70. *Diels-Alder* Reactions of (1*H*-Indol-3-yl)-enacetamides and -endiacetamides: A Selective Access to Acetylamino-Functionalized [*b*]Annelated Indoles and Carbazoles[1])

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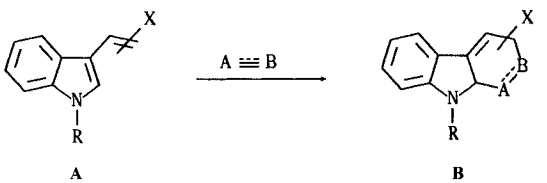
Diels-Alder reactions of the (1*H*-indol-3-yl)-enacetamides and -endiacetamides **1a–d** with some carbodienophiles and 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione give rise to the novel amino-functionalized carbazoles **4–6** and **8** (*Scheme 3*). Ethenetetracarbonitrile reacts with **1b** to furnish the *Michael*-type adduct **7** (*Scheme 3*). Structural aspects of the starting materials **1**, which exhibit above all 3-vinyl-1*H*-indole reactivity, are discussed with regard to the prediction of a *Diels-Alder* process.

Introduction. – *Diels-Alder* reactions of 2- and 3-vinyl-1*H*-indoles as 4π-electron components are now well established as a versatile procedure for the regio- and stereoselectively controlled syntheses of [*b*]annelated indoles and/or carbazoles [1–5]. This methodology should also be useful for the synthesis of compounds **B** functionalized with alkoxy, alkylthio, or amino groups (see **A** → **B**, *Scheme 1*) which could be of interest as building blocks in alkaloid chemistry [6] and/or in the development of pharmacologically active lead compounds [7]. The *Diels-Alder* reactivity of the precursor 3-vinyl-1*H*-indoles **A** has only been sparsely explored in the case of alkoxy- [8a] [9], trialkylsilyloxy- [10], alkylthio- [11], or amino-functionalized [8b] [12] derivatives. Hence, in continuation of our synthetic investigations on pericyclic reactions with vinylindoles [1–5] [7] [8] or indole-2,3-quinodimethanes [13] and as an extension of our preliminary communication

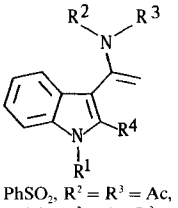
Scheme 1



A **B**

X = R'O, R'_3SiO, R'S, R'_2N

A ≡ B = carbo- or heterodienophile



1a $R^1 = PhSO_2$, $R^2 = R^3 = Ac$, $R^4 = H$
b $R^1 = PhSO_2$, $R^2 = Ac$, $R^3 = R^4 = H$
c $R^1 = R^2 = R^3 = Ac$, $R^4 = H$
d $R^1 = PhSO_2$, $R^2 = R^3 = Ac$, $R^4 = Me$

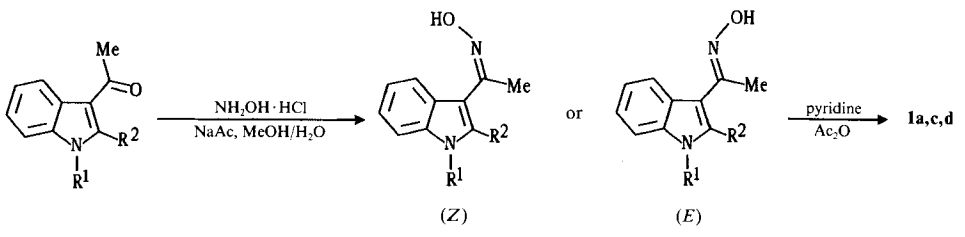
[1]) This work is dedicated to Prof. Dr. Dr. *Ernst Mutschler*, Frankfurt/Main, on the occasion of his 60th birthday.

[8b], we now report further new results on the *Diels-Alder* reactions of the (1*H*-indol-3-yl)-enamides **1a–d** with a variety of carbo- and heterodienophiles.

Although this methodology was first described in [12], we have now extended the scope of the procedure and explored the limitations of synthetic applications and the reactivity of this special class of 3-vinyl-1*H*-indoles. As the structure of **1** encompasses the 3-[(dialkylamino)methyl]-1*H*-indole moiety of *Aspidosperma* alkaloids [14], the *Diels-Alder* adducts of **1** and carbodienophiles represent interesting building blocks for the syntheses of this class of alkaloids. An exemplary X-ray structure analysis of **1c**, molecular-mechanics calculations for conformational analysis, and π-SCF-MO calculations gave valuable information for the prediction of the *Diels-Alder* reactivity of acetylamino-functionalized 3-vinyl-1*H*-indoles of type **1** in general.

Results and Discussion. – *Synthesis and Structure of 3-Vinyl-1*H*-indoles* **1a–d**. As described in [12], but using a slightly modified procedure, the 3-vinyl-1*H*-indoles **1a**, **1c**, and **1d** were prepared from the readily available 3-acetyl-1*H*-indoles **2a–c** *via* **3a–c** (*Scheme 2*). Methanolysis of **1a** in the presence of excess silica gel proceeded smoothly to furnish **1b** (96% yield). It was shown that the previously unknown stereoselectivity of step **2** → **3** depends on the substituents R^1 and R^2. Thus, **2a** and **2c** gave exclusively the (*E*)-isomers **3a** and **3c**, respectively, and **2b** the (*Z*)-isomer **3b** (HPLC). The (*E*)- or (*Z*)-configuration of the oximes **3** was determined unequivocally with the help of H,H-NOE measurements.

Scheme 2

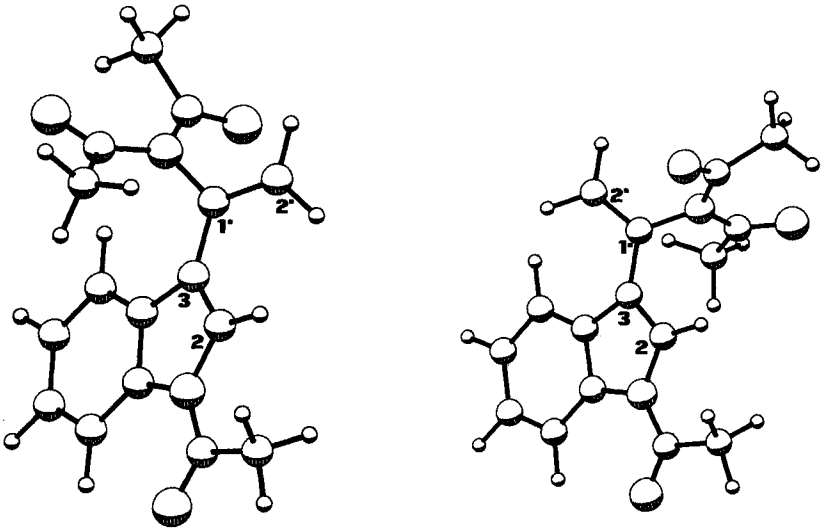


2a $R^1 = R^2 = H$
b $R^1 = PhSO_2$, $R^2 = H$
c $R^1 = PhSO_2$, $R^2 = Me$

3a $R^1 = R^2 = H$, $(E)/(Z) = 1:0$
b $R^1 = PhSO_2$, $R^2 = H$, $(E)/(Z) = 0:1$
c $R^1 = PhSO_2$, $R^2 = Me$, $(E)/(Z) = 1:0$

In general, for the prediction of the outcome of the *Diels-Alder* process of a diene regarding its reactivity, the steric and electronic properties play an important role [15]. A high population of the s-*cis*-conformation of a diene in the reaction medium and, according to the FMO concept [16], a small HOMO-LUMO energy difference of the reactants, including optimal frontier molecular orbital overlap in a [4π s + 2π s] transition state, considerably enhance concerted *Diels-Alder* reactions. However, molecular-mechanics calculations[2]) revealed that a fully coplanar s-*cis*-conformation of the diene unit

[2]) For molecular-mechanics and the following π-VESCF MO calculations, the full version of the MMX program from *Serena Software Ltd.*, Bloomington, IN, was used. The molecular-mechanics program was established from the MM2 and MMP1 programs (*Allinger* QCPE 395 and QCPE 318) by *K. E. Gilbert* and *J. J. Gajewski*. MO calculations were performed with full geometry optimization on the s-*cis*-synclinal conformations of **1**, and the MO method is described in [17].



C D

Fig. 1. *Energy minimum conformations of* **1c** *calculated by molecular mechanics*[2]. **C** = s-*cis*-synclinal conformer, torsional angle C(2)–C(3)–C(1′)–C(2′) = 30°; **D** = s-*trans*-synclinal conformer, torsional angle C(2)–C(3)–C(1′)–C(2′) = −144°. The starting geometry was taken from an X-ray analysis of conformer **I** (*Table*).

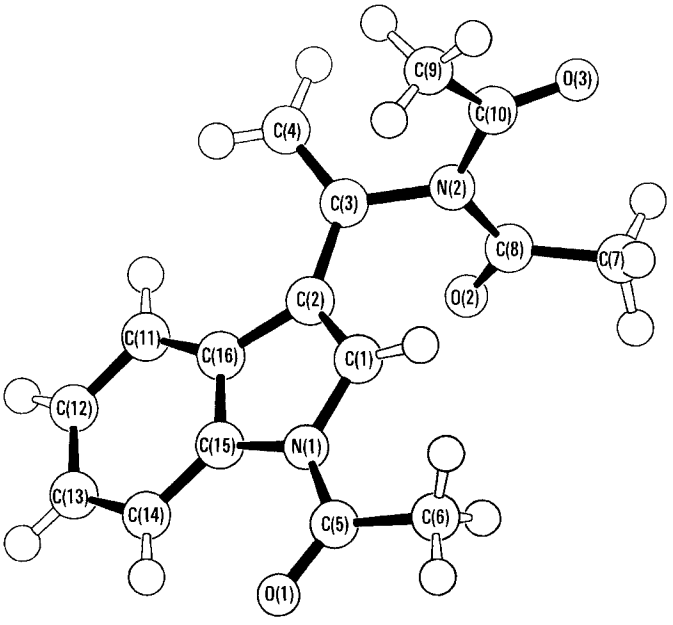


Fig. 2. *SCHAKAL* [30] *drawing of one of the two independent molecules of* **1c** *in the crystal state.* Arbitrary numbering.

in **1a–d** is energetically disfavored. Two local minimum conformations which show an s-*cis*-synclinal or an s-*trans*-synclinal arrangement of the 1-aminobutadiene moiety (torsion around the C(3)–C(1′) σ-bond) were calculated for all four compounds **1** (see *Fig. 1* for **1c**). These calculations revealed that the conformational equilibrium in the vacuum state is dependent on the bulk of the substituents R^1 to R^4 of **1**. Hence, *e.g.*, the s-*trans*-synclinal conformation of **1b** is favored over the s-*cis*-synclinal conformation by 3.91 kcal·mol^{-1}, whereas for **1c** the s-*cis*-synclinal conformation is favored over the s-*trans*-synclinal form by 0.41 kcal·mol^{-1}.

However, an X-ray structure analysis of **1c** revealed that the s-*trans*-synclinal conformation is energetically favored in the solid state. *Fig. 2* shows one of the two very similar independent molecules of **1c** in the crystal state. Selected bond lengths, bond angles, and torsional angles for both forms are given in the *Table*. As a consequence of the centrosymmetric space group, enantiomeric forms of both molecules are also present in the cell.

Table. *Selected Interatomic Distances* [pm], *Bond Angles, and Torsional Angles* [°] *for Both Independent Molecules* **I** *and* **II** *of* **1c** *from an X-Ray Analysis*

	I	**II**		**I**	**II**
N(1)–C(1)	139.4(3)	140.8(3)	C(2)–C(16)	145.3(3)	143.9(4)
N(1)–C(15)	141.1(3)	141.0(3)	C(3)–C(4)	132.2(4)	131.1(4)
N(1)–C(5)	139.3(3)	139.8(4)	C(3)–N(2)	145.1(3)	145.0(3)
C(1)–C(2)	135.1(4)	134.5(4)	N(2)–C(8)	140.3(3)	140.8(4)
C(2)–C(3)	145.7(4)	147.1(4)	N(2)–C(10)	140.3(4)	140.9(4)
C(1)–N(1)–C(15)	107.4(2)	107.5(2)	C(1)–N(1)–C(5)–O(1)	175.2(2)	178.4(2)
N(1)–C(1)–C(2)	110.8(2)	109.9(2)	C(1)–C(2)–C(3)–C(4)	−151.9(3)	−156.8(3)
C(1)–C(2)–C(3)	125.7(2)	124.9(2)	C(1)–C(2)–C(3)–N(2)	27.1(4)	21.7(4)
C(1)–C(2)–C(16)	106.6(2)	107.9(2)	C(2)–C(3)–N(2)–C(8)	66.1(3)	72.5(3)
C(16)–C(2)–C(3)	127.7(2)	127.2(2)	C(2)–C(3)–N(2)–C(10)	−119.0(3)	−110.3(3)
C(2)–C(3)–N(2)	115.2(2)	115.4(2)	C(3)–N(2)–C(8)–O(2)	12.4(3)	2.8(4)
C(2)–C(3)–C(4)	125.8(3)	125.7(2)	C(3)–N(2)–C(10)–O(3)	−161.1(2)	−160.3(3)
N(2)–C(3)–C(4)	118.9(2)	118.8(3)			
C(8)–N(2)–C(10)	123.6(2)	125.6(2)			

The indole-ring system of **1c** is approximately planar (maximum deviation from the best plane = 4(1) pm). The Ac group at the indole N(1) atom is nearly coplanar, the torsional angle C(1)–N(1)–C(5)–C(6) being 6.4(4)° [– 2.2(4)°][3]). The conformation of the diene unit C(1)=C(2)–C(3)=C(4) is s-*trans*-synclinal with a torsional angle of −151.9(3)° [−156.8(3)°][3]). The bond angles at C(2) and C(3) are relatively large, nearly 125° (*Table*), the bond length of the central C(2)–C(3) bond has the typical butadiene value of 146 pm. The orientation of the acetylamino group at C(3) is nearly perpendicular with respect to the indole plane (*Figs. 2* and *3*), the angle between the N(2)–C(8) bond and the indole plane is 79.5(2)° [82.5(2)°][3]), indicative of its quasiaxial position. The shortest intermolecular contact distance, 239 pm, is between O(1) and *H*–C(1) in the second independent molecule.

One of the conformations of **1c** calculated by MMX molecular mechanics[2]) is in sufficient agreement with the conformation **II** observed by crystallography (*Fig. 1*, con-

[3]) The corresponding values for the second independent molecule are given in brackets.

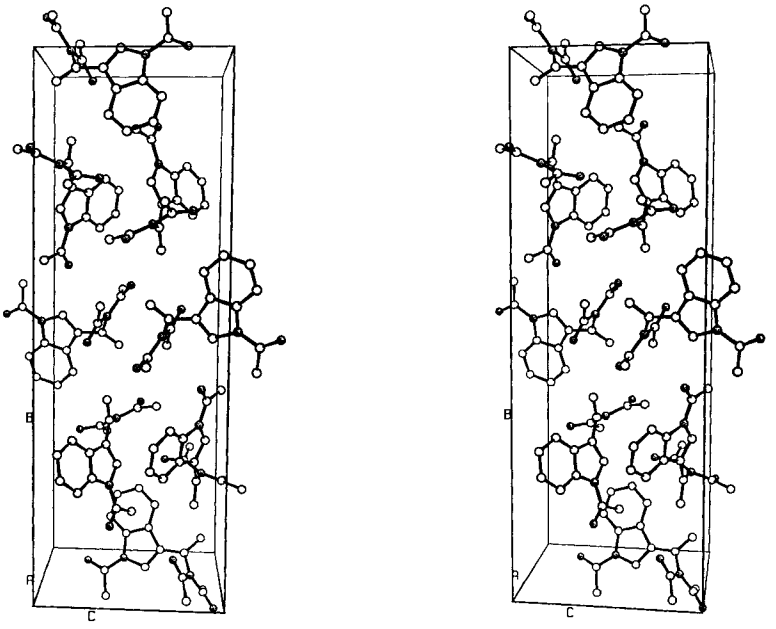


Fig. 3. *Stereoview of the unit cell of* **1c**

formation **D** torsional angle C(2)–C(3)–C(1′)–C(2′) = −144°)[4]). But it does seem remarkable that the orientations of both Ac moieties at N(2) in the theoretical structure **D** (*Fig. 1*) are reversed with respect to those determined by X-ray crystallography.

^{1}H-NMR NOE measurements (400 MHz, (D_6)DMSO) reveal that, on the NMR time scale, compounds of type **1** undergo rapid conformational exchange in solution. Furthermore, we also can assume that the population of the sufficiently reactive s-*cis*-synclinal conformers in solution is large enough for *Diels-Alder* reactions to occur in all cases; this assumption is supported by observations of *Dreiding* models. In addition, molecular-mechanics calculations on the '*endo*'- and '*exo*'-*Diels-Alder* transition states of the reaction of **1c** with *N*-phenylmaleimide[2]) demonstrate that no special steric hindrance is in operation in both orientations of the reactants (difference of transition-state potential energies $\Delta E^{\neq}$('*endo*','*exo*') = 0.14 kcal·mol^{-1}; a bond order of 0.3 for the two σ-bonds to be generated was used). Moreover, π-VESCF-MO calculations performed in **1a–d** [17][2]) revealed a HOMO topology in the 1-aminobutadiene unit which corresponds fully to that in the parent 3-vinyl-1*H*-indole [18][5]). Thus, we may predict a HOMO(diene)-LUMO-(dienophile)-controlled process for the *Diels-Alder* reactions of **1** with electron-deficient dienophiles.

In summary, the structural properties of **1a–d** permit us to predict that these compounds possess sufficient *Diels-Alder* reactivity under normal electron demand [15].

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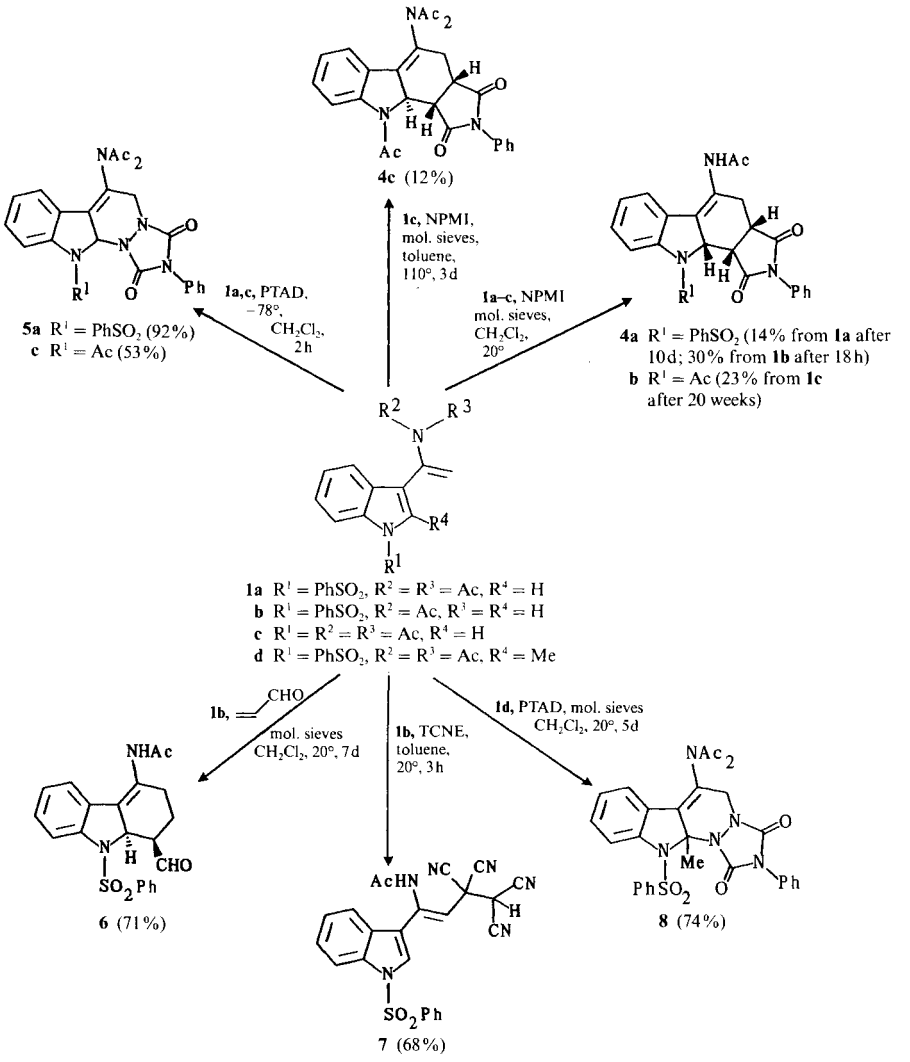
[4]) E(steric) of X-ray conformation **I** (*Table*), 40.1 kcal·mol^{-1}; E(steric) after refinement by molecular mechanics of X-ray geometry **I** (*Table*), 22.6 kcal·mol^{-1}.

[5]) For the example of **1c**, E(HOMO) = −11.15 eV, c(N(1)) = 0.2425, c(C(2)) = −0.3848, c(C(3)) = −0.3844, c(C(1′)) = 0.2425, c(C(2′)) = 0.3802; the calculations were based on the geometry **C** shown in *Fig. 1*.

Diels-Alder Reactions of **1a–d** *and Structure of the Products.* The reactivity of the 3-vinyl-1*H*-indoles **1a–c** was tested in reactions with *N*-phenylmaleimide (NPMI), 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (PTAD), acrylaldehyde, and tetracyanoethene (= ethenetetracarbonitrile; TCNE). The results obtained clearly demonstrate that compounds **1** belong to the group of generally less reactive 3-vinyl-1*H*-indoles. Special reaction conditions were necessary in some cases in order to prevent solvolysis of the enamides **1** to the more stable 3-acetyl-1*H*-indoles. At higher temperatures (with the

Scheme 3



NPMI = *N*-Phenylmaleimide
PTAD = 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione
TCNE = Ethenetetracarbonitrile

exception of reactions in toluene), **1** usually underwent polymerization, before any reaction with the dienophile could take place. However, under well controlled conditions (inert-gas atmosphere, highly activated molecular sieves (4 Å)[6]) as nonacidic catalyst, highly pure and anhydrous solvents, and strict absence of any acidic components), some novel [*b*]annelated indoles and indole derivatives were obtained (*Scheme 3*).

Thus, **1a–c** all reacted with NPMI at room temperature to furnish exclusively the '*endo*'-cycloadducts **4a** or **4b** (10 days to 20 weeks were required for reasonable results; see *Scheme 3*). In the case of **1a** and **1c**, concomitant transformation of the endiacetamide moiety to an enacetamide occurred. TLC monitoring of this time-dependent reaction suggested that the initial cycloaddition to a product with an endiacetamide functionality is more rapid at room temperature than the probable solvolysis of these endiacetamides to the more stable and exclusively isolated enacetamides **4a** or **4b**. Moreover, TLC analysis of the crude reaction mixtures revealed that these solvolyses do not take place during the workup procedure. The thermally more stable **1c** reacted with NPMI in toluene under reflux exclusively to the '*exo*'-cycloadduct **4c** besides polymeric products (*Scheme 3*).

With the highly dienophilic PTAD compounds **1a** and **1c** gave, under kinetically controlled conditions (after merely 2 h in the absence of molecular sieves), the [*b*]annelated indolines **5a** and **5c**, respectively. The 3-vinyl-1*H*-indole **1b** underwent [4 + 2] cycloaddition with acrylaldehyde in a regioselective and '*endo*'-controlled process to provide the functionalized carbazole derivative **6** which was first described in [12].

On the other hand and in spite of several variations of the conditions, reactions of **1** with TCNE did not produce any cycloadducts. The reaction of **1b** with TCNE gave rise to the stereoselective formation of the novel *Michael*-type adduct **7** (*Scheme 3*) [20].

For the purpose of investigating the influence of a Me group at C(2) on the reactivity of 3-vinyl-1*H*-indoles, we have investigated the *Diels-Alder* reactivity of **1d.** However, only the addition with the highly reactive PTAD was successful in our hands, giving the [4 + 2] cycloadduct **8** in reasonable yield (*Scheme 3*). Hence, it seems probable that, as yet, the presence of further substituents on the 1-aminobutadiene moiety does not hinder the build up of a *Diels-Alder* transition state; this is in full accord with observations of *Dreiding* models.

The constitutions and relative configurations of the products **4–8** were established unequivocally on the basis of 400-MHz ^{1}H-NMR spectral investigations. For the elucidation of the '*endo*'- and/or '*exo*'-configurations and the (*Z*)-configuration of **7**, additional differential H,H-NOE measurements were performed. A low-energy conformation of **4a** as calculated by molecular mechanics[2]) is exemplarily depicted in *Fig. 4*. The vicinal H,H-coupling constants of the bis-annelated cyclohexene rings (see *Exper. Part*) and the differential H,H-NOE's, *e.g.*, from H–C(10b) to H–C(10a) and to H–C(3a) and *vice versa*, in the '*endo*'-products clearly established the given configuration (*Fig. 4*). Calculations of polar dihedral maps (*Weiler* plots) [21] of **4a** and **4b** revealed that the bis-annelated cyclohexene ring adopts a slightly twisted boat conformation in these two cases, and this is fully compatible with the observed H,H-coupling constants. In the case of

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[6]) The molecular sieves employed belonged to the zeolite group; the catalytic effect should be of a physical nature (concentration of the reactants in the cavities of the material), see [19].

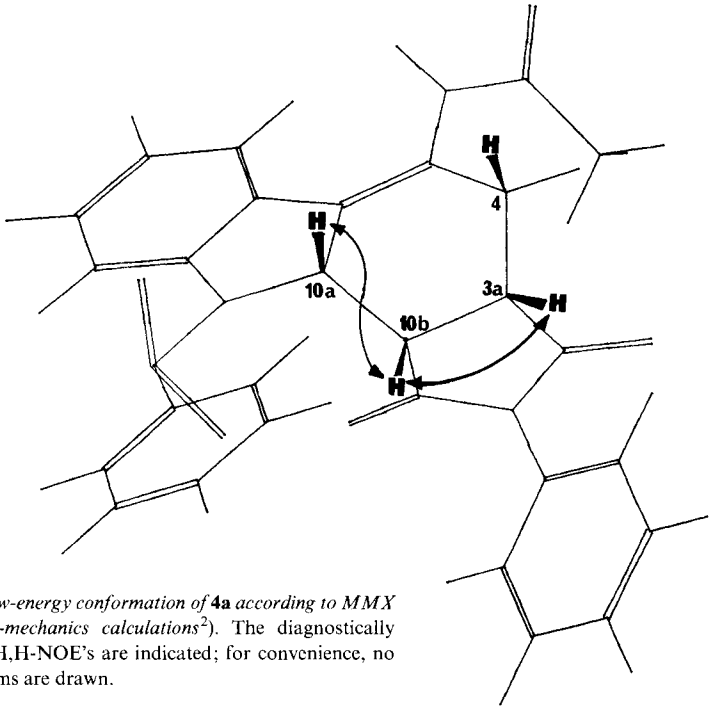

Fig. 4. *Low-energy conformation of* **4a** *according to MMX molecular-mechanics calculations*[2]). The diagnostically relevant H,H-NOE's are indicated; for convenience, no other atoms are drawn.

compound **7**, an NOE from the vinyl proton to indole H–C(2) and indole H–C(4) is also indicative of the postulated configuration and constitution.

According to the π-SCF-MO calculations [17], the '*endo*'-selectivity and the regiochemistry[7]) observed in the reaction of **1b** with acrylaldehyde is fully compatible with the predictions of the FMO concept [16]. The formation of the '*endo*'-cycloadducts **4a** and **4b** under mild (kinetically controlled) conditions can be accounted for by an energetically favored secondary HOMO(diene)-LUMO(dienophile) orbital interaction in the *Diels-Alder* transition state [23][8]). The one-bond formation in the reaction of **1b** with the electrophilic TCNE should be the result of a polarity-controlled mechanism, although steric effects which make the formation of a six-membered ring difficult may also play an important role.

Addendum. – Meanwhile a single-crystal X-ray analysis of **4b** was performed [31], showing that the established configuration and conformation of **4b** is fully compatible with the ^{1}H-NMR results. Additionally, the '*endo*'-configuration for **4a** and **4b** is unambiguously proved in this cycloadduct series.

We are grateful to the *Deutsche Forschungsgemeinschaft*, Bonn, Germany, for financial support of this work.

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[7]) The regioselectivity in the reaction of **1b** with acrylaldehyde can also be explained by a polarity-controlled orientation of the reactants; in a two-step process, a biradical or a zwitterionic intermediate can be formed, whereas in a one-step process, a highly unsymmetrical transition state may arise [22].

[8]) The '*endo*'-selectivity of *Diels-Alder* reactions has also generally been explained by attractive *van der Waals* [24], dipole-dipole [25], and steric [26] interactions and closed-shell repulsions [27] between the dienophile substituents and the diene in the transition state.

Experimental Part

General. All reactions must be performed in highly pure, anh. solvents under inert-gas atmospheres. Column chromatography (CC): silica gel *60* (*Merck*, 0.063–0.200 mm particle size). Flash chromatography (FC): silica gel *60* (*Merck*, 0.040–0.063 mm particle size). HPLC: *RP-18* column (*Merck*); *Merck-Hitachi L 6200*, *L-4000* UV detector. Eluents: petroleum ether (40–60°)/AcOEt. M.p.: *Büchi SMP-20*; not corrected. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100.6 MHz) spectra: *Bruker-WM-400* spectrometer; δ [ppm] scale, coupling constants J in Hz, TMS as internal standard. EI-MS (70 eV): *Varian MAT 7*, data given as m/z (%). FD-MS (70 eV): *Varian MAT 711*, data given as m/z (%). C,H,N Analyses: *Carlo-Erba-Strumentazione-1106* apparatus.

N-{*1-[1-(Phenylsulfonyl)-1*H*-indol-3-yl]vinyl*}*diacetamide* (**1a**). A soln. of **3b** [12] (1.0 g, 3.2 mmol) in pyridine (90 ml) and Ac_2O (60 ml) was heated under reflux for 48 h. The residue obtained after concentration under high vacuum was extracted with Et_2O. The org. phase was washed with aq. 1N Na_2CO_3, dried (Na_2SO_4), and evaporated. The residue was then purified by FC (petroleum ether/AcOEt 1:1): 650 mg (55%) of **1a**. Colorless crystals. M.p. 158° (AcOEt). ^{1}H-NMR ((D_6)DMSO): 2.33 (*s*, 2 Me); 5.51 (*d*, J = 0.8, 1 olef. H); 6.09 (*d*, J = 0.8, 1 olef. H); 7.34 (*dd*, J = 7.8, 7.9, H–C(5) or H–C(6)); 7.57 (*dd*, J = 7.5, 7.6, H–C(3′), H–C(5′) ($PhSO_2$)); 7.68 (*dd*, J = 7.4, 7.4, H–C(4′)); 7.85 (*d*, J = 7.9, H–C(7)); 7.98–8.03 (*m*, H–C(2), H–C(4), H–C(2′), H–C(6′)). ^{13}C-NMR ((D_6)DMSO): 25.72 (2 Me); 113.49 (C(7)); 117.57 (C=*C*H_2); 119.81 (C(3)); 120.74 (C(5)); 124.23 (C(4)); 125.37 (C(6), C(2)); 126.68 (C(3′), C(5′) ($PhSO_2$)); 127.07 (C(3a)); 129.74 (C(2′), C(6′)); 134.73 (C(4′)); 134.96 (C(7a)); 136.60 (*C*=CH_2); 137.39 (C(1′)); 171.98 (2 C=O). EI-MS: 382 (24, M^+), 339 (100), 298 (18), 208 (98). Anal. calc. for $C_{20}H_{18}N_2O_4S$ (382.44): C 62.81, H 4.74, N 7.33; found: C 62.83, H 4.65, N 7.45.

N-{*1-[1-(Phenylsulfonyl)-1*H*-indol-3-yl]vinyl*}*acetamide* (**1b**). Product **1a** (300 mg, 0.8 mmol) was dissolved in MeOH (60 ml). Highly activated silica gel *60* (*Merck*, particle size 0.063–0.200 mm, dried at 160°/600 Torr) was added until the mixture was dry. After 10 h, CH_2Cl_2 (60 ml) was added, the mixture filtered, and the org. phase concentrated under high vacuum. The residue was crystallized from petroleum ether/AcOEt: 260 mg (96%) of **1b**. Colorless crystals. M.p. 148°. ^{1}H-NMR ((D_6)DMSO): 2.03 (*s*, Me); 5.08 (*s*, 1 olef. H); 5.83 (*s*, 1 olef. H); 7.30 (*dd*, J = 7.7, 7.8, H–C(5) or H–C(6)); 7.38 (*dd*, J = 7.2, 7.3, H–C(6) or H–C(5)); 7.59 (*dd*, J = 7.5, 7.4, H–C(3′), H–C(5′) ($PhSO_2$)); 7.68–8.05 (*m*, H–C(2), H–C(4), H–C(7), H–C(2′), H–C(4′), H–C(6′)); 9.32 (*s*, NH). EI-MS: 340 (60, M^+), 325 (30), 298 (39), 200 (100). Anal. calc. for $C_{18}H_{16}N_2O_3S$ (340.40): C 63.45, H 4.70, N 8.22; found: C 63.20, H 4.75, N 7.97.

N-{*1-(1-Acetyl-1*H*-indol-3-yl)vinyl]diacetamide* (**1c**). A soln. of **3a** (1.5 g, 8.6 mmol) in pyridine (250 ml) and Ac_2O (140 ml) was heated under reflux for 72 h. Workup as described for **1a** and purification by FC (AcOEt): 800 mg (33%) of **1c**. Colorless crystals. M.p. 150° (AcOEt). ^{1}H-NMR ((D_6)DMSO): 2.36 (*s*, 2 Ac); 2.65 (*s*, 1 Ac); 5.55 (*s*, 1 olef. H); 6.10 (*s*, 1 olef. H); 7.34–7.42 (*m*, H–C(5), H–C(6)); 7.87 (*dd*, $^3J(6,7)$ = 7.2, $^4J(5,7)$ = 1.2, H–C(7)); 7.97 (*s*, H–C(2)); 8.41 (*dd*, $^3J(5,4)$ = 8.0, $^4J(6,4)$ = 1.1, H–C(4)). ^{13}C-NMR ($CDCl_3$): 23.9 (*Me*CO); 26.2 (2 Me); 116.9 (C(7)); 117.2 (C=*C*H_2); 119.5 (C(3)); 119.6 (C(5)); 123.7 (C(4)); 124.3 (C(2)); 125.9 (C(6)); 127.1 (C(3a)); 136.5 (C(7a)); 138.5 (*C*=CH_2); 168.3 (Me*C*O); 172.7 (2 Me*C*O). EI-MS: 284 (18, M^+), 242 (100), 200 (78), 185 (68), 159 (70), 143 (31). Anal. calc. for $C_{16}H_{16}N_2O_3$ (284.32): C 67.59, H 5.67, N 9.85; found: C 67.50, H 5.79, N 9.68.

N-{*1-[1-(Phenylsulfonyl)-2-methyl-1*H*-indol-3-yl]vinyl*}*diacetamide* (**1d**). A soln. of **3c** (1.2 g, 3.53 mmol) in pyridine (100 ml) and Ac_2O (60 ml) was heated under reflux for 96 h. Workup as described for **1a** and purification by FC (petroleum ether/AcOEt 1:1): 300 mg (21%) of **1d**. Colorless crystals. M.p. 143° (AcOEt). ^{1}H-NMR ((D_6)DMSO): 2.25 (*s*, 2 Me); 2.66 (*s*, Me–C(2)); 5.62 (*s*, 1 olef. H); 5.67 (*s*, 1 olef. H); 7.23–7.37 (*m*, H–C(5), H–C(6), H–C(7)); 7.57 (*dd*, J = 7.6, 7.5, H–C(3′), H–C(5′) ($PhSO_2$)); 7.67 (*dd*, J = 7.4, 7.5, H–C(4′)); 7.85 (*dd*, J = 7.5, 7.5, H–C(2′), H–C(6′)); 8.09 (*d*, J = 8.2, H–C(4)). ^{13}C-NMR ((D_6)DMSO): 13.5 (*Me*–C(2)); 25.8 (2 Me); 114.3 (C(7)); 117.4 (C=*C*H_2); 118.8 (C(4)); 121.2 (C(3)); 124.2 (C(5)); 124.5 (C(6)); 126.2 (C(3′), C(5′) ($PhSO_2$)); 127.3 (C(3a)); 129.9 (C(2′), C(6′)); 134.6 (C(4′)); 135.1 (C(7) or C(2)); 135.9 (C(2) or C(7)); 163.1 (*C*=CH_2); 137.5 (C(1′)); 172.56 (2 C=O). EI-MS: 396 (78, M^+), 213 (100), 144 (37). Anal. calc. for $C_{21}H_{20}N_2O_4S$ (396.47): C 63.62, H 5.08, N 7.08, S 8.09; found: C 63.60, H 5.12, N 7.10, S 8.00.

*(*E*)-1-(1*H*-Indol-3-yl)ethanone Oxime* (**3a**). Compound **2a** (1.3 g, 8 mmol) was dissolved by warming in MeOH (280 ml). A mixture of $NH_2OH \cdot HCl$ (13.9 g, 0.2 mol) and NaOAc (14.7 g) in H_2O (100 ml) was added. The mixture was then heated under reflux for 12 h. After cooling, the mixture was evaporated, the residue mixed with H_2O (30 ml) and extracted several times with Et_2O, the org. phase washed with aq. 1N $NaHCO_3$, dried (Na_2SO_4), and evaporated, and the residue recrystallized from MeOH: 900 mg (65%) of **3a**[9]. Colorless crystals. M.p. 147° (MeOH). ^{1}H-NMR ((D_6)DMSO): 2.18 (*s*, Me); 7.04 (*dd*, J = 7.5, 7.4, H–C(5) or H–C(6)); 7.12 (*dd*, J = 7.3, 7.1,

[9]) The stereoselective synthesis of **3a** was confirmed by HPLC (*RP-18* column, ∅ 12.5 cm, MeCN/H_2O 7:2, UV detector (254 nm)).

H–C(6) or H–C(5)); 7.38 (*d*, *J* = 8.0, H–C(7)); 7.64 (*s*, H–C(2)); 8.14 (*d*, *J* = 7.9, H–C(4)); 10.51 (*s*, OH); 11.29 (*s*, NH). EI-MS: 174 (100, $M^{+\cdot}$), 157 (41), 142 (31), 117 (62). Anal. calc. for $C_{10}H_{10}N_2O$ (174.20): C 68.95, H 5.79, N 16.08; found: C 69.11, H 5.75, N 16.11.

(Z)-1-[1-(Phenylsulfonyl)-1H-indol-3-yl]ethanone Oxime (**3b**). A soln. of **2b** (3.0 g, 10 mmol) in MeOH (300 ml) was warmed and a mixture of $NH_2OH \cdot HCl$ (17.5 g, 0.26 mol) and NaOAc (18.25 g) added. The mixture was heated under reflux for 15 min, cooled, and the solvent evaporated. The residue was suspended in H_2O (30 ml) and extracted several times with Et_2O. The combined org. phases were washed with aq. 1N $NaHCO_3$, dried (Na_2SO_4), and concentrated. The residue was crystallized from MeOH: 2.94 g (94%) of **3b**[10]. Colorless crystals. M.p. 142°. ^{1}H-NMR ((D$_6$)DMSO): 2.22 (*s*, Me); 7.28 (*dd*, *J* = 7.9, 8.0, H–C(5) or H–C(6)); 7.37 (*dd*, *J* = 8.3, 8.4, H–C(6) or H–C(5)); 7.59 (*dd*, *J* = 7.5, 7.5, H–C(3′), H–C(5′) ($PhSO_2$)); 7.68 (*dd*, *J* = 7.3, 7.3, H–C(4′)); 7.94 (*d*, *J* = 8.2, H–C(7)); 8.04 (*d*, *J* = 8.1, H–C(2′), H–C(6′)); 8.13 (*s*, H–C(2)); 8.18 (*d*, *J* = 7.7, H–C(4)); 11.20 (*s*, OH). EI-MS: 314 (100, $M^{+\cdot}$), 173 (96), 141 (14), 132 (70), 115 (30), 77 (89). Anal. calc. for $C_{16}H_{14}N_2O_3S$ (314.36): C 61.13, H 4.49, N 8.91; found: C 61.30, H 4.45, N 8.90.

(E)-1-[1-(Phenylsulfonyl)-2-methyl-1H-indol-3-yl]ethanone Oxime (**3c**). Synthesized according to the procedure to compound **3a** from **2c** (5 g, 16 mmol) in MeOH (650 ml), $NH_2OH \cdot HCl$ (28 g, 0.4 mol) and NaOAc (29 g) in 200 ml water. The mixture was heated under reflux for 20 h. Yield: 3.3 g (62.8%) of **3c**. Colorless crystals. M.p. 162° (MeOH). ^{1}H-NMR ((D$_6$)DMSO): 2.14 (*s*, Me); 2.63 (*s*, Me–C(4)); 7.22–7.92 (*m*, 8 arom. H); 8.10 (*d*, *J* = 7.7, H–C(4)); 11.32 (*s*, OH). EI-MS: 328 (62, $M^{+\cdot}$), 187 (48), 170 (100), 146 (52), 128 (20), 77 (81). Anal. calc. for $C_{17}H_{16}N_2O_3S$ (328.39): C 62.18, H 4.91, N 8.53, S 9.76; found: C 62.10, H 5.09, N 8.51, S 9.70.

(±)-N-[1,2,3,3aβ,4,10,10aβ,10bβ-Octahydro-1,3-dioxo-2-phenyl-10-(phenylsulfonyl)pyrrolo[3,4-a]carbazol-5-yl]acetamide (**4a**). To a soln. of **1a** (190 mg, 0.5 mmol) and *N*-phenylmaleimide (86 mg, 0.5 mmol) in CH_2Cl_2 (30 ml), highly activated molecular sieves (4 Å; 5 g) were added, and the mixture was stirred at 20° for 10 days. The molecular sieves were then filtered off and the solvent evaporated. The residue was purified by FC (AcOEt): 38 mg (14%) of **4a**. Colorless crystals. M.p. 179° (AcOEt).

In the same way, **4a** was obtained from **1b** (340 mg, 1 mmol) and *N*-phenylmaleimide (172 mg, 1 mmol) in CH_2Cl_2 (30 ml) in the presence of molecular sieves (5 g). The mixture was stirred at 20° for 18 h and the product purified by FC: 150 mg (30%) of **4a**. ^{1}H-NMR ($CDCl_3$): 2.04 (*s*, Me); 2.56 (*dd*, ^2J = 15.9, ^3J = 7.2, H_β–C(4)); 3.26 (*d*, ^2J = 15.9, H_α–C(4)); 3.31–3.35 (*m*, H_β–C(3a)); 4.18 (*dd*, ^3J = 8.9, 6.8, H_β–C(10a)); 6.93–7.87 (*m*, 1 arom. H). ^{1}H-NMR ((D$_6$)DMSO): 9.58 (NH). EI-MS: 513 (24, $M^{+\cdot}$), 372 (20), 340 (11), 330 (100), 199 (67). Anal. calc. for $C_{28}H_{23}N_3O_5S$ (513.20): C 65.47, H 4.48, N 8.18, S 6.24; found: C 65.60, H 4.39, N 7.91, S 5.96.

(±)-N-(10-Acetyl-1,2,3,3aβ,4,10,10aβ,10bβ-octahydro-1,3-dioxo-2-phenylpyrrolo[3,4-a]carbazol-5-yl)acetamide (**4b**). As described for **4a**, from **1c** (200 mg, 0.7 mmol), *N*-phenylmaleimide (120 mg, 0.7 mmol), CH_2Cl_2 (20 ml), and molecular sieves (4 Å; 5 g; standing at r.t. for 20 weeks). The residue was purified by CC (AcOEt): 68 mg (23%) of **4b**. Colorless crystals. M.p. 188° (AcOEt). ^{1}H-NMR ($CDCl_3$): 2.13 (*s*, *Ac*NH); 2.55 (*s*, Ac–N(10)); 2.60 (*dd*, ^2J = 15.9, ^3J = 7.0, H_β–C(4)); 3.17 (*d*, ^2J = 15.8, H_α–C(4)); 3.32 (*dd*, ^3J = 7.0, 8.1, H–C(3a)); 4.43 (*dd*, ^3J = 8.3, 7.1, H_β–C(10b)); 4.95 (*d*, ^3J = 7.0, H_β–C(10a)); 6.89–7.42 (*m*, 9 arom. H). EI-MS: 415 (46, $M^{+\cdot}$), 373 (15), 330 (52), 242 (30), 200 (82). Anal. calc. for $C_{24}H_{21}N_3O_4$ (415.17): C 69.43, H 5.09, N 10.12; found: C 69.38, H 5.15, N 10.08.

(±)-N-(10-Acetyl-1,2,3,3aβ,4,10,10aα,10bβ-octahydro-1,3-dioxo-2-phenylpyrrolo[3,4-a]carbazol-5-yl)diacetamide (**4c**). To a soln. of **1c** (370 mg, 1.3 mmol) in toluene (20 ml) were added molecular sieves (4 Å; 3.0 g) and *N*-phenylmaleimide (190 mg, 1.09 mmol). The mixture was heated under reflux for 3 days, allowed to cool and filtered, the filtrate evaporated, and the residue purified by CC (petroleum ether/AcOEt 1:1): 71 mg (12%) of **4c**. Colorless crystals. M.p. 240° (petroleum ether/AcOEt). ^{1}H-NMR ((D$_6$)DMSO): 2.28, 2.29, 2.41 (3*s*, 3 Me); 2.64 (*dd*, *J* = 9.9, 9.7, H_β–C(3a)); 2.73 (*dd*, *J* = 15.4, 8.6, H_α–C(4)); 2.88 (*dd*, *J* = 15.4, 9.6, H_β–C(4)); 3.61 (*dd*, *J* = 9.1, 9.0, H_β–C(10b)); 5.40 (*d*, *J* = 10.4, H_α–C(10a)); 7.16 (*dd*, *J* = 7.6, 7.4, 1 H–C(6) or H–C(7)); 7.22 (*d*, *J* = 6.9, H–C(5) or H–C(8)); 7.38 (*m*, H–C(2′), H–C(6′) (Ph) H–C(7) or H–C(6)); 7.43 (*dd*, *J* = 7.4, 7.4, H–C(4′)); 7.53 (*dd*, *J* = 7.8, 7.4, H–C(3′), H–C(5′)); 7.92 (*d*, *J* = 7.9, H–C(8) or H–C(5)). EI-MS: 457 ($M^{+\cdot}$). HR-MS: 457.4229 ($C_{26}H_{23}N_3O_5$, calc. 457.4848).

(±)-N-[2,3,11,11aβ-Tetrahydro-1,3-dioxo-2-phenyl-11-(phenylsulfonyl)-1H,5H-[1,2,4]triazolo[1,2-a]pyridazino[3,4-b]indol-6-yl]diacetamide (**5a**). To a soln. of **1a** (120 mg, 0.32 mmol) in CH_2Cl_2 (20 ml) at –78°, 4-phenyl-3*H*-1,2,4-triazol-3,5(4*H*)-dione (60 mg, 0.34 mmol) in CH_2Cl_2 (10 ml) was added from a syringe and the mixture stirred at –78° for 0.5 h followed by 1 h at r.t. The org. solvent was evaporated and the residue crystallized from petroleum ether/AcOEt: 165 mg (92%) of **5a**. Slightly yellow crystals. M.p. 168° (AcOEt). ^{1}H-NMR ($CDCl_3$): 2.06 (*s*, Me); 2.50 (*s*, Me); 4.28 (*dd* ^2J = 16.4, ^5J = 1.1, H_α–C(5) or H_β–C(5)); 4.57 (*dd*, ^2J = 16.4,

[10]) The stereoselective synthesis of **3b** was confirmed by HPLC (see *Footnote* [9]) for details).

^5J = 2.0, H_β–C(5) or H_α–C(5)); 6.36 (*d*, ^5J = 1.5, H–C(11a)); 7.06–7.60 (*m*, 12 arom. H); 8.03 (*d*, ^3J = 8.0, 2 arom. H). FD-MS: 557 (100, $M^{+\cdot}$), 497 (20), 474 (10), 415 (32), 379 (22). Anal. calc. for $C_{28}H_{23}N_5O_6S$ (557.59): C 60.31, H 4.16, N 12.56; found: C 60.05, H 4.25, N 12.32.

*(±)-*N*-(11-Acetyl-2,3,11,11aβ-tetrahydro-2-phenyl-1*H*,5*H*-[1,2,4]triazolo[1,2-a]pyridazino[3,4-b]indol-6-yl)diacetamide* (**5c**). As described for **5a**, from **1c** (100 mg, 0.35 mmol), CH_2Cl_2 (20 ml), 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (65 mg, 0.37 mmol), CH_2Cl_2 (10 ml; 0.5 h at −78°, 2 h at r.t.) The residue was purified by CC (AcOEt): 85 mg (53%) of **5c**. Slightly yellowish crystals. M.p. 188°. ^{1}H-NMR ($CDCl_3$): 2.37 (*s*, Me); 2.41 (*s*, Me); 2.58 (*s*, Me); 4.36 (*d*, ^2J = 16.2, H_α–C(5) or H_β–C(5)); 4.74 (*d*, ^2J = 16.2, H_β–C(5) or H_α–C(5)); 6.31 (*s*, H–C(11a)); 7.08–7.42 (*m*, 9 arom.). FD-MS: 459 (100, $M^{+\cdot}$), 398 (57). Anal. calc. for $C_{24}H_{21}N_5O_5$ (459.19): C 62.77, H 4.57, N 15.24; found: C 62.69, H 4.60, N 15.19.

*(±)-*N*-[1-Formyl-1β,2,3,9aβ-tetrahydro-9-(phenylsulfonyl)-9*H*-carbazol-4-yl]acetamide* (**6**). To a suspension of **1b** (100 mg, 0.34 mmol) in acrylaldehyde (30 ml, 0.50 mmol), molecular sieves (4 Å; 5 g) were added. The mixture was stirred at r.t. for 7 days. The mixture was filtered, the filtrate concentrated, and the residue purified by FC (AcOEt): 96 mg (71%) of **6**. Slightly yellowish crystals. M.p. 154° [12]. ^{1}H-NMR ($CDCl_3$): 1.69–1.82 (*m*, 1 H, CH_2); 2.06 (*s*, Me); 2.18–2.24 (*m*, 1 H, CH_2); 2.31–2.37 (*m*, 1 H, CH_2); 2.88 (*dd*, ^2J = 19.0, ^3J = 3.2, 1 H, CH_2); 3.64–3.65 (*m*, H–C(1)); 4.53 (*d*, ^3J = 3.2, H–C(9a)); 6.89 (*s*, NH); 7.23–7.75 (*m*, 7 arom. H); 7.87 (*d*, *J* = 8.2, H–C(5)); 9.86 (*s*, CHO). EI-MS: 396 (11, $M^{+\cdot}$), 340 (10), 255 (23), 199 (69), 183 (53), 77 (100). Anal. calc. for $C_{21}H_{20}N_2O_4S$ (396.52): C 63.62, H 5.08, N 7.07; found: C 63.56, H 5.00, N 6.95.

*(Z)-*N*-{1-[1-(Phenylsulfonyl)-1*H*-indol-3-yl]-3,3,4,4-tetracyanobut-1-en-1-yl}acetamide* (**7**). To a suspension of **1b** (100 mg, 0.34 mmol) and ethenetetracarbonitrile (45 mg, 0.35 mmol) in toluene (50 ml), molecular sieves (4 Å; 7 g) were added. The mixture was stirred at r.t. for 3 days, and filtered, the filtrate evaporated, and the residue purified by CC (AcOEt/petroleum ether 1:1): 188 mg (68%) of **7**. Slightly yellowish crystals. M.p. 219° (dec. with blue coloring of crystals; from AcOEt). ^{1}H-NMR ((D_6)DMSO): 1.85 (*s*, Me); 5.43 (*s*, H–C(2)); 7.35 (*dd*, *J* = 7.9, 7.2, H–C(5′) or H–C(6′) (indol)); 7.42 (*dd*, ^3J = 7.2, 7.7, H–C(6′) or H–C(5′)); 7.62 (*dd*, ^3J = 7.8, 7.7, H–C(3″), H–C(5″) ($PhSO_2$)); 7.72 (*dd*, ^3J = 7.4, 7.5, H–C(4″)); 7.80 (*d*, ^3J = 7.9, H–C(7′)); 7.97 (*d*, *J* = 8.3, H–C(4′)); 8.07 (*dd*, *J* = 7.5, 7.5, H–C(2″), H–C(6″)); 8.15 (*s*, H–C(2″)); 8.25 (*s*, H–C(4), exchangeable with D_2O); 10.01 (*s*, NH, exchangeable with D_2O). EI-MS: 468 (13, $M^{+\cdot}$), 398 (21), 351 (31), 258 (30), 141 (29), 77 (100). Anal. calc. for $C_{24}H_{16}N_6O_3S$ (468.50): C 61.53, H 3.44, N 17.94; found: C 60.97, H 3.38, N 17.85.

*(±)-*N*-[2,3,11,11aβ-Tetrahydro-11aβ-methyl-1,3-dioxo-2-phenyl-11-(phenylsulfonyl)-[1,2,4]triazolo[1,2-a]-pyridazino[3,4-b]indol-6-yl]diacetamide* (**8**). To a soln. of **1d** (100 mg, 0.25 mmol) in CH_2Cl_2 (20 ml), 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (90 mg, 5.1 mmol) in CH_2Cl_2 (10 ml) was added and the mixture stirred at 20° for 5 days. The solvent was then evaporated and the residue purified by FC (petroleum ether/AcOEt 1:1): 105 mg (74%) of **8**. Colorless crystals. M.p. 188° (AcOEt). ^{1}H-NMR ($CDCl_3$): 1.60 (*s*, Me–C(11a)); 2.11 (*s*, MeCO); 2.54 (*s*, 3 H, MeCO); 4.20 (*s*, CH_2); 7.12–7.78 (*m*, 14 arom. H). ^{13}C-NMR ($CDCl_3$): 24.4 (Me–C(11a)); 26.4 (Me); 26.5 (Me); 49.1 (C(5)); 82.4 (C(11a)); 119.4 (C(10)); 123.6 (C(7)); 124.6 (C(6a)); 125.8 (C(6)); 126.1 (C(8)); 126.2 (C(2′), C(6′) (Ph–N(2))); 127.9 (C(2″), C(6″) ($PhSO_2$)); 128.8 (C(9)); 128.9 (C(3′), C(5′)); 129.3 (C(3″), C(5″)); 138.5 (C(10a)); 139.6 (C(1′)); 141.7 (C(1″)); 149.9 (C=O); 154.2 (C=O); 170.10 (C=O); 172.8 (C=O). EI-MS: 571 (5, $M^{+\cdot}$), 470 (13), 210 (49), 154 (18), 119 (100). Anal. calc. for $C_{29}H_{25}O_6S$ (571.15): C 60.93, H 4.41, N 12.26, S 5.60; found: C 60.90, H 4.52, N 12.32, S 5.61.

Crystal-Structure Determination of **1c** ($C_{16}H_{16}N_2O_3$). A dark yellow crystal of **1c** (approximate dimensions: 0.65 × 0.57 × 0.40 mm) was investigated using a 4-circle diffractometer (*Enraf Nonius CAD 4*, CuK_α radiation, graphite monochromator). The monoclinic lattice constants were refined from 25 high angle reflections to *a* = 1052.6(2), *b* = 2819.4(3), *c* = 982.8(3) pm, β = 92.94(2)°. From systematic extinctions, the space group $P2_1/c$ with *Z* = 8 was derived. Thus, the structure – resolved by direct methods (SHELXS-86 [28]) – contains two very similar independent molecules in the asymmetric unit. The refinement (457 parameters) was performed using full-matrix least-squares methods (SHELX76 [29]) based on 3245 unique reflections ($F_o > 3\sigma$, Θ 2–55°) and using the weighting factor $w = 1/\sigma^2(F_o)$. Anisotropic temperature factors were assigned to all non-H-atoms. The H-atoms were located in a difference *Fourier* map, whereas, for the indole system, they were fixed at 'riding' positions. For each different type of H-atoms, a common isotropic temperature factor was refined. The final residuals converged to *R* = 0.046 and *wR* = 0.039, the largest parameter shift in the last cycle was 0.02 e.s.d., the max/min peaks in a difference *Fourier* map were 0.14/ − 0.21 e/Å^2. Additional information, the resulting atomic parameters, and the structure factor tables have been deposited[11]).

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[11]) This material is available on request from the *Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH*, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55162, the names of the authors, and the journal citation.

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