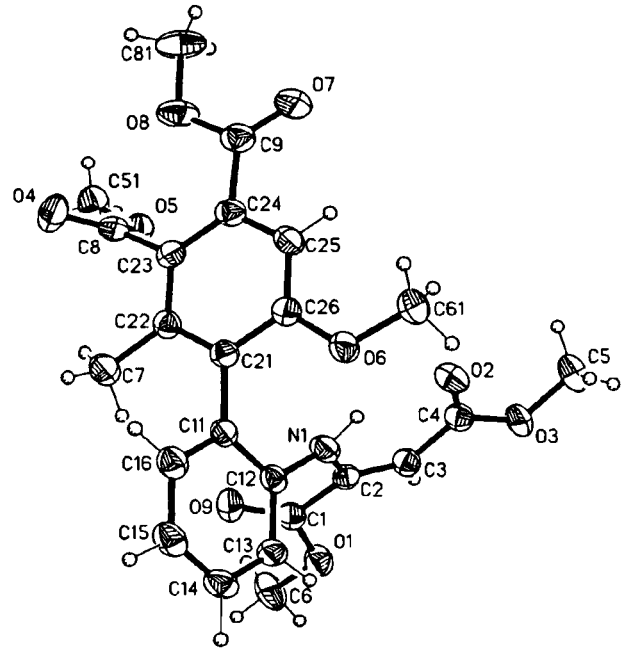


Figure 1. XP-Drawing [27] of a molecule of **6** in the crystal. Thermal ellipsoids at the 50% probability level; H atoms with arbitrary radii.

Structure Determination Summary

Crystal Data	
Empirical Formula	$C_{24}H_{25}NO_9$
Color	yellow
Crystal Size (mm)	0.4•0.3•0.3
Crystal System	Triclinic
Space Group	$P\bar{1}$
Unit Cell Dimensions	a = 9.673(2) Å
	b = 11.286(2) Å
	c = 11.565(2) Å
	α = 71.52(3)°
	β = 86.73(3)°
	γ = 72.62(3)°
Volume	1141.8(4) Å^3
Z	2
Formula Weight	471.5
Density(calc.)	1.371 Mg/m^3
Absorption Coefficient	0.89 mm^{-1} no correction
F(OOO)	496
Data Collection	
Diffractometer Used	CAD4 (Enraf-Nonius)
Radiation	CuKα (λ = 1.54178 Å)
Temperature (K)	193
Monochromator	Highly oriented graphite crystal
2θ Range	8.0 to 110.0°
Scan Type	ω
Measuring Time	Variable; max. 30 s/reflection
Scan Range (ω)	(1.0+0.14tgθ)°
Background Measurement	Additional 25% before and after each reflection
Standard Reflections	2 measured every 60 minutes for intensity
	2 measured every 250 refl. for orientation
Index Ranges	$-10 \le h \le 10$, $-11 \le k \le 11$
	$-12 \le \ell \le 1$
Reflections Collected	3033
Independent Reflections	2839 (R_{int} = 1.13%)
Observed Reflections	2658 ($F > 3.0\sigma(F)$)
Solution and Refinement	
System Used	Siemens SHELXTL PLUS (VMS)
Solution	Direct methods
Refinement Method	Full-Matrix Least-Squares
Quantity Minimized	$\Sigma w(F_o - F_c)^2$
Extinction Correction	$\chi = 0.0357(12)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
Hydrogen Atoms	H's located but kept riding
Weighting Scheme	$w^{-1} = \sigma^2(F)$
Number of Parameters Refined	310
Final R Indices (obs. data)	R = 3.34 %, wR = 3.80 %
R Indices (all data)	R = 3.57 %, wR = 3.81 %
Goodness-of-Fit	4.81
Largest and Mean Δ/σ	0.003, 0.001
Data-to-Parameter Ratio	8.6:1
Largest Difference Peak	0.20 eÅ 3
Largest Difference Hole	-0.18 eÅ

steric energy barriers of 83 and 67 kcal•mol^{-1}, respectively, which separate, among others, the enantiomeric rotamers. Thus, these high energy barriers indicate that **6** should indeed exist as stable, rotational conformers in the sense of atropisomers [23]. AM1 calculations on **6** [20] performed in an analogous manner predicted rotational barriers as $\Delta H^{\ddagger}$ ($\Delta\Delta H_f$) of 58 and 64 kcal•mol^{-1}. Interestingly, the 400 MHz

Table 1

Atomic Coordinates (x10^5) and Equivalent Isotropic Displacement Coefficients (pm^2)

	x	y	z	U(eq)
O(1)	27400(13)	32553(13)	56928(12)	392(6)
O(2)	68461(13)	41274(13)	30147(13)	397(6)
O(3)	77927(13)	23016(13)	45764(12)	418(6)
O(4)	21922(15)	116132(13)	22257(13)	486(7)
O(5)	36091(13)	101157(12)	38085(11)	356(6)
O(6)	50394(12)	64260(12)	6631(11)	346(6)
O(7)	73114(15)	96568(14)	14233(16)	598(8)
O(8)	54165(15)	110811(14)	19219(13)	474(7)
O(9)	18205(13)	53995(13)	47029(12)	391(6)
N(1)	39001(15)	50985(14)	29469(14)	317(7)
C(1)	27441(19)	43722(19)	48417(17)	307(8)
C(2)	40673(18)	42293(17)	40949(16)	281(8)
C(3)	53542(18)	34052(17)	46234(17)	314(8)
C(4)	66912(19)	33444(19)	39903(19)	336(9)
C(5)	91810(20)	22223(22)	40320(22)	570(11)
C(6)	15680(21)	33825(23)	65381(19)	503(10)
C(7)	11965(19)	90669(19)	24656(18)	382(9)
C(8)	30579(19)	105584(19)	26650(18)	334(8)
C(9)	60500(22)	99900(19)	16462(18)	381(9)
C(11)	22896(18)	69324(17)	14303(16)	272(7)
C(12)	26196(18)	56332(17)	21849(16)	274(8)
C(13)	17391(18)	48703(18)	21420(16)	303(8)
C(14)	5407(19)	53910(19)	13460(17)	350(9)
C(15)	2145(20)	66678(20)	5814(18)	375(9)
C(16)	10880(19)	74294(19)	6258(17)	339(8)
C(21)	32153(18)	77634(17)	14939(16)	273(7)
C(22)	26938(18)	87900(17)	19803(16)	286(7)
C(23)	36136(19)	95261(17)	20544(16)	299(8)
C(24)	50166(19)	92406(17)	16224(16)	315(8)
C(25)	55189(19)	82181(18)	11373(17)	329(8)
C(26)	46337(18)	74771(17)	10872(16)	297(8)
C(51)	32330(22)	110216(21)	44949(20)	480(10)
C(61)	64948(20)	60463(20)	2631(19)	433(9)
C(81)	63417(26)	118380(23)	20384(21)	575(11)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 2

Bond Lengths (pm)

O(1)-C(1)	133.2 (2)	O(1)-C(6)	145.8 (2)
O(2)-C(4)	122.6 (2)	O(3)-C(4)	134.4 (2)
O(3)-C(5)	144.1 (2)	O(4)-C(8)	120.3 (2)
O(5)-C(8)	133.6 (2)	O(5)-C(51)	143.8 (3)
O(6)-C(26)	136.8 (3)	O(6)-C(61)	143.9 (2)
O(7)-C(9)	120.3 (2)	O(8)-C(9)	133.0 (3)
O(8)-C(81)	144.6 (3)	O(9)-C(1)	120.3 (2)
N(1)-C(2)	136.2 (2)	N(1)-C(12)	142.0 (2)
C(1)-C(2)	150.0 (3)	C(2)-C(3)	135.0 (2)
C(3)-C(4)	144.4 (3)	C(7)-C(22)	150.3 (3)
C(8)-C(23)	150.0 (3)	C(9)-C(24)	149.6 (3)
C(11)-C(12)	139.8 (2)	C(11)-C(16)	139.1 (2)
C(11)-C(21)	149.7 (3)	C(12)-C(13)	139.2 (3)
C(13)-C(14)	138.1 (3)	C(14)-C(15)	138.2 (3)
C(15)-C(16)	138.6 (3)	C(21)-C(22)	139.5 (3)
C(21)-C(26)	140.2 (2)	C(22)-C(23)	140.9 (3)
C(23)-C(24)	140.0 (2)	C(24)-C(25)	138.8 (3)
C(25)-C(26)	137.8 (3)		

^{1}H nmr spectrum of **6** at room temperature contained only one, relatively sharp set of proton signals. However, upon addition of (*S*)-(+)-1-(9-anthryl)-2,2,2-trifluoroethanol as a

Table 3

Bond Angles (°)

C(1)-O(1)-C(6)	114.4(1)	C(4)-O(3)-C(5)	115.6(1)
C(8)-O(5)-C(51)	116.7(1)	C(26)-O(6)-C(61)	118.2(2)
C(9)-O(8)-C(81)	116.9(2)	C(2)-N(1)-C(12)	126.3(2)
O(1)-C(1)-O(9)	124.4(2)	O(1)-C(1)-C(2)	112.6(1)
O(9)-C(1)-C(2)	123.0(2)	N(1)-C(2)-C(1)	115.4(1)
N(1)-C(2)-C(3)	124.2(2)	C(1)-C(2)-C(3)	119.8(2)
C(2)-C(3)-C(4)	122.1(2)	O(2)-C(4)-O(3)	121.8(2)
O(2)-C(4)-C(3)	125.5(1)	O(3)-C(4)-C(3)	112.7(2)
O(4)-C(8)-O(5)	124.0(2)	O(4)-C(8)-C(23)	125.9(2)
O(5)-C(8)-C(23)	110.1(1)	O(7)-C(9)-O(8)	123.5(2)
O(7)-C(9)-C(24)	123.9(2)	O(8)-C(9)-C(24)	112.6(2)
C(12)-C(11)-C(16)	118.6(2)	C(12)-C(11)-C(21)	120.3(2)
C(16)-C(11)-C(21)	121.1(2)	N(1)-C(12)-C(11)	118.6(2)
N(1)-C(12)-C(13)	121.1(1)	C(11)-C(12)-C(13)	120.2(2)
C(12)-C(13)-C(14)	120.1(2)	C(13)-C(14)-C(15)	120.3(2)
C(14)-C(15)-C(16)	119.7(2)	C(11)-C(16)-C(15)	121.1(2)
C(11)-C(21)-C(22)	120.7(2)	C(11)-C(21)-C(26)	119.2(2)
C(22)-C(21)-C(26)	120.1(2)	C(7)-C(22)-C(21)	120.4(2)
C(7)-C(22)-C(23)	120.7(2)	C(21)-C(22)-C(23)	118.9(2)
C(8)-C(23)-C(22)	117.6(2)	C(8)-C(23)-C(24)	122.3(2)
C(22)-C(23)-C(24)	120.1(2)	C(9)-C(24)-C(23)	123.4(2)
C(9)-C(24)-C(25)	116.3(2)	C(23)-C(24)-C(25)	120.3(2)
C(24)-C(25)-C(26)	119.8(2)	O(6)-C(26)-C(21)	114.9(2)
O(6)-C(26)-C(25)	124.4(2)	C(21)-C(26)-C(25)	120.8(2)

Table 4

Anisotropic Displacement Coefficients (pm^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	324(7)	409(8)	391(8)	-77(6)	71(6)	-97(7)
O(2)	296(8)	478(9)	423(9)	-148(6)	9(6)	-121(8)
O(3)	224(7)	422(8)	543(9)	-24(6)	-26(6)	-124(7)
O(4)	487(9)	317(8)	620(10)	-1(7)	-183(8)	-175(7)
O(5)	382(8)	358(8)	357(8)	-96(6)	-8(6)	-159(6)
O(6)	296(7)	374(8)	426(8)	-105(6)	84(6)	-212(7)
O(7)	340(9)	480(10)	991(13)	-198(7)	-22(8)	-177(9)
O(8)	540(9)	545(10)	550(9)	-362(8)	113(7)	-286(8)
O(9)	329(8)	390(8)	425(8)	-8(7)	-12(6)	-178(7)
N(1)	234(8)	353(9)	356(10)	-95(7)	-10(7)	-91(8)
C(1)	287(10)	351(12)	319(11)	-87(9)	-51(8)	-152(10)
C(2)	277(10)	280(10)	328(11)	-89(8)	-16(8)	-141(9)
C(3)	294(11)	327(11)	322(11)	-81(9)	-20(9)	-107(9)
C(4)	269(11)	373(12)	411(13)	-89(9)	-47(9)	-181(11)
C(5)	262(11)	603(15)	793(18)	-41(11)	43(11)	-237(14)
C(6)	327(12)	652(15)	427(13)	-86(11)	122(10)	-104(12)
C(7)	306(11)	438(12)	460(13)	-107(9)	30(9)	-226(10)
C(8)	293(11)	335(12)	426(13)	-146(10)	-18(9)	-133(10)
C(9)	365(13)	381(12)	403(12)	-158(10)	-58(10)	-74(10)
C(11)	235(9)	301(11)	311(10)	-73(8)	13(8)	-147(9)
C(12)	222(10)	333(11)	301(11)	-64(8)	25(8)	-166(9)
C(13)	289(10)	327(11)	349(11)	-116(9)	43(9)	-164(9)
C(14)	301(11)	470(13)	400(12)	-174(9)	47(9)	-252(11)
C(15)	282(10)	511(13)	383(12)	-100(10)	-49(9)	-213(11)
C(16)	288(10)	375(12)	350(11)	-79(9)	-23(9)	-122(10)
C(21)	264(10)	273(10)	274(10)	-82(8)	-38(8)	-64(9)
C(22)	264(10)	298(11)	287(11)	-64(8)	-28(8)	-88(9)
C(23)	324(11)	263(10)	304(11)	-87(8)	-52(9)	-68(9)
C(24)	303(11)	322(11)	319(11)	-120(9)	-40(9)	-65(9)
C(25)	257(10)	365(12)	354(11)	-99(9)	25(8)	-94(9)
C(26)	297(10)	305(11)	290(11)	-83(9)	-3(8)	-98(9)
C(51)	447(13)	539(14)	532(14)	-78(11)	-15(11)	-330(12)
C(61)	351(12)	454(13)	506(13)	-103(10)	158(10)	-208(11)
C(81)	775(17)	674(16)	510(14)	-524(14)	8(12)	-211(13)

The anisotropic displacement factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

chiral shift reagent [31] at room temperature, the spectrum clearly revealed two sets of proton signals of equal intensity for the methoxy groups and the vinyl proton, arising *via* complexation of **6**. In the aromatic proton region also, some double sets of signals began to become evident but there was some superposition with the resonance signals of the chiral shift reagent. This phenomenon should indeed be due to the existence of enantiomeric atropisomers in solution now being visible as diastereomeric complexes whereas, within the limits of the nmr time scale, the aryl rings flip rapidly from torsional angles of about (+)40°–(+)140° or (–)40°–(–)140°. The resultant rotamers are "separated" by the high energy barriers of the coplanar conformers.

In contrast to compound **6**, the biaryl derivative **11** exhibits sterically unhindered rotation about the central σ-bond because there is only one *ortho* group on each aromatic ring. MAXIMIN2 molecular mechanics calculations [28] on **11** revealed a lower steric energy barrier to rotation of 34 kcal•mol^{-1}. No atropisomeric forms have yet been detected experimentally by nmr spectroscopy using the above-mentioned chiral shift reagent.

Table 5

H-Atom Coordinates (x10^4) and Isotropic Displacement Coefficients (pm^2x10^{-1})

	x	y	z	U
H(1)	4739	5107	2561	40(2)
H(3)	5392	2917	5355	40(2)
H(51)	9855	1387	4489	79(2)
H(52)	9514	2970	4047	79(2)
H(53)	9156	2185	3195	79(2)
H(61)	1748	2453	7128	79(2)
H(62)	616	3698	6056	79(2)
H(63)	1570	3970	7013	79(2)
H(71)	1096	9475	3061	79(2)
H(72)	967	8252	2878	79(2)
H(73)	468	9537	1798	79(2)
H(13)	2065	3951	2650	40(2)
H(14)	-77	4822	1315	40(2)
H(15)	-630	7080	-13	40(2)
H(16)	855	8358	95	40(2)
H(25)	6446	8021	828	40(2)
H(511)	3635	10532	5348	79(2)
H(512)	2244	11543	4353	79(2)
H(513)	3643	11631	4232	79(2)
H(611)	6598	5227	49	79(2)
H(612)	7185	5832	983	79(2)
H(613)	6685	6757	-420	79(2)
H(811)	5666	12639	2184	79(2)
H(812)	6814	12064	1297	79(2)
H(813)	6926	11345	2742	79(2)

EXPERIMENTAL

Materials and Techniques.

All reactions were performed in a special apparatus developed in our laboratories [19]. Solvents of the highest purity grade were used and all reactions were carried out under an argon atmos-

phere. Flash chromatography was performed with silica gel 60 (Merck, 0.040-0.063 mm particle size) and petroleum ether (40-60°)/ethyl acetate mixtures as eluent. Melting points were determined on Büchi SMP-20 and Electrothermal IA 920 apparatus and are not corrected. Elemental analyses were performed using Perkin Elmer 240 and Haereus CHN rapid elemental analyzer. The infrared spectra were recorded on a Beckmann IR 4220 spectrophotometer. The mass spectra were measured with Varian MAT CH 7A (for 70 eV ei-ms) and Varian MAT 711 (for fd-ms) spectrometers, data are given as m/e (%). The proton magnetic resonance spectra (400 and 200 MHz) and ^{13}C nmr (100.6 and 50.3 MHz) spectra were recorded on Bruker AM 400 and Bruker AC 200 spectrometers using tetramethylsilane as internal standard (δ scale). The ^{13}C nmr spectra were obtained employing the APT technique; notations used: C_p (primary), C_s (secondary), C_t (tertiary), C_q (quaternary).

General Procedure for the Synthesis of Compounds **3-6**, **8-11**, and **13**.

A solution of 30.0 mmoles of tetrafluoroboric acid (4.1 ml of a 54% solution of tetrafluoroboric acid in diethyl ether) was added dropwise to a solution of 31.3 mmoles of the respective trialkyl orthoacetate in 10 ml of dichloromethane at -10°. After stirring and cooling to -78°, a colorless precipitate of the dialkoxy(methyl)carbenium tetrafluoroborate was formed in the reaction vessel [19].

This precipitate was filtered, washed several times with cold diethyl ether under argon, then suspended in 10 ml of dichloromethane, and the suspension cooled to 0°. A solution of 20.5 mmoles of the indole in 15 ml of dichloromethane was added rapidly with vigorous stirring to the carbenium salt suspension. After 30-60 minutes, a colored precipitate of **1** had separated. This precipitate was filtered, washed several times with cold diethyl ether under argon, and then suspended in 30 ml of ethylene glycol dimethyl ether. Dimethyl acetylenedicarboxylate (4.0 ml, 32.7 mmoles) or *N*-phenylmaleimide (5.0 g, 33 mmoles) was then added. The suspension was cooled to 0° and a suspension of sodium hydride (700 mg, 29.2 mmoles) in 10 ml of ethylene glycol dimethyl ether was added dropwise over a period of 30 minutes. The mixture was stirred for a further 40 minutes, allowed to warm to room temperature, and filtered. The filtrate was poured onto ice and the aqueous layer extracted three times with diethyl ether. The combined organic layers were dried with magnesium sulfate and concentrated under reduced pressure. The products **3a**, **6**, **9**, and **13** crystallized after concentration of the mother liquor. In order to obtain products **3b**, **4**, **5**, **8**, **10**, and **11** and to increase the yields of **3a**, **6**, **9**, and **13**, the concentrated mother liquors were worked up by "flash" chromatography (petroleum ether/ethyl acetate, 2/1 v/v or 2/3 for **6** and 3/1 for **8**). The yields cited below are based on the indole starting materials.

Dimethyl 4-Methoxy-9-methyl-9*H*-carbazole-1,2-dicarboxylate (**3a**).

Compound **3a** was obtained as colorless, matted crystals in 45% yield (3.00 g), mp 170° (methanol); ir (potassium bromide): ν 2950 (w), 1730 (s), 1710 (s), 1590 (m), 1235 (s), 720 (s) cm^{-1}; ^1H nmr (200 MHz, hexadeuterioacetone): δ 3.83 (s, 3H, NCH_3), 3.91 (s, 3H, $COOCH_3$), 3.98 (s, 3H, $COOCH_3$), 4.16 (s, 3H, OCH_3), 7.26 (d pseudo-t, ^3J = 7.92 Hz, ^4J = 1.44 Hz, 1H, C6-H or C7-H), 7.32 (s, 1H, C3-H), 7.48-7.60 (m, 2H, C8-H and C7-H or C6-H), 8.33 (dd, ^3J = 7.82 Hz, ^4J = 0.99 Hz, 1H, C5 H); ^{13}C nmr (50.3 MHz, hexadeuterioacetone): δ C_p 31.0 (NCH_3), 52.8 ($COOCH_3$), 52.9 ($COOCH_3$), 56.2 (OCH_3); δ Ct 101.9, 109.8, 120.8, 124.3, 127.5, δ C_q 106.6, 112.5, 116.0, 121.4, 138.7, 143.3, 156.6, δ C=O 167.4, 169.2; ms: ei m/z (%) 327 ($M^{+\cdot}$, 100), 296 (40), 281 (13), 280 (18), 209 (39), 167 (12).

Anal. Calcd. for $C_{18}H_{17}NO_5$ (327.34): C, 66.05; H, 5.23; N, 4.28. Found: C, 65.95; H, 5.07; N, 4.30.

Dimethyl 3,9-Dimethyl-9*H*-carbazole-1,2-dicarboxylate (**3b**).

Compound **3b** was obtained as white, very fine needles in 2% yield (100 mg), mp 183° (ethanol/water); ^1H nmr (200 MHz, hexadeuterioacetone): δ 2.92 (s, 3H, CH_3), 3.87 (s, 3H, NCH_3), 3.90 (s, 3H, $COOCH_3$), 4.00 (s, 3H, $COOCH_3$), 7.30-7.35 (m, 1H, aromatic H), 7.54-7.67 (m, 2H, aromatic H), 7.64 (s, 1H, C4-H), 8.27 (d, ^3J = 7.96 Hz, 1H, C8-H); ^{13}C nmr (50.3 MHz, hexadeuterioacetone): δ C_p 21.0 (CH_3), 30.0 (NCH_3), 52.7 ($COOCH_3$), 52.9 ($COOCH_3$), δ C_t 110.1 (C8), 120.8 (C6), 122.3 (C5), 124.0 (C7), 127.9 (C4), δ C_q 122.6, 125.8, 127.5, 134.2, 134.8, 137.9, 144.8, δ C=O: 168.8, 169.3; ms: ei m/z (%) 311 ($M^{+\cdot}$, 100) 280 (52), 264 (28), 193 (85), 180 (10), 140 (16).

Anal. Calcd. for $C_{18}H_{17}NO_4$ (311.34): C, 69.44; H, 5.50; N, 4.50. Found: C, 69.21; H, 5.37; N, 4.31.

Dimethyl 4-Methoxy-9*H*-carbazole-1,2-dicarboxylate (**4**).

Compound **4** was obtained as colorless needles in 11% yield (700 mg), mp 130-132° (petroleum ether/ethyl acetate); ir (potassium bromide): ν 3460 (m), 2875 (m), 1740 (s), 1710 (s), 1600 (s), 1590 (s), 1515 (m), 1460 (m), 1450 (m), 1430 (s), 1415 (m) cm^{-1}, ^1H nmr (400 MHz, deuteriochloroform): δ 3.95 (s, 3H, $COOCH_3$), 3.96 (s, 3H, $COOCH_3$), 4.12 (s, 3H, OCH_3), 6.75 (s, 1H, C3-H), 7.24-7.28 (m, 1H, aromatic), 7.41-7.49 (m, 2H aromatic), 8.27 (d, ^3J = 7.81 Hz, 1H, C5-H or C8-H), 9.84 (s, 1H, exchangeable, NH); ms: ei m/z (%) 313 ($M^{+\cdot}$, 100), 281 (97), 223 (39), 195 (65), 180 (10), 153 (15), 152 (14), 77 (10).

Anal. Calcd. for $C_{17}H_{15}NO_5$ (313.31): C, 65.17; H, 4.83; N, 4.47. Found: C, 65.13; H, 4.65; N, 4.32.

Dimethyl 2-[4-Methoxy-1,2-bis(methoxycarbonyl)-9*H*-carbazol-9-yl]-(*Z*)-butenedioate (**5**).

Compound **5** was obtained as colorless needles in 34% yield (3.20 g), mp 225° (methanol or ethanol); ir (potassium bromide): ν 3060 (w), 2960 (w), 1735 (s), 1710 (s), 1590 (m), 1450 (m), 1405 (m), 1285 (s), 1240 (s), 780 (m), 750 (m) cm^{-1}; ^1H nmr (200 MHz, dideuteriodichloromethane): δ 3.64 (s, 3H, $COOCH_3$), 3.90 (s, 3H, $COOCH_3$), 3.91 (s, 3H, $COOCH_3$), 3.92 (s, 3H, $COOCH_3$), 4.16 (s, 3H, OCH_3), 6.75 (s, 1H, C3-H), 7.30-7.42 (m, 2H, C5'-H and C6'-H or C7'-H), 7.36 (s, 1H, C3'-H), 7.51 (d pseudo-t, ^3J = 7.67 Hz, ^4J = 1.15 Hz, 1H, C7'-H or C6'-H), 8.37 (d, ^3J = 7.45, 1H, C8'-H); ^{13}C nmr (100.6 MHz, dideuteriodichloromethane): δ C_p 52.9, 53.2, 53.3 (2x), 56.4, δ C_t 103.5, 109.9, 122.1, 124.1, 127.6, 134.5, δ C_q 113.2, 117.4, 121.9, 128.1, 132.7, 138.0, 142.5, 156.5, δ C=O 162.6, 164.9, 167.2, 168.0; ms: ei m/z (%) 455 ($M^{+\cdot}$, 100), 380 (19), 307 (11).

Anal. Calcd. for $C_{23}H_{21}NO_9$ (455.42): C, 60.66; H, 4.65; N, 3.08; Found: C, 60.41; H, 4.67; N, 3.15.

Dimethyl 2-Amino-*N*-[6'-methoxy-3',4'-bis(methoxycarbonyl)-2'-methylbiphenyl-2-yl]-(*E*)-butenedioate (**6**).

Compound **6** was obtained as light yellow crystals in 10% yield (1.01 g), mp 158° (methanol); ir (potassium bromide): ν 3260 (m), 2960 (m), 1745 (s), 1725 (s), 1670 (s), 1610 (s), 1600 (s),

1440 (s), 1330 (s) cm^{-1}; ^1H nmr (400 MHz, dideuteriodichloromethane): δ 2.03 (s, 3H, CH_3), 3.62 (s, 3H, $COOCH_3$), 3.65 (s, 3H, $COOCH_3$), 3.87 (s, 3H, $COOCH_3$), 3.91 (s, 3H, $COOCH_3$), 3.93 (s, 3H, OCH_3), 5.30 (s, 1H, C3-H), 6.88 (dd, ^3J = 7.82 Hz, ^4J = 1.09 Hz, 1H, C3'-H), 7.01 (dd, ^3J = 7.85 Hz, ^4J = 1.11 Hz, 1H, C6'-H), 7.21 (pseudo-t, ^3J = 8.01 Hz, 1H, C4'-H or C5"-H), 7.32 (pseudo-t, ^3J = 7.99 Hz, C5"-H or C4'-H), 7.47 (s, 1H, C5'-H), 9.38 (s, 1H, exchangeable with D_2O, NH); ^{13}C nmr (50.3 MHz, hexadeuterioacetone): δ C_p 17.6 (CH_3), 51.3 ($COOCH_3$), 52.5 ($COOCH_3$), 52.9 ($COOCH_3$), 53.0 ($COOCH_3$), 56.5 (OCH_3), δ C_t 93.8 (C3), 109.6, 122.7, 125.6, 129.5, 131.8, δ C_q 129.9, 130.3, 130.4, 132.7, 136.9, 139.9, 149.3, 157.9, δ C=O 165.0, 166.8, 169.7, 170.2; ms: ei m/z (%) 471 ($M^{+\bullet}$, 75), 440 (26), 412 (67), 409 (24), 380 (100), 349 (11), 321 (8).

Anal. Calcd. for $C_{24}H_{25}NO_9$ (471.46): C, 61.14; H, 5.34; N, 2.97. Found: C, 61.34; H, 5.47; N, 3.16.

Dimethyl (1*Z*,3*Z*)-4-(1,2-Dimethylindol-3-yl)-4-methoxy-1,3-butadiene-1,2-dicarboxylate and (1*Z*,3*E*)-Isomer (**8**).

Compound **8** was obtained as a yellowish amorphous powder (1:2 mixture of the π-diastereomers **A** and **B**) in 7% yield (500 mg), mp 103-105° (petroleum ether/ethyl acetate); ir (potassium bromide): ν 3000 (w), 2950 (m), 2840 (w), 1715 (s), 1620 (m), 1600 (m), 1540 (m), 1080 (s), 755 (m) cm^{-1}; ^1H nmr (400 MHz, hexadeuterioacetone): δ 2.33 (s, 3H, C2'-CH_3, **A**), 2.43 (s, 3H, C2'-CH_3, **B**), 3.33 (s, 3H, NCH_3, **A**), 3.37 (s, 3H, NCH_3, **B**), 3.48 (s, 3H, $COOCH_3$, **A**), 3.70 (s, 3H, $COOCH_3$, **A**), 3.73 (s, 3H, OCH_3, **A**), 3.75 (s, 3H, $COOCH_3$, **B**), 3.79 (s, 3H, OCH_3, **B**), 5.25 (d, ^4J = 1.65 Hz, 1H, vinyl, **A**), 5.70 (d, ^4J = 1.56 Hz, 1H, vinyl, **B**), 5.80 (d, ^4J = 1.54 Hz, 1H, vinyl, **A**), 6.27 (d, ^4J = 1.68 Hz, 1H, vinyl, **B**), 7.06-7.44 (m, 4H + 4H, aromatic, **A** + **B**); ^{13}C nmr (100.6 MHz, deuteriochloroform): δ C_p 11.2 (**B**), 11.4 (**A**), 51.2 (**B**), 51.4 (**A**), 51.7 (**A**, 2x), 52.1 (**B**, 2x), 56.7 (**B**), 57.4 (**A**), δ C_t 110.2 (**B**), 110.2 (**A**), 119.5 (**B**), 119.8 (**A**), 121.1 (**B**), 121.2 (**A**), 122.1 (**B**), 122.4 (**A**), 124.8 (**B**), 125.5 (**A**), 125.5 (**B**), 126.2 (**A**), δ C_q 106.1 (**B**), 106.3 (**A**), 112.3 (**B**), 113.4 (**A**), 127.4, 127.7, 137.8, 137.9, 138.2, 139.0, 139.9, 140.5; δ C=O 167.8 (**A**), 168.1 (**B**), 168.0 (**A**), 168.3 (**B**); ms: ei m/z (%) 343 ($M^{+\bullet}$, 50), 329 (21), 328 (100), 312 (19), 269 (11), 268 (12), 240 (18), 194 (12), 182 (18), 181 (13), 172 (26), 158 (61), 69 (11), 57 (14).

Anal. Calcd. for $C_{19}H_{21}NO_5$ (343.38): C, 66.46; H, 6.16; N, 4.08. Found: C, 66.37; H, 6.13; N, 3.96.

Dimethyl 4-Ethoxy-9-methyl-9*H*-carbazole-1,2-dicarboxylate (**9**).

Compound **9** was obtained as light yellow plates in 33% yield (2.23 g), mp 162-163° (methanol); ir (potassium bromide): ν 2980 (w), 2950 (w), 1730 (s), 1710 (s), 1620 (m), 1585 (s), 1270 (s), 1240 (s), 1045 (s), 750 (s) cm^{-1}; ^1H nmr (200 MHz, dideuteriodichloromethane): δ 1.66 (t, ^3J = 6.95 Hz, 3H, CH_2-CH_3), 3.80 (s, NCH_3), 3.92 (s, 3H, $COOCH_3$), 4.00 (s, 3H, $COOCH_3$) 4.37 (q, ^3J= 6.98 Hz, 2H, CH_2-CH_3), 7.24-7.32 (m, 1H, aromatic), 7.30 (s, 1H, C3-H), 7.41-7.57 (m, 2H, aromatic), 8.40 (dd, ^3J = 7.81 Hz, ^4J = 1.04 Hz, 1H, C8-H); ^{13}C nmr (50.3 MHz, dideuteriodichloromethane): δ C_p 15.1, 30.9, 52.8, 53.0, δ Cs 64.6, δ C_t 102.3, 108.9, 120.3, 124.0, 126.9; δ C_q 115.7, 121.1, 122.3, 126.6, 142.4, 146.4, 155.5, δ C=O 167.3, 169.7; ms: ei m/z (%) 341 ($M^{+\bullet}$, 100), 310 (20), 223 (12), 195 (17)

Anal. Calcd. for $C_{19}H_{19}NO_5$ (341.36): C, 66.85; H, 5.61; N, 4.10. Found: C, 66.89; H, 5.62; N, 4.09.

Dimethyl 6-[1,2-(*Z*)-Bis(methoxycarbonyl)ethenyl]-4-ethoxy-9-methyl-9*H*-carbazole-1,2-dicarboxylate (**10**).

Compound **10** was obtained as an amorphous yellowish powder in 5% yield (450 mg), mp 184-186° (petroleum ether/ethyl acetate); ir (potassium bromide): ν 2995 (m), 2975 (m), 2910 (w), 1725 (br s), 1615 (s), 1470 (s), 1440 (s), 1365 (s), 1270 (s), 1170 (s), 1070 (s), 770 (s) cm^{-1}; ^1H nmr (200 MHz, deuteriochloroform): δ 1.23 (t, ^3J = 7.05 Hz, 3H, CH_2-CH_3), 3.72 (q, ^3J= 7.04 Hz, 2H, CH_2-CH_3), 3.74 (s, 3H, NCH_3), 3.77 (s, 3H, $COOCH_3$), 3.87 (s, 3H, $COOCH_3$), 3.94 (s, 3H, $COOCH_3$), 3.96 (s, 3H, $COOCH_3$), 6.65 (s, 1H, C2'-H), 7.21-7.59 (m, 2H, aromatic), 7.43 (d, ^3J = 8.35 Hz, 1H, C7-H or C8-H), 7.84 (s, 1H, C3-H), 8.24 (d, ^3J = 8.09 Hz, 1H, C8-H or C7-H); ms: fd m/z (%) 483.4 ($M^{+\bullet}$, 100).

Anal. Calcd. for $C_{25}H_{25}NO_9$ (483.47): C, 62.11; H, 5.21; N, 2.90; Found: C, 61.80; H, 5.17; N, 2.73.

Dimethyl 2-Amino-*N*-[2'-ethoxy-4',5'-bis(methoxycarbonyl)-biphenyl-2-yl]-*N*-methyl-(*E*)-butenedioate (**11**).

Compound **11** was obtained as yellowish, fine needles in 4% yield (380 mg), mp 134-136° (diethyl ether/*n*-hexane); ir (potassium bromide): ν 2990 (w), 2980 (w), 2920 (w), 1740 (s), 1660 (m), 1620 (m), 1610 (m), 1520 (m), 765 (s) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 1.21 (t, ^3J = 7.00 Hz, 3H, CH_2-CH_3), 3.69 (q, ^3J = 7.03 Hz, 2H, CH_2-CH_3), 3.76 (s, 3H, NCH_3), 3.86 (s, 3H, $COOCH_3$), 3.87 (s, 3H, $COOCH_3$), 3.93 (s, 3H, $COOCH_3$), 4.07 (s, 3H, $COOCH_3$), 6.36 (s, 1H, C3-H), 7.22-7.24 (m, 1H, C4'-H or C5'-H), 7.24 (s, 1H, C6"-H), 7.42 (d, ^3J = 8.32 Hz, 1H, C6'-H), 7.54 (pseudo-t, ^3J = 7.70 Hz, 1H, C5'-H or C4'-H), 7.83 (s, 1H, C3"-H), 8.23 (d, ^3J = 8.01 Hz, C3'-H); ^{13}C nmr (100.6 MHz, deuteriochloroform): δ C_p 18.4, 30.4, 52.3, 52.6, 52.8, 52.9, δ C_s 58.4, δ C_t 109.1, 120.3, 120.9, 123.2 (2x), 126.8, 128.1, δ C_q 119.2, 124.2, 125.1, 130.2, 136.6, 143.1, 144.3, δ C=O 165.3, 166.3, 166.6, 169.2; fd-ms: m/e (%) 485.4 ($M^{+\bullet}$, 100).

Anal. Calcd. for $C_{25}H_{27}NO_9$ (485.49): C, 61.85; H, 5.61; N, 2.89. Found: C, 61.84; H, 5.53; N, 2.60.

10-Methyl-2-phenyl-1,2,3,3aβ,4,5,10,10bβ-octahydropyrrolo[3,4-*a*]carbazole-1,3,5-trione and Enantiomer (**13**).

Compound **13** was obtained as a colorless, amorphous powder in 18% yield (1.25 g), mp 213-215° (acetone); ir (potassium bromide): ν 3080 (w), 2980 (w), 1790 (m), 1730 (s), 1650 (s), 1640 (s), 1505 (m), 1490 (s), 1420 (m), 1385 (s), 775 (m) 765 (s), 710 (m) cm^{-1}; ^1H nmr (400 MHz, deuteriochloroform): δ 2.94 (dd, ^3J = 8.04 Hz, ^2J = 17.13 Hz, 1H, C4-H), 3.16 (dd, ^3J = 5.88 Hz, ^2J = 17.12 Hz, 1H, C4-H), 3.82-3.98 (m, 1H, C3a-H_β), 4.02 (s, 3H, NCH_3), 4.64 (d, ^3J = 8.28 Hz, 1H, C10b-H_β), 7.21-7.50 (m, 8H, aromatic), 8.25-8.30 (m, 1H, aromatic); ms: ei m/z (%) 344 ($M^{+\bullet}$, 81), 197 (100), 168 (25).

Anal. Calcd. for $C_{21}H_{16}N_2O_3$ (344.37): C, 73.24; H, 4.68; N, 8.13. Found: C, 73.19; H, 4.60; N, 7.95.

Crystal Structure Determination of **6** ($C_{24}H_{25}NO_9$).

A yellow crystal of **6** (approximate dimensions: 0.4 x 0.3 x 0.3 mm) was investigated at a temperature of 193 K using a 4-circle diffractometer (Enraf Nonius CAD 4, CuK_α radiation, graphite monochromator). The space group is $P\bar{1}$, Z = 2; the cell dimensions were refined to a = 967.3(2), b = 1128.6(2), c = 1156.5(2) pm, α = 71.52(3)°, β = 86.73(3)°, γ = 72.62(3)°. 2839 unique reflections were collected up to sin Θ/λ = 0.53, from which 2685 with $F_o > 3\sigma(F)$ were used for the calculations. The structure was solved by direct methods and refined with anisotropic temperature factors for all non-H atoms (SHELXTL-plus [27]) using weighting factors $w = 1/\sigma^2(F_o)$. All hydrogen atoms were located in

difference Fourier maps and could be refined with isotropic temperature factors common by groups. In the last cycles, they were kept "riding". The final residuals converged to $R = 0.033$ and $wR = 0.038$, the largest parameter shift was 0.003 e.s.d., the max/min peaks in a difference Fourier map were 0.20/-0.18 e/Å^3.

Addendum

Meanwhile, in the case of compound **6** chiral hplc analysis (γ-cyclodextrine, methanol/water 70:30) was able to separate two enantiomeric atropisomers analyticallly

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