A Novel Route to 1-Substituted 3-(Dialkylamino)-9-oxo-9*H*-indeno[2,1-*c*]-pyridine-4-carbonitriles

by **Thomas Landmesser**[1]), **Anthony Linden**, and **Hans-Jürgen Hansen***

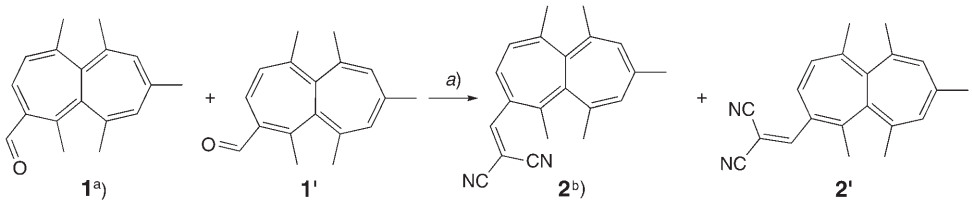
Organisch-chemisches Institut der Universität, Winterthurerstrasse 190, CH-8057 Zürich

Heptalenecarbaldehydes **1**/**1′** as well as aromatic aldehydes react with 3-(dicyanomethylidene)-indan-1-one in boiling EtOH and in the presence of secondary amines to yield 3-(dialkylamino)-1,2-dihydro-9-oxo-9*H*-indeno[2,1-*c*]pyridine-4-carbonitriles (*Schemes 2* and *4*, and *Fig. 1*). The 1,2-dihydro forms can be dehydrogenated easily with $KMnO_4$ in acetone at 0° (*Scheme 3*) or chloranil (=2,3,5,6-tetrachlorocyclohexa-2,5-diene-1,4-dione) in a 'one-pot' reaction in dioxane at ambient temperature (*Table 1*). The structures of the indeno[2,1-*c*]pyridine-4-carbonitriles **5′** and **6a** have been verified by X-ray crystal-structure analyses (*Fig. 2* and *4*). The inherent merocyanine system of the dihydro forms results in a broad absorption band in the range of 515–530 nm in their UV/VIS spectra (*Table 2* and *Fig. 3*). The dehydrogenated compounds **5**, **5′**, and **7a**–**7f** exhibit their longest-wavelength absorption maximum at *ca.* 380 nm (*Table 2*). In contrast to **5** and **5′**, **7a**–**7f** in solution exhibit a blue-green fluorescence with emission bands at around 460 and 480 nm (*Table 4* and *Fig. 5*).

1. Introduction. – In the course of our investigations of thermally and photochemically switchable π-donor,π-acceptor-substituted heptalenes [1–3], we became interested in *Knoevenagel*-type condensation reactions of heptalene-carbaldehydes with π-acceptor-carrying methylidene compounds such as malononitrile or 3-(dicyanomethylidene)indan-1-one, a method to prepare the corresponding ethenylheptalenes. Whereas we encountered no problems to synthesize β,β-dicyanoethenyl-substituted heptalenes (*Scheme 1*) [4] by this route, the reaction with the indan-1-one did not work very well during our first attempts. We isolated in this case, in low yield, violet crystals of a compound, the spectra of which were not at all in accordance with the expected product **3** or its double-bond-shifted (DBS) isomer **3′** (*Scheme 2*). Moreover, the spectra indicated that the *Knoevenagel* catalyst, piperidine, had become an integral part of the unknown structure. A crystallographic analysis of the violet crystals revealed finally the structure of an 1-heptalenyl-substituted 1,2-dihydro-9-oxo-3-(piperidin-1-yl)-9*H*-indeno[2,1-*c*]pyridine-4-carbonitrile **4′** (*Fig. 1*). On standing in solution, **4′** slowly underwent dehydrogenation, a process, which could be performed cleanly with $KMnO_4$ in acetone at 0° (*Scheme 3*). The two yellow-to-orange-colored DBS isomers **5** and **5′** were obtained as a 1:3 mixture, which we could not separate chromatographically. However, both compounds crystallized in morphologically different forms, so that the conglomerate of crystals could be separated manually. The structure of **5′** was again secured by an X-ray crystal-diffraction analysis (*Fig. 2*).

[1]) Part of the Ph.D. thesis of *T. L.*, University of Zurich, 2001; current address: *Siegfried AG*, Untere Brühlstrasse 4, CH-4800 Zofingen.

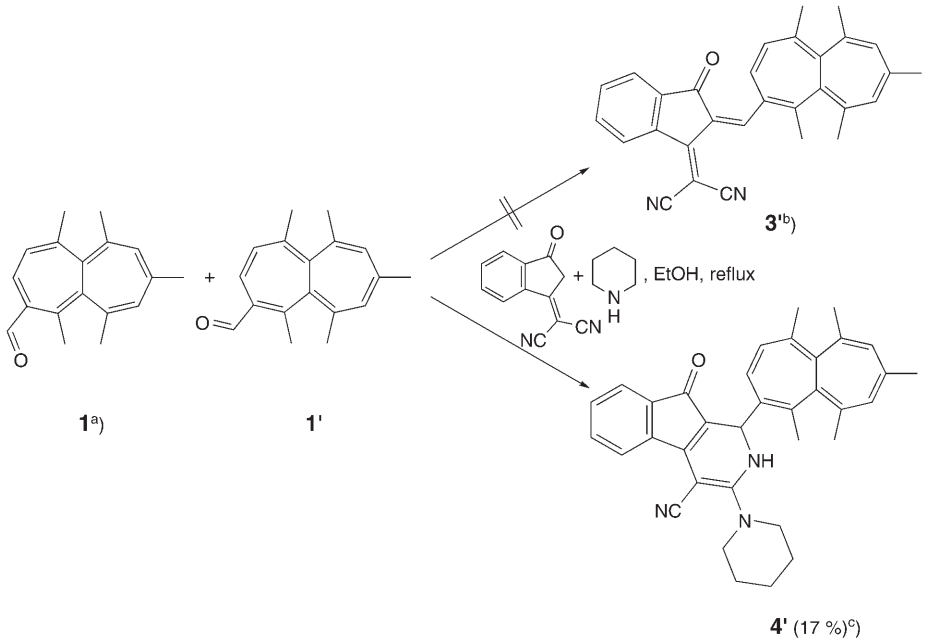
Scheme 1



a) $CH_2(CN)_2$, cat. Piperidine, EtOH, reflux; 31% [4][b]).

[a]) A mixture of 57% of **1** and 43% of **1′** was used. [b]) Yields up to 86% of a 1:3 mixture of **2**/**2′** are obtained with $TiCl_4$/pyridine at 0° to r.t.

Scheme 2



[a]) See *Footnote a* of *Scheme 1*. [b]) Neither **3′** nor its DBS isomer **3** were found. [c]) The crystallized form represented pure **4′**.

Since the formation of **4′**, followed by dehydrogenation to **5**/**5′** seemed to represent a new path for the synthesis of 1-substituted 3-(dialkylamino)-9-oxo-9*H*-indeno[2,1-*c*]pyridine-4-carbonitriles, we reacted 3-(dicyanomethylidene)indan-1-one, which is easily available from indane-1,3-dione and malononitrile [5], with other aldehydes and secondary amines, and here we report on these investigations.

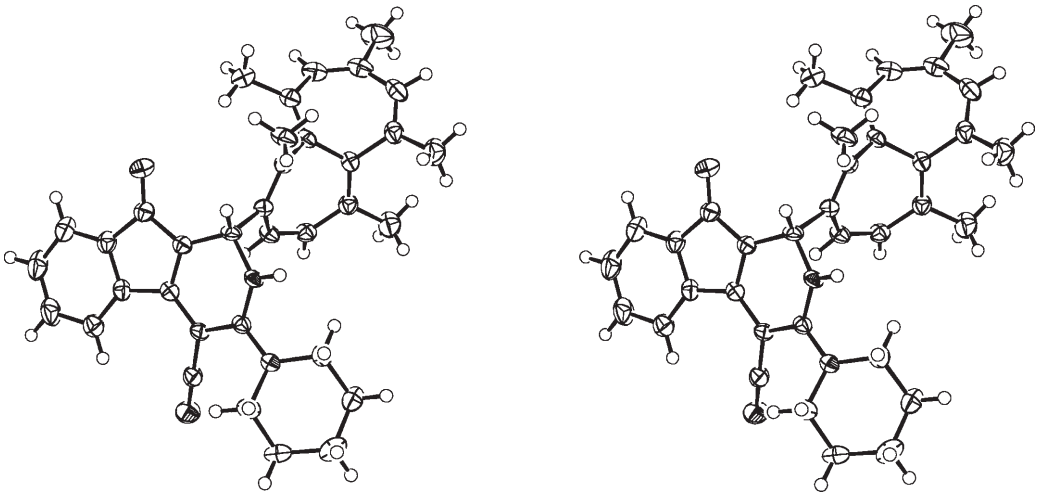
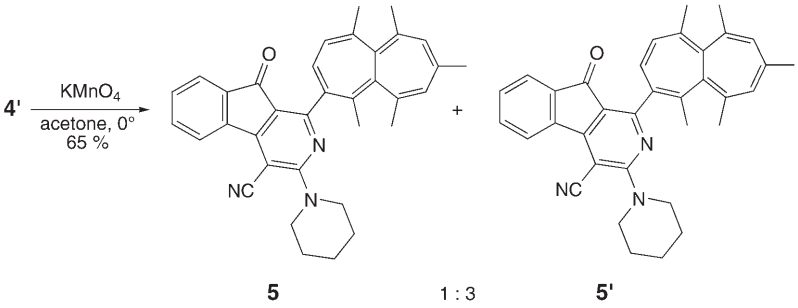


Fig. 1. *Stereoscopic view of the X-ray crystal structure of* **4′**. The (*P*,1*S*)-configuration is shown (atoms with 50% probability ellipsoids).

Scheme 3



2. Results. – 2.1. *Product Formation.* The formation of **4′** from heptalenecarbaldehydes **1**/**1′**, 3-(dicyanomethylidene)indan-1-one, and piperidine in boiling EtOH is indeed a general reaction of the indanone, aromatic aldehydes, and secondary amines. In these cases, however, the primary compounds **6** were accompanied by their dehydrogenated forms **7**, or the latter represented the solely found form (*Scheme 4*). Attempts to realize the formation of **6** or just **7** with other aldehydes such as methanal, propanal, 2,2-dimethylpropanal (pivalaldehyde), and 3,3-dimethylpropenal (senecioaldehyde) were less successful, since complex inseparable mixtures, which may have contained small amounts of compounds of type **6** and **7**, were formed in low yields.

In further experiments, we tried to develop a more convenient one-pot procedure for the formation of the stable aromatized forms **7**. Benzoquinones such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or *o*- and *p*-chloranil are generally excellent dehydrogenating reagents for 1,2- or 1,4-dihydroaromatic compounds [6], which can be applied in solvents such as 1,4-dioxane, wherein the [5 + 1] cyclocondensation reaction

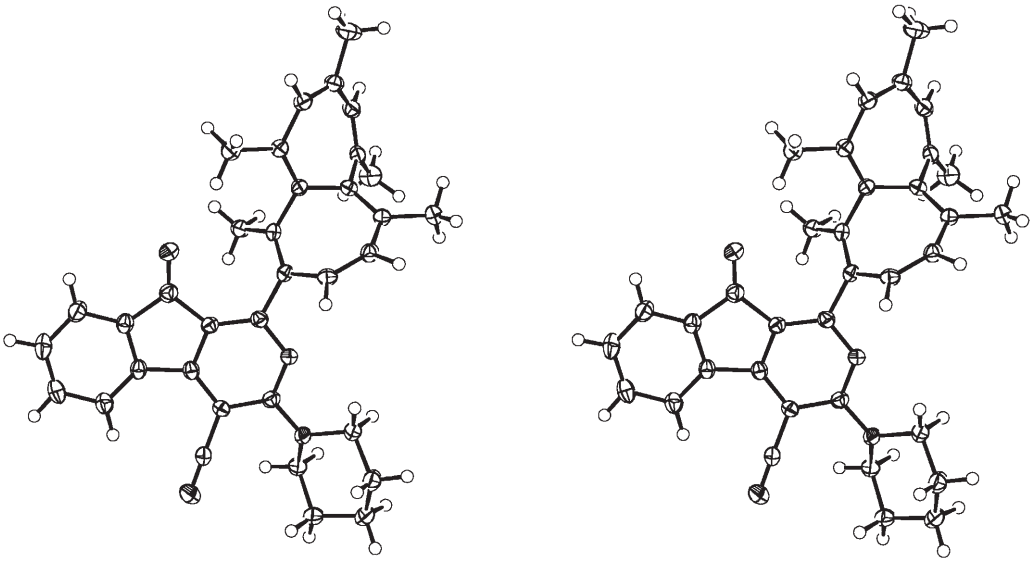
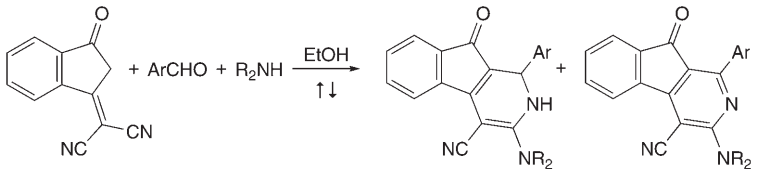


Fig. 2. *Stereoscopic view of the X-ray crystal structure of* **5′**. The (*P*)-configuration is shown (atoms with 50% probability ellipsoids).

Scheme 4

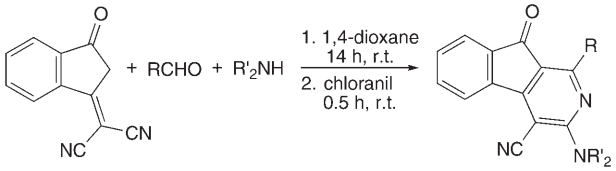


6 **7**

	Ar	R	Yield [%]	Yield [%]
a	Ph	$-(CH_2)_5-$	49	8
b	Ph	Et	51	12
c	Thien-2-yl	$-(CH_2)_5-$	37	27
d	Pyrid-4-yl	$-(CH_2)_5-$	0	25

to **6** also took place. We found that the indeno[2,1-*c*]pyridine-4-carbonitriles **7** were indeed the sole products, when the reaction of the indanone, aldehyde, and secondary amine was performed in 1,4-dioxane at room temperature, followed by the addition of chloranil (=2,3,5,6-tetrachlorocyclohexa-2,5-diene-1,4-dione; *Table 1*). The yields of **7** were *grosso modo* the same as the total yields of **6** and **7** in EtOH. The yield of the DBS isomers **5** and **5′** was distinctly higher than in EtOH, but still lower than for the aromatic aldehydes with the exception of pyridine-4-carbaldehyde and cinnamaldehyde. The slightly different basicity of the tested secondary amines, Et_2NH (pK_a 10.5), piperidine

Table 1. *One-Pot Formation of 1-Substituted 3-(Dialkylamino)-9-oxo-9*H*-indeno[1,2-*c*]pyridine-4-carbonitriles with Chloranil as Dehydrogenating Reagent*[a])



R	R′	Product	Yield [%][b])
1,5,6,8,10-Pentamethylheptalen-2- and -4-yl	$-(CH_2)_5-$	**5**, **5′**	44[c])
Ph	$-(CH_2)_5-$	**7a**	66
Ph	Et	**7b**	63
Ph	$-(CH_2)_4-$	**7e**	68
Thien-2-yl	$-(CH_2)_5-$	**7c**	60
Pyridin-4-yl	$-(CH_2)_5-$	**7d**	26
(*E*)-Styryl	$-(CH_2)_5-$	**7f**	12[d])

[a]) 1 mol-equiv. of the indanone was reacted with 1.2 mol-equiv. of aldehyde and *sec*-amine; after 14 h, 1.1 mol-equiv. of chloranil were added. [b]) Yield of chromatographically purified material. [c]) 1 : 1 Mixture of the two DBS isomers **5** and **5′**. [d]) Reaction time 18 h without subsequent addition of chloranil.

(pK_a 11.1), and pyrrolidine (pK_a 11.3), does not play an important role, since all three amines gave with benzaldehyde and the indanone similar yields of **7b**, **7a**, and **7e**, respectively, with a weak trend following the increasing basicity of the amines.

The formation of **7f** represented a special case, since **7f**, on heating in solution, was easily transformed into the 1-phenyl-substituted indeno[2,1-*c*]pyridine-4-carbonitrile **7a** under formal loss of acetylene. The temperature had, therefore, to be the room temperature, also during the procedure of workup and isolation of **7f**. The yield did not exceed 12%, and the addition of chloranil was not necessary. Obviously, the primary product **6f** was already dehydrogenated under the reaction conditions in 1,4-dioxane[2]).

2.2. *Spectroscopic and Structural Characteristics of the New Indeno[2,1-*c*]pyridine-4-carbonitriles and Their 1,2-Dihydro Forms.* Most noticeable is the change of color from red to yellow in going from the 1,2-dihydro-9*H*-indeno[2,1-*c*]pyridine-4-carbonitriles to their dehydrogenated forms, which indicates a fundamental difference of the two chromophoric systems. Indeed, whereas the 9*H*-indeno[2,1-*c*]pyridines exhibit absorption bands *grosso modo* comparable with those of fluorenones (*cf.*, *e.g.*, [7]), however, with larger molar extinction coefficients due to the presence of auxochromic

[2]) We undertook no further experiments to uncover the reason for the ease of dehydrogenation in this case. Air was not excluded in the experiments. Therefore, O_2 could be responsible for the dehydrogenation. But this would not explain the low yield of **7f**. Another hydrogen acceptor could be the reactant 3-(dicyanomethylidene)indan-1-one, an assumption in agreement with the low yield of **7f**. A further driving force for the ready dehydrogenation of **6f** may be found in the perfect planar s-*cis*-conformation of the ethenyl group of the (*E*)-configured styryl (=2-phenylethenyl) moiety with respect to the C(1)=N(2) bond of **7f** according to AM1 calculations, which guarantees an optimal π-stabilization (see also *Sect. 2.2*).

groups, their 1,2-dihydro forms show a broad symmetric absorption band at 516–531 nm (see *Fig. 3* and *Table 2*), which is best explained as charge-transfer (CT) transition of the inherent merocyanine-type partial structure, composed of the two amino N-atoms on one end and the C=O group on the other.

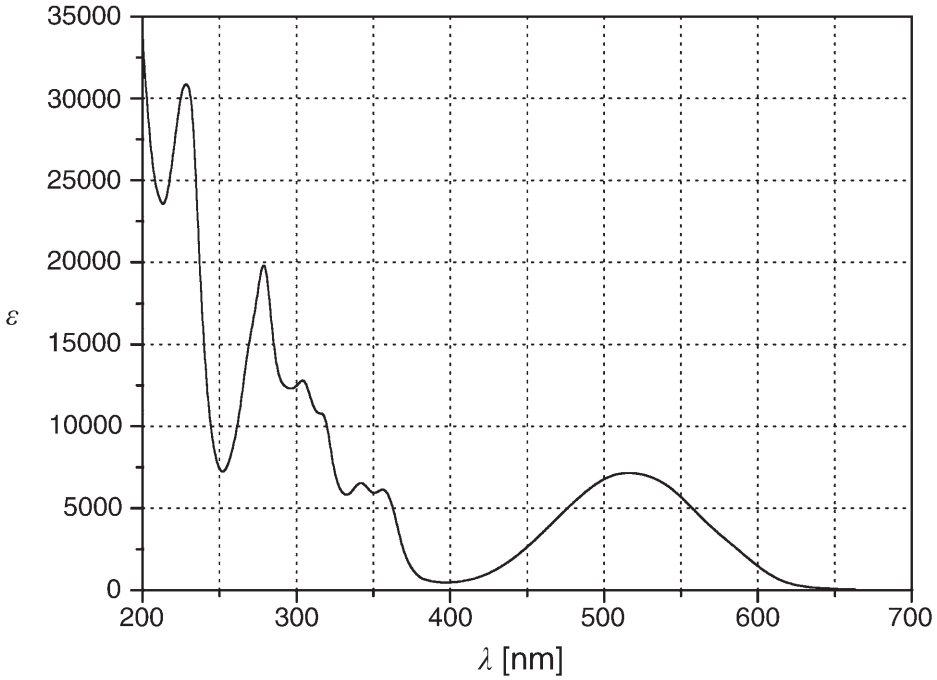


Fig. 3. *UV/VIS Spectrum* (MeCN) *of* **6a**

Table 2. *Characteristic UV/VIS and IR Data of the New 1,2-Dihydro-indeno[2,1-c]pyridine-4-carbonitriles and Indeno[2,1-c]pyridine-4-carbonitriles*

Fluorenone	UV/VIS[a]) [nm (log ε)]	IR[b]) [cm^{-1}]		Fluorenone	UV/VIS[c]) [nm (log ε)]	IR[b]) [cm^{-1}]	
		$\tilde{\nu}$(C=O)	$\tilde{\nu}$(C≡N)			$\tilde{\nu}$(C=O)	$\tilde{\nu}$(C≡N)
4′	531 (3.80)	1673*s*	2184*s*	**5′**	367 (4.11)	1707*s*	2213*m*
4[d])				**5**	371 (4.13)	1706*s*	2209*m*
6a	516 (3.85)	1667*s*	2184*s*	**7a**	375 (4.11)	1705*s*	2207*m*
6b	516 (3.86)	1665*s*	2171*s*	**7b**	373 (4.10)	1700*s*	2210*m*
6c	510 (3.87)	1668*s*	2185*s*	**7c**	390 (4.22)	1691*s*	2208*m*
6d[d])				**7d**	380 (4.10)	1706*s*	2208*w*
6e[e])				**7e**	373 (4.13)	1701*s*	2215*m*
6f[d])				**7f**	392 (4.27)	1691*s*	2217*m*

[a]) Longest-wavelength CT band in MeCN. [b]) IR Spectra in KBr. [c]) Longest-wavelength band in cyclohexane. [d]) Not found; see text. [e]) Not prepared.

Further structural factors that contribute to the long-wavelength absorption of the 1,2-dihydro structures are the cross-conjugated benzo ring and the CN group at C(4).

Additional spectroscopic information on the strong conjugative interaction of the merocyanine system of the 1,2-dihydro forms is derived from a comparison of the bond stretching frequencies of the C=O and the C≡N group with those of the corresponding dehydrogenated forms (*Table 2*). Whereas $\tilde{\nu}$(C=O) of the latter lies *ca.* 20 cm^{-1} below that of indeno[2,1-*c*]pyridine itself (1720–1725 cm^{-1} ($CHCl_3$) [8][9]), mainly due to the dialkylamino group at C(3), one finds, for the 1,2-dihydro forms, wavenumbers of 1665–1673 cm^{-1}, which indicate a strong conjugative interaction within the merocyanine partial structure in the ground state. That the CN group at C(4) participates in the merocyanine system can again be seen by a comparison of its wavenumbers, which change from *ca.* 2180 to 2210 cm^{-1} on dehydrogenation, again in good agreement with $\tilde{\nu}$(C≡N) of 2226 cm^{-1} of benzonitrile (film [10]), taking into account the *ortho*-neighborhood of the dialkylamino substituent. The strong conjugation within the merocyanine part of the 1,2-dihydro forms can also be recognized by comparison of the chemical shift of H–C(5) and H–C(8), which lie in both structures fully within the deshielding area of the C≡N and the C=O group, respectively, thus exposed to a downshift of *ca.* 0.5 ppm on dehydrogenation of the 1,2-dihydro forms (*Table 3*).

Table 3. *Chemical Shifts* δ [ppm] *of H–C(5) and H–C(8) of the 1,2-Dihydroindeno-pyridines and Indeno-pyridines*[a])

1,2-Dihydro-indeno-pyridines	H–C(5)	H–C(8)[b])	Indeno-pyridines	H–C(5)	H–C(8)
4′	7.85	*ca.* 7.3	**5′**	8.39	7.71
6a	7.83	*ca.* 7.3	**7a**	8.42	7.71
6b	7.93	*ca.* 7.3	**7b**	8.49	7.71
6c	7.85	*ca.* 7.3	**7c**	8.39	7.74

[a]) In $CDCl_3$. [b]) The signals of H–C(6,7,8) are superimposed in the narrow range of 7.4–7.2 ppm.

A closer inspection of the X-ray crystal structure of **4′** (*Fig. 1*) provides a deeper insight into the structural characteristics of the 1-substituted 3-(dialkylamino)-1,2-dihydroindeno[2,1-*c*]pyridine-4-carbonitriles. The crystal structure of **4′** shows a single diastereoisomer with a relative (*P*)-configuration of the heptalene part and (1*S*)-configuration at the dihydro-indeno-pyridine part. The benzene ring is planar as expected. The connected 1,2-dihydropyridine ring, however, forms a shallow boat conformation with the heptalenyl substituent at C(1) in flagpole position. The bottom plane contains the atoms N(2), C(3), C(4a), and C(8a), with C(1) and C(4) as bow and stern atoms. The dihedral angles between the bottom plane and those of the planes formed by C(9a), C(1), and N(2), and C(3), C(4), and C(4a) amount to 15.8(2)° and 6.7(2)°, respectively. Moreover, N(2) shows almost no pyramidalization, since its deviation from the plane of C(1), H–N(2), and C(3) is 0.023(2) Å. In other words, it is sp^2-hybridized and thus fully integrated in the conjugation of the merocyanine system. The situation of the N-atom of the piperidine ring linked to C(3) is somewhat different. It deviates by 0.178(2) Å from the plane formed by C(3) and the two adjacent C-atoms of the piperidine ring, and, in addition, the interplane angle with N(2), C(3), and C(4) amounts to 37.7(3)°, *i.e.*, the N-atom of the piperidine ring is almost sp^3-hybridized, and its conjugative contribution to the merocyanine system must therefore be distinctly smaller than that of the other endocyclic N-atom. The distance between the closest H-

atom in the equatorial position of the piperidine chair conformation and the C-atom of the CN group is 2.36 Å. Therefore, it is this steric interaction that hinders the coplanar arrangement of the N-atom of the piperidine ring with C(3)=C(4) of the dihydropyridine moiety.

The latter situation is not very much changed by dehydrogenation (*cf. Fig. 2*). The pyridine ring of **5′** is almost planar, however, slightly tilted against the benzene ring (*Θ* (C(4)–C(4a)–C(4b)–C(5)) amounts to 7.2(3)°). The N-atom of the CN group is 0.475(2) Å out of the pyridine plane, since H–C(5) is pointing toward the C-atom of the CN group ($d = 2.64$ Å), and the distance to the closest equatorial H-atom of the piperidine chair is 2.36 Å. The N-atom of the piperidine ring is 0.197(2) Å out of the plane of its three surrounding atoms, and the pyridine plane and the plane of the piperidine N-atom with its two adjacent C-atoms form a tilt angle of 38.1(2)°.

Since all new 3-(dialkylamino)indeno[2,1-*c*]pyridine-4-carbonitriles, except for **5** and **5′** with the heptalenyl substituent at C(1), showed a distinct blue-green fluorescence under normal light, which was most intense for **7f** with the (*E*)-styryl substituent at C(1) (see below), we performed a further X-ray crystal-structure analysis of **7a** (*Fig. 4*). The structural characteristics of **7a** are similar to those of **5′** with the exception that, for **7a**, the piperidine N-atom is 0.068(2) Å out of the plane of its three surrounding atoms, so it is close to being planar. In other words, its conjugative interaction with the π-system of the 9-oxo-9*H*-indeno[2,1-*c*]pyridine-4-carbonitrile backbone is much stronger as in the case of **5′**. This structure also has an interplane angle of 19.4(2)° between the pyridine and the piperidine part, which is just half as large as in the case of **5′**. As a further result, the distance between the closest equatorial H-atom of the piperidine chair and the C-atom of the CN group has shrunk to 2.24 Å compared with the distance in **5′**. The distance between H–C(5) and the C-atom of the CN group ($d = 2.59$ Å) is within the estimated standard deviations the same as in **5′**, however, with the tendency of being a bit shorter. The same is true for the torsion angle *Θ* (C(4)–C(4a)–C(4b)–C(5)), which amounts in this case to 4.8(3)°. Furthermore,

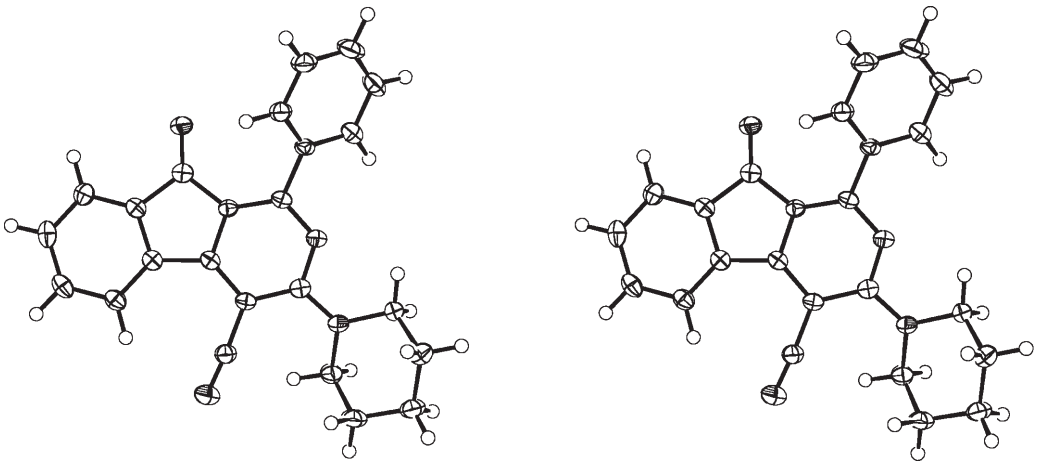


Fig. 4. *Stereoscopic view of the X-ray crystal structure of* **7a** (atoms with 50% probability ellipsoids)

the bond angles at C(3), C(4), and the amino-N atom are all distorted with the larger angle always such that it appears the piperidine ring is trying to get away from the CN group, the N-atom of which is as in **5′** 0.456(2) Å out of the plane of the pyridine ring. It is also of interest to note that the interplane angle between the pyridine ring and its 1-Ph substituent amounts to 37.6(2)°, which indicates a conjugation between both aromatic systems.

Comparing the crystal structures of **5′** and **7a**, it can be said that both structures have to compensate for steric interactions between the piperidin-1-yl substituent at C(3) and the CN group at C(4), the latter being under the influence of a certain buttressing effect of H–C(5). Therefore, C(4) slightly deviates from the plane of the pyridine ring, which is documented by the size of deviation of Θ (C(4)–C(4a)–C(4b)–C(5)) from 0° and more clearly seen by the deviation of the N-atom of the CN group from the plane of the pyridine ring. On the other hand, the change of the electron-donating heptalenyl substituent (12π-electron system) to the electron-accepting Ph substituent as an aromatic 6π-electron system at C(1) leads to a more planar pyridine ring and also to a more effective conjugative interaction of the N-atom of the piperidine moiety with the indeno-pyridine part. This latter should also be effective in the case of the other amino substituents at C(3), as well as of the other aromatic or hetero-aromatic substituents at C(1).

The new indeno-pyridine-carbonitriles **7a**–**7f** show, as mentioned above, a blue-green fluorescence. When we measured their emission spectra in cyclohexane, we were amazed to find that all compounds exhibited two closely lying emission maxima of almost equal intensity in the vicinity of 460 and 480 nm (*Table 4*). As an example, the absorption and emission spectra of **7f** are shown in *Fig. 5*. The energy gap of the two emission bands amounts to 2–3 kcal mol^{-1}. Since we conducted no further experiments, we can only speculate on the origin of the two bands. The two bands are mostly superimposed with a tailing to longer wavelength. It seems that the two emission bands belong to two S_1 states of the 3-amino-indeno-pyridines, which are slightly different in energy and which show an almost unresolved vibration fine structure. It can be assumed that one of the states is a π,π^* state with charge-transfer contribution of the amino group (*cf.* the jump of acidity by ΔpK_a *ca.* 6 of phenols and aromatic ammonium ions or amines on excitation [11]). On the other hand, 2-aminopyridine is a stronger base than pyridine itself (*cf.* pK_a 6.82 and 5.25 (H_2O) [12]), so that the second fluorescent state could be an n,π^* state.

2.3. *Formation of Indeno[2,1-c]pyridine-4-carbonitriles.* Well-established procedures for the formation of indeno[2,1-*c*]pyridines are the ring closure of 4-aryl nicotinic acid derivatives with polyphosphoric acid at 200° and above (see [8][13][14] and earlier literature cited there)[3]). 9-Oxo-9*H*-indeno[2,1-*c*]pyridine itself has been obtained *inter alia* by dichromate oxidation of 9*H*-indeno[2,1-*c*]pyridine, which is formed in excellent yield by flash vacuum pyrolysis at 500° of (phenyl)(pyridin-4-yl)diazomethane by a series of carbene–carbene rearrangements [8]. Close to our synthesis is the reaction of 3-(dicyanomethylidene)indan-1-one with diaryl formamidines in boiling $CHCl_3$, which leads in good yields *via* **8** and **9** to 3-(arylamino)-9-oxo-9*H*-indeno[2,1-*c*]pyridine-4-carbonitriles **10** (*Scheme 5*) [17], whereby the step **9** → **10** corresponds to a *Dimroth*

[3]) See also [15][16] for the synthesis of more complex indeno-pyridines.

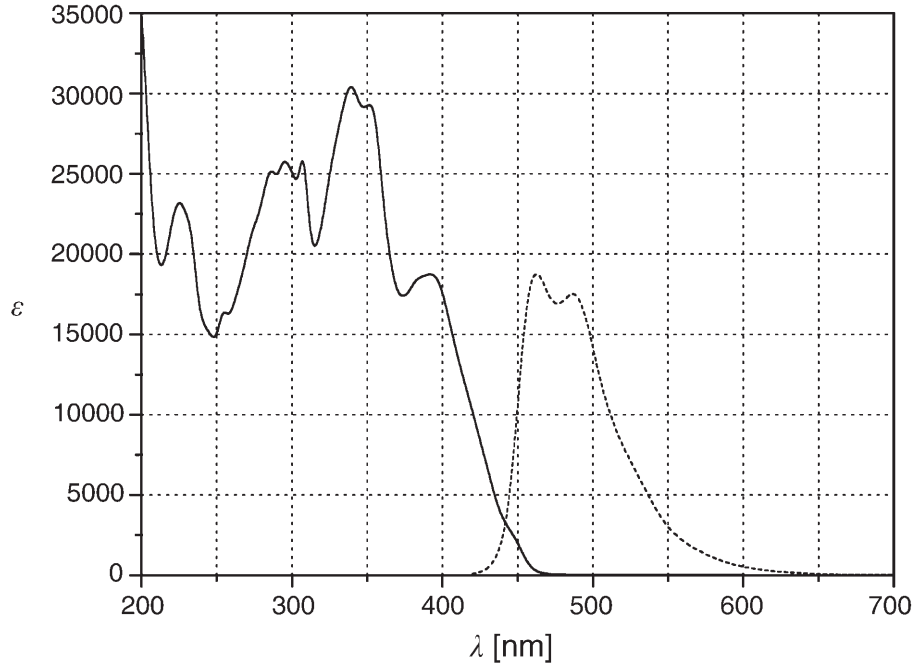


Fig. 5. *UV/VIS* (—) *and Fluorescence* (----) *spectra of* **7f** (cyclohexane)

Table 4. *Fluorescence Data of the New 3-(Dialkylamino)indeno-pyridine-carbonitriles*[a])

Fluorenone	λ_{emiss} [nm]	$\Delta\lambda$ [nm]	ΔE [kcal · mol^{-1}]
6a	476, 460	16	2.1
6b	475, 454	21	2.8
6c	487, 463	24	3.0
6d	476, 459	17	2.2
6e	475, 452	23	3.1
6f	487, 462	25	3.2

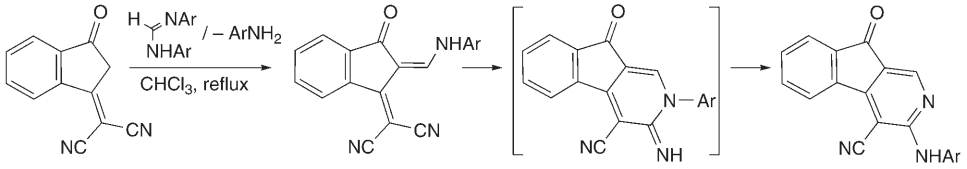
[a]) In cyclohexane.

rearrangement. The global transformation can be described as a [4 + 2] cyclocondensation reaction in contrast to our synthesis, which has to be regarded as a [5 + 1] cyclocondensation reaction, whereby the N-atom of the involved CN group becomes the pyridine N-atom[4]).

In the present case, we assume that the product formation starts with a normal *Knoevenagel* reaction between the indanone and the aldehyde, followed by a nucleophilic attack of the secondary amine at the CN group in the inward position

[4]) Pyridine syntheses with cyano groups as the N-atom donor in the ring-forming process are numerous (see [18–20] and earlier literature cited there).

Scheme 5



8 **9** **10**

with respect to the ensuing ring formation (*Scheme 6*). It is an open question whether the thus generated zwitterionic imidide **12** is trapped in a concerted manner by the present enone part to form the zwitterionic enolate **14**, which then yields the 1,2-dihydro-indeno-pyridines by intermolecular H^+ shift, or whether the imidide **12** has a certain life-time, so that it can undergo intermolecular H^+ shift to the neutral 1-azahexatriene intermediate **13**, which then experiences an electrocyclic disrotatory ring closure to the products. *Boutome* and *Hartmann* observed a comparable formation of a complex pyridine compound by treatment of the 2-oxonaphtho[1,2-*b*]pyran-3-carbonitrile **15** with piperidine in boiling MeCN with concomitant autoxidation (*Scheme 6*) [18].

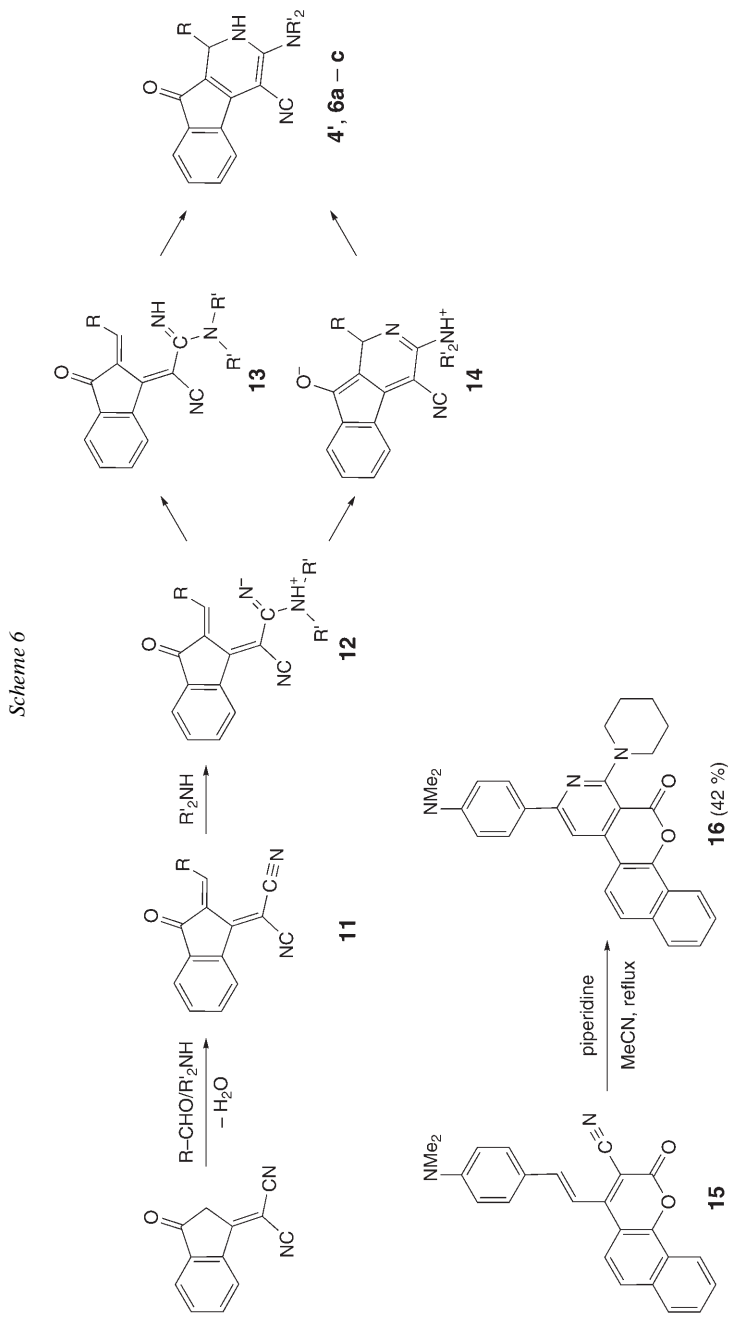
3. Concluding Remarks. – We described a new reaction between 3-(dicyanomethylidene)indanone, and aldehydes without H-atoms at C(α) and secondary amines that leads by a [5 + 1] cyclocondensation to 1-substituted 3-(dialkylamino)-1,2-dihydro-9-oxo-9*H*-indeno[2,1-*c*]pyridine-4-carbonitriles. Aldehydes with H-atoms at C(α) or α,β-unsaturated aldehydes with H-atoms at C(γ) do not undergo the [5 + 1] cyclocondensation reaction. The primary 1,2-dihydro products can easily be dehydrogenated to the pyridine forms, which show with aromatic or heteroaromatic substituents at C(1) a blue-green fluorescence with two emission maxima of similar intensity around 460 and 480 nm.

We thank our NMR laboratory for specific and sometimes laborious NMR measurements, our MS laboratory for mass spectra, and our laboratory for microanalysis. Financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. M.p.: Homemade apparatus with a heating table and microscope; uncorrected. TLC: aluminum sheets coated with silica gel *60 F_{254}* (*Merck*) or plastic sheets coated with alumina *N/UV_{254}* (*POLYGRAM®*, *Macherey-Nagel*); spot visualization with UV light (254 or 366 nm) or with appropriate spray reagents. Column chromatography (CC): silica gel *C-560* (0.040 – 0.063 mm; *Chemie Uetikon AG*) or on alumina, type *5016A*, basic (0.05 – 0.15 mm; *Fluka*). UV/VIS Spectra: *Lambda 19* UV/VIS/NIR spectrophotometer (*Perkin-Elmer*); maxima and minima, λ_{max} and λ_{min}, in nm; molar extinction coefficients ε [1000 $cm^2 \cdot mol^{-1}$] in log ε. Fluorescence spectra (FL): luminescence spectrometer *LS 50 B* (*Perkin-Elmer*); maxima of emission, λ_{em}, in nm. IR Spectra: *FT 1600* instrument or *Spectrum One* FT-IR spectrophotometer (both *Perkin-Elmer*), in KBr pills (*ca.* 1 mg substrate/150 mg KBr); absorption bands in cm^{-1}; intensities as residual transmission. NMR Spectra: ^{1}H-NMR on *Bruker* instruments (*AC-300*, *ARX-300*, or *AMX-600*) in $CDCl_3$ and TMS as internal standard; chemical shifts (δ) in ppm, coupling constants (*J*) in Hz; ^{13}C-NMR on *ARX-300* or *AMX-600* instruments; as internal standard the

Scheme 6


R–CHO/R'2NH
– H2O
R'2NH
piperidine
MeCN, reflux
4', 6a – c
11
12
13
14
15
16 (42 %)

corresponding solvent signal, *i.e.*, $CDCl_3$ (*t*, $J(C,D) = 31.5$ Hz, $\delta(C) = 77.00$ ppm), (D_6)acetone (*sept.*, $J(C,D) = 19.3$ Hz, $\delta(C) = 29.73$); DEPT spectra for the determination of the multiplicities of the ^{13}C fragments; C_q, quaternary C-atom. MS: *MAT-95* instrument (*Finnigan*), EI at 70 eV, source temp. 250°, CI with NH_3, ions in *m*/*z*, in parentheses relative peak intensities in %. GC/MS on a *GC-8000Top* apparatus (*CE Instruments*), coupled with a *Voyager* mass spectrometer (*Finnigan*) with combined CI/EI source (70 eV); *OV-5* capillary column (*Restek*; 15 m × 0.25 mm, 0.25 μm; 95% dimethyl- and 5% diphenylpolysiloxane).

1. *Formation of the 1,2-Dihydro-indeno-pyridine-carbonitriles.* 1.1. *1,2-Dihydro-9-oxo-1-(1,5,6,8,10-pentamethylheptalen-2-yl)-3-(piperidin-1-yl)-9*H-*indeno[2,1-*c*]pyridine-4-carbonitrile* (**4′**). The 57:43 mixture of the heptalenecarbaldehydes **1** and **1′** (252.4 mg, 1.00 mmol) and 3-(dicyanomethylidene)indan-1-one (194.2 mg 1.00 mmol) [6] were placed in dry EtOH (30 ml) in a 50 ml round-bottom flask. Under stirring, piperidine (0.20 ml, 2.0 mmol) was added, whereby a red color appeared at once, and the indanone dissolved slowly. The mixture was heated for 3 h at reflux, in which time the color turned more and more to violet. EtOH and excess piperidine were distilled off *in vacuo*. The residue was separated by CC (silica gel; toluene and successively increasing amounts of AcOEt (100:1, 50:1, 20:1, 10:1, 5:1, 2:1, 1:1, 1:2; each time 100 ml)). The first wine-red fraction gave after evaporation of the solvent mixture a violet solid, which was crystallized from toluene at −15° to yield pure **4′** (87.4 mg, 17%). A sample for analysis was dissolved in CH_2Cl_2 and precipitated by addition of pentane and then dried *in vacuo*. M.p. 164–166°. R_f (AcOEt/MeOH 10:1) 0.84. UV/VIS (MeCN): λ_{max} 590 (sh, 3.50), 531 (3.80), 357 (sh, 3.77), 341 (sh, 3.90), 317 (sh, 4.24), 305 (4.29), 278 (4.40), 259 (4.45), 233 (4.56); λ_{min} 413 (2.78), 295 (4.27), 276 (4.40), 248 (4.43), 213 (4.49). IR: 3424*w* (N–H, free), 3287*m* (N–H, ass.), 3065*w*, 3003*w*, 2938*m*, 2857*m*, 2184*s* (C≡N), 1673*s* (C=O), 1652 (sh), 1604*s*, 1578v*s*, 1552*s*, 1457*s*, 1445*s*, 1411v*s*, 1376*s*, 1364*s*, 1322*w*, 1310*m*, 1275*m*, 1252*s*, 1237 (sh), 1186*s*, 1162*m*, 1147*m*, 1118*m*, 1078*m*, 1043*w*, 1015*m*, 956*w*, 938*w*, 915*w*, 855*m*, 819*w*, 804*w*, 785*w*, 758*m*, 728*w*, 702*w*, 690*w*, 673*w*, 625*w*, 589*w*, 547*w*, 531*w*, 472*w*. ^{1}H-NMR (300 MHz): 7.85 (*dm*, $^3J(5,6) = 7.0$, H–C(5)); 7.34–7.21 (*m*, 3 arom. H); 6.44 (*d*, $^3J = 11.9$, H–C(3′)); 6.27 (*d*, $^3J = 11.9$, H–C(4′)); 6.07 (*s*, H–C(9′)); 5.96 (*s*, H–C(7′)); 5.66 (*d*, $^3J(1,2) = 3.5$, H–C(1)); 5.40 (br. *d*, $^3J(2,1) = 3.5$, H–N(2)); 3.64–3.42 (*m*, 2 NCH_2CH_2); 2.16 (*s*, Me); 1.96 (*d*, $^4J = 1.2$, Me); 1.94 (*d*, $^4J = 1.0$, Me); 1.71 (br. *s*, 2 $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$); 1.68 (*s*, 2 Me). EI-MS: 513 (32, $M^{+\bullet}$), 511 (25, $[M-H_2]^{+\bullet}$), 496 (17), 290 (100, $[M-\text{hept}]^+$), 234 (25), 224 (23), 209 (18), 193 (16), 184 (50), 170 (20), 149 (13), 123 (14), 105 (15), 91 (48), 69 (30), 57 (31), 43 (31), 41 (36).

The structure of **4′** was finally established by an X-ray crystal-structure analysis (*cf. Fig. 1* and *Table 5*).

1.2. *1,2-Dihydro-9-oxo-1-phenyl-3-(piperidin-1-yl)-9*H-*indeno[2,1-*c*]pyridine-4-carbonitrile* (**6a**). In analogy to *Sect. 1.1*, the indanone (1.00 mmol), PhCHO (0.10 ml, 1.0 mmol), and piperidine (0.20 mmol) were heated under reflux in EtOH during 2 h. The residue was separated by CC (silica gel; first hexane/Et_2O 1:1, then Et_2O, and finally Et_2O/MeOH 10:1, then 1:1; each time 250 ml). This procedure resulted in clean yellow and violet colored fractions, which gave dark red crystals of **6a** (173.3 mg, 49%) and **7a** as a yellow solid (28.8 mg, 8%). A sample for analysis of **6a** was dissolved in CH_2Cl_2 and precipitated by addition of pentane and then dried *in vacuo*.

Data of **6a**. M.p. 130–133°. R_f (AcOEt/MeOH 10:1) 0.82. UV/VIS (MeCN): λ_{max} 516 (3.85), 356 (3.79), 342 (3.81), 317 (sh, 4.03), 304 (4.11), 279 (4.30), 228 (4.49); λ_{min} 398 (2.67), 351 (3.77), 333 (3.77), 296 (4.09), 252 (3.86), 213 (4.37). IR: 3401*w* (N–H, free), 3278*m* (N–H, ass.), 3062*w*, 3027*w*, 2940*m*, 2857*m*, 2184*s* (C≡N), 1667*s* (C=O), 1603v*s*, 1576v*s*, 1553 (sh), 1492*m*, 1459v*s*, 1443v*s*, 1415v*s*, 1367*s*, 1326*m*, 1273*s*, 1243*s*, 1189*s*, 1162*s*, 1148*m*, 1119*s*, 1078*m*, 1046*w*, 1015*m*, 961*m*, 939*w*, 914*w*, 856*m*, 820*w*, 796*w*, 771*m*, 733*s*, 698*m*, 681*m*, 635*w*, 602*w*, 572*w*, 544*m*, 528*w*, 493*w*, 472*w*. ^{1}H-NMR (300 MHz): 7.83 (*dm*, $^3J(5,6) = 7.0$, H–C(5)); 7.36–7.20 (*m*, 8 arom. H); 5.77 (br. *d*, $^3J(2,1) = 4.6$, H–N(2)); 5.64 (*d*, $^3J(1,2) = 4.6$, H–C(1)); 3.68–3.49 (*m*, 2 NCH_2CH_2); 1.73 (br. *s*, 2 $NCH_2CH_2CH_2$, $NCH_2CH_2CH_2$). EI-MS: 367 (54, $M^{+\bullet}$), 365 (56, $[M-H_2]^{+\bullet}$), 336 (55), 322 (24), 310 (22), 296 (14), 290 (100, $[M-C_6H_5]^+$), 282 (29), 253 (12), 234 (17), 227 (16), 161 (16), 103 (10), 91 (11), 84 (20, $C_5H_{10}N^+$), 73 (15), 61 (10), 44 (20).

Data of **7a**. See *Sect. 2.2*.

1.3. 3-*(Diethylamino)-1,2-dihydro-9-oxo-1-phenyl-9*H-*indeno[2,1-*c*]pyridine-4-carbonitrile* (**6b**). The above described amounts of the indanone, PhCHO, and Et_2NH (2.0 mmol) were heated in EtOH (25 ml)

during 4 h under reflux. The obtained residue was separated on silica gel with 1. hexane/Et_2O 1:1, 1:10; 2. Et_2O; 3. Et_2O/MeOH 10:1, 5:1, 2:1, 1:1 (each time 200 ml). The first fraction delivered **7b** (41.5 mg, 12%) as yellow solid. The following violet-colored fractions gave dark red needles of **6b** (182.0 mg, 51%).

Data of **6b**. M.p. 215–217° (CH_2Cl_2). R_f (AcOEt/MeOH 10:1) 0.78. UV/VIS (MeCN): λ_{max} 516 (3.86), 355 (3.75), 341 (3.78), 316 (sh, 4.03), 303 (4.12), 278 (4.31), 230 (4.50); λ_{min} 395 (2.63), 350 (3.73), 332 (3.73), 297 (4.11), 252 (3.89), 214 (4.37). IR: 3429 (sh, N–H, free), 3341*m* (N–H, ass.), 3082*w*, 3061*w*, 3030*w*, 2977*m*, 2934*w*, 2890 (sh), 2874*w*, 2171*s* (C≡N), 1665v*s* (C=O), 1604*s*, 1577v*s*, 1553*s*, 1503*m*, 1491*m*, 1457v*s*, 1407v*s*, 1380*s*, 1353*s*, 1343*s*, 1290*m*, 1264*s*, 1241*s*, 1202*s*, 1186*m*, 1170*s*, 1152*m*, 1112*m*, 1076*m*, 1047*w*, 1029*w*, 1011*w*, 1002*w*, 967*m*, 930*w*, 885*w*, 858*w*, 823*w*, 793*w*, 785*w*, 774*m*, 759*m*, 738*m*, 711*m*, 696*m*, 684*w*, 647*w*, 631*w*, 587*w*, 571*w*, 546*m*, 534*w*, 486*w*, 478*w*. ^{1}H-NMR (300 MHz): 7.93 (*dm*, $^3J(5,6) = 7.0$, H–C(5)); 7.38–7.20 (*m*, 8 arom. H); 5.65–5.62 (*m*, H–C(1), H–N(2)); 3.63 (*q*, $^3J = 7.1$, 2 NCH_2Me); 1.32 (*t*, $^3J = 7.1$, 2 NCH$_2$*Me*). EI-MS: 355 (51, $M^{+\cdot}$), 326 (19), 324 (27), 310 (9), 278 (100, $[M - C_6H_5]^+$), 250 (14), 234 (8), 227 (12), 222 (16), 86 (13), 84 (22), 77 (8, $C_6H_5^+$), 51 (15), 49 (35).

1.4. *1,2-Dihydro-9-oxo-3-(piperidino-1-yl)-1-(thien-2-yl)-9*H*-indeno[2,1-*c*]pyridine-4-carbonitrile* (**6c**). The same amounts as described before and thiophen-2-carbaldehyde (1.0 mmol) were heated in EtOH (25 ml) during 4 h under reflux. The residue was separated by CC (silica gel; 1. hexane/Et_2O 1:1, 1:10, 1:100; 2. Et_2O; 3. Et_2O/MeOH 100:1, 10:1, 5:1; each time 200 ml) to yield a yellow and then a violet-colored fraction. The oily residue of the latter was dissolved in toluene, and the soln. was cooled to −20° to give dark-red crystalline **6c** (137.7 mg, 37%). A sample for analysis of **6c** was dissolved again in CH_2Cl_2 and precipitated by addition of pentane. The yellow-colored fraction gave a brown-yellow solid of **7c**, which was recrystallized from cyclohexane (99.7 mg, 27%).

Data of **6c**. M.p. 132–135°. R_f (AcOEt/MeOH 10:1) 0.78. UV/VIS (MeCN): λ_{max} 510 (3.87), 355 (3.82), 342 (3.84), 316 (sh, 4.03), 304 (4.09), 278 (4.28), 231 (4.53); λ_{min} 398 (2.74), 351 (3.81), 332 (3.79), 296 (4.07), 254 (3.91), 209 (4.30). IR: 3401 (sh, N–H, free), 3276*m* (N–H, ass.), 3107*w*, 3069*w*, 3014*w*, 2940*m*, 2857*m*, 2185*s* (C≡N), 1668*s* (C=O), 1603*s*, 1575v*s*, 1553 (sh), 1457v*s*, 1444*s*, 1416v*s*, 1369*s*, 1327*w*, 1296*m*, 1280*m*, 1246*s*, 1226*m*, 1187*s*, 1163*m*, 1145*m*, 1118*s*, 1079*m*, 1037*w*, 1014*m*, 954*m*, 938*w*, 854*m*, 834 (sh), 800*w*, 755*m*, 736*m*, 706*m*, 681*w*, 636*w*, 606*w*, 574*w*, 544*w*, 530 (sh), 472*w*. ^{1}H-NMR (300 MHz): 7.85 (*dm*, $^3J(5,6) = 7.1$, H–C(5)); 7.41–7.24 (*m*, 3 arom. H); 7.19 (*dd*, $^3J(5',4') = 5.0$, $^4J(5',3') = 1.2$, H–C(5′)); 6.99 (*dm*, $^3J(3',4') = 3.6$, H–C(3′)); 6.93 (*dd*, $^3J(4',3') = 3.6$, $^3J(4',5') = 5.0$, H–C(4′)); 5.92 (*d*, $^3J(1,2) = 4.6$, H–C(1)); 5.72 (br. *d*, $^3J(2,1) = 4.6$, H–N(2)); 3.71–3.54 (*m*, 2 NCH_2CH$_2$); 1.76 (br. *s*, 2 NCH$_2$CH_2CH$_2$, NCH$_2$CH$_2$CH_2). EI-MS: 373 (35, $M^{+\cdot}$), 371 (100, $[M - H_2]^{+\cdot}$), 342 (86), 328 (39), 316 (39), 303 (22), 288 (51), 261 (16), 245 (16), 233 (20), 215 (15), 188 (15), 97 (14), 84 (75, $C_5H_{10}N^+$), 56 (19), 41 (44), 39 (20).

1.5. *Attempted Formation of 1,2-Dihdro-9-oxo-3-(piperidin-1-yl)-1-(pyridin-4-yl)-9*H*-indeno[2,1-*c*]pyridine-4-carbonitrile* (**6d**). The reaction in EtOH was performed with freshly distilled pyridine-4-carbaldehyde as described in *1.2* for **6a**. The workup procedure yielded only **7d** (45.6 mg, 25%). Yellow solid.

Data of **7d**. See *Sect. 2.5*.

2. *Formation of the Indeno-pyridine-carbonitriles.* 2.1. *9-Oxo-1-(1,5,6,8,10-pentamethylheptalen-4-yl)-3-(piperidin-1-yl)-9*H*-indeno[2,1-*c*]pyridine-4-carbonitrile* (**5**) *and 9-Oxo-1-(1,5,6,8,10-pentamethylheptalen-2-yl)-3-(piperidin-1-yl)-9*H*-indeno[2,1-*c*]pyridine-4-carbonitrile* (**5′**). *Method A*. Compound **4′** (25.7 mg, 0.05 mmol) was dissolved in acetone (10 ml) in a 25-ml round-bottom flask. The soln. was cooled to 0°, and a 0.04M soln. of $KMnO_4$ in acetone was added dropwise. The color of the mixture has slowly changed to yellow-brown within 1 h stirring. MeOH (5 ml) was added, and stirring was continued for a further h. The suspension formed was filtered through *Celite*®, and the filter cake was washed with acetone. The residue of the yellow colored filtrate was purified by CC (silica gel; toluene/AcOEt 25:1). Evaporation of the yellow eluate gave a dark yellow oil, which crystallized on stirring with a glass rod and a small amount of Et_2O. The dried crystals (16.7 mg, 65%) represented a 1:3 mixture of **5** and **5′** according to ^{1}H-NMR analysis.

Method B. The indanone (97.1 mg, 0.50 mmol), the 57:43 mixture **1**/**1′** (151.4 mg, 0.60 mmol), piperidine (0.6 ml, 0.6 mmol), and, later, chloranil were reacted according to the analogous reaction with PhCHO (see below, *Sect. 2.2*). The dark yellow oil, which was obtained after CC, was taken up in hexane/Et_2O and yielded on evaporation a conglomerate of crystals of **5** and **5′** (112.0 mg, 44%) in a ratio of 1:1

(^{1}H-NMR). The conglomerate could be separated by manual selection of the differently crystallized and colored DBS isomers **5** and **5′**.

Data of **5**. Yellow crystals. M.p. 206–207° (hexane). R_f (toluene/AcOEt 5:1) 0.83. UV/VIS (cyclohexane): λ_{max} 371 (4.13), 328 (4.30), 306 (4.32), 253 (4.58), 218 (4.59); λ_{min} 347 (4.08), 318 (4.26), 303 (4.32), 233 (4.45), 207 (4.56). IR: 2936*s*, 2915*s*, 2855*m*, 2209*m* (C≡N), 1706v*s* (C=O), 1594*s*, 1566v*s*, 1533v*s*, 1465*s*, 1444*s*, 1394*m*, 1368*m*, 1317*w*, 1289*m*, 1275*w*, 1253*s*, 1229*m*, 1208v*s*, 1173*w*, 1157*m*, 1144*m*, 1120*m*, 1087*w*, 1016*m*, 966*w*, 868*m*, 851*m*, 839*m*, 771*m*, 758*m*, 699*w*, 686*w*. ^{1}H-NMR (300 MHz): 8.37 (*dm*, $^3J(5,6) = 7.5$, H–C(5)); 7.71 (*dm*, $^3J(8,7) = 7.3$, H–C(8)); 7.58 (*td*, $^3J(6,5) \approx {}^3J(6,7) = 7.5$, $^4J(6,8) = 1.0$, H–C(6)); 7.50 (*tm*, $^3J(7,6) \approx {}^3J(7,8) = 7.3$, H–C(7)); 6.72 (*d*, $^3J(3',2') = 5.9$, H–C(3′)); 6.23 (*dm*, $^3J(2',3') = 5.9$, H–C(2′)); 6.13 (*s*, H–C(9′)); 5.97 (*s*, H–C(7′)); 3.85 (br. *s*, 2 NCH_2CH$_2$); 2.05 (*s*, Me); 2.02 (*s*, Me); 2.00 (*s*, Me); 1.75 (*s*, Me); 1.70 (br. *s*, 2 NCH$_2$CH_2CH$_2$, NCH$_2$CH$_2$CH_2); 1.56 (*s*, Me). EI-MS: 511 (41, $M^{+\bullet}$), 496 (25, $[M - Me]^+$), 351 (17), 322 (38), 296 (18), 198 (23), 184 (100), 169 (18), 91 (12), 84 (17, $C_5H_{10}N^+$). Anal. calc. for $C_{35}H_{33}N_3O$ (511.67): C 82.16, H 6.50, N 8.21; found: C 82.11, H 6.49, N 8.11.

Data of **5′**. Orange prisms. M.p. 177–180° (cyclohexane/toluene). R_f (toluene/AcOEt 5:1) 0.83. UV/VIS (cyclohexane): λ_{max} 367 (4.11), 352 (4.10), 327 (4.34), 307 (4.32), 257 (4.62), 217 (4.60); λ_{min} 359 (4.08), 343 (4.05), 319 (4.25), 304 (4.31), 233 (4.37), 205 (4.58). IR (KBr): 2999*w*, 2939*m*, 2855*m*, 2213*m* (C≡N), 1707v*s* (C=O), 1597*m*, 1570v*s*, 1527v*s*, 1489*s*, 1465*s*, 1450*s*, 1368*s*, 1315*w*, 1288*m*, 1274*w*, 1250*s*, 1208*s*, 1170*w*, 1160*m*, 1147*m*, 1120*m*, 1086*w*, 1070*w*, 1022*m*, 988*w*, 972*w*, 955*w*, 941*w*, 887*w*, 870*m*, 848*w*, 822*w*, 799*w*, 782*w*, 761*m*, 746*w*, 724*w*, 698*w*, 688*w*. ^{1}H-NMR (300 MHz): 8.39 (*dm*, $^3J(5,6) = 7.6$, H–C(5)); 7.71 (*dm*, $^3J(8,7) = 6.9$, H–C(8)); 7.60 (*tm*, $^3J(6,5) \approx {}^3J(6,7) = 7.6$, H–C(6)); 7.51 (*tm*, $^3J(7,6) \approx {}^3J(7,8) =$ 7.4, H–C(7)); 6.38 (*d*, $^3J = 11.7$, H–C(3′ oder 4′)); 6.30 (*d*, $^3J = 11.7$, H–C(4′ oder 3′)); 6.17 (*s*, H–C(9′)); 6.03 (*s*, H–C(7′)); 3.95 (br. *s*, 2 NCH_2CH$_2$); 2.12 (*s*, Me); 2.02 (*s*, Me); 1.86 (*s*, Me); 1.81 (*s*, Me); 1.77 (br. *s*, 2 NCH$_2$CH_2CH$_2$, NCH$_2$CH$_2$CH_2); 1.56 (*s*, Me). CI-MS (NH_3): 512 (100, $[M + H]^+$). EI-MS: 511 (12, $M^{+\bullet}$), 198 (18), 184 (100), 169 (19), 91 (13), 84 (32, $C_5H_{10}N^+$), 69 (13). Anal. calc. for $C_{35}H_{33}N_3O$ (511.67): C 82.16, H 6.50, N 8.21; found: C 81.90, H 6.62, N 8.10.

The structure of **5′** was finally established by an X-ray crystal-diffraction analysis (*cf. Fig. 2* and *Table 5*).

2.2. *9-Oxo-1-phenyl-3-(piperidin-1-yl)-9*H-*indeno[2,1-*c*]pyridine-4-carbonitrile* (**7a**). 3-(Dicyanomethylidene)indan-1-one (97.1 mg, 0.50 mmol) was dissolved in 1,4-dioxane (25 ml) in a 50-ml round-bottom flask. Freshly distilled PhCHO (0.06 ml, 0.60 mmol) and piperidine (0.06 ml, 0.60 mmol) were added in quick succession. The color of the soln. turned to red upon addition of piperidine. The soln. was stirred during 14 h at r.t. Then, chloranil (=2,3,5,6-tetrachlorocyclohexa-2,5-diene-1,4-dione; 132.5 mg, 0.55 mmol) was added to the wine-red soln., which was stirred for another 0.5 h, whereby the color changed to a turbid yellow-black. The soln. was poured on ice, stirred for 30 min, and then extracted several times with toluene. The combined extracts were successively washed with 4% aq. NaOH, H_2O, and finally sat. NaCl soln. The dried ($MgSO_4$) soln. was evaporated, and the brown residue was purified by CC (silica gel; hexane/Et_2O 10:1). The obtained yellow colored fraction gave on evaporation **7a** (121.1 mg, 66%). Yellow prisms.

Data of **7a**. M.p. 161–163° (cyclohexane/toluene). R_f (toluene/AcOEt 5:1) 0.78. UV/VIS (cyclohexane)[5]): λ_{max} 375 (4.11), 333 (4.19), 276 (4.50), 223 (4.41); λ_{min} 347 (3.95), 325 (4.11), 239 (4.14), 216 (4.36). FL (cyclohexane): λ_{em} 477. IR: 3055*w*, 3029*w*, 3014*w*, 2932*m*, 2852*m*, 2207*m* (C≡N), 1705v*s* (C=O), 1596*s*, 1567v*s*, 1532v*s*, 1492*s*, 1467*s*, 1451*s*, 1402*m*, 1386*m*, 1362*m*, 1350*m*, 1294*m*, 1275*m*, 1254*s*, 1227*m*, 1208v*s*, 1172*m*, 1157*m*, 1146*m*, 1123*m*, 1022*m*, 1003*m*, 996*m*, 954*w*, 900*w*, 870*m*, 854*w*, 815*w*, 778*w*, 754*s*, 708*m*, 698*m*, 684*w*, 634*w*, 612*w*, 546*w*, 465*w*, 435*w*. ^{1}H-NMR (300 MHz): 8.42 (*dm*, $^3J(5,6) = 7.6$, H–C(5)); 7.93–7.90 (*m*, 2 arom. H); 7.71 (*dm*, $^3J(8,7) = 7.4$, H–C(8)); 7.61 (*td*, $^3J(6,5) \approx {}^3J(6,7) = 7.6$, $^4J(6,8) = 1.4$, H–C(6)); 7.52 (*td*, $^3J(7,6) \approx {}^3J(7,8) = 7.4$, $^4J(7,5) = 0.9$, H–C(7)); 7.51–7.43 (*m*, 3 arom. H); 3.99 (br. *s*, 2 NCH_2CH$_2$); 1.78 (br. *s*, 2 NCH$_2$CH_2CH$_2$, NCH$_2$CH$_2$CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 187.78 (CO); 160.70 (C_q); 160.51 (C_q); 159.21 (C_q); 138.31 (C_q); 136.49 (C_q); 135.55 (C_q); 134.00 (CH); 132.15 (CH); 130.46 (CH); 129.89 (2 CH); 127.63 (2 CH); 123.71 (CH); 123.23 (CH); 117.23 (C_q); 115.48

---

[5]) For **7a** and the other derivatives, a number of faintly visible sh, most of them interpretable as vibration fine structure of the main absorption bands, are recognizable. They appear for **7a** at 206 (4.46), 267 (4.44), 292 (4.41), 304 (4.29), 319 (4.15), 362 (4.04), 392 (3.95), 406 (3.80), and 430 (3.45).

(C_q, CN); 83.95 (C_q); 49.50 (2 N*C*H_2CH$_2$); 26.09 (2 CH_2); 24.42 (CH_2). CI-MS (NH_3): 366 (100, $[M+H]^+$). EI-MS: 365 (100, $M^{+\bullet}$), 336 (77), 322 (37), 309 (33), 296 (34), 282 (36), 253 (13), 227 (14), 84 (20, $C_5H_{10}N^+$), 56 (13). Anal. calc. for $C_{24}H_{19}N_3O$ (365.44): C 78.88, H 5.24, N 11.50; found: C 78.88, H 5.33, N 11.56.

The structure of **7a** was further secured by an X-ray crystal-diffraction analysis (see *Fig. 4* and *Table 5*).

2.3. *3-(Diethylamino)-9-oxo-1-phenyl-9*H-*indeno[2,1-*c*]pyridine-4-carbonitrile* (**7b**). The indanone (0.5 mmol), PhCHO (0.6 mmol), and Et_2NH (0.6 mmol) were reacted as described in *2.2*. A red solid precipitated in the course of the reaction, which later on dissolved again. The crude product was purified by CC (silica gel; hexane/Et_2O 10:1) to give **7b**. (111.3 mg, 63%). Yellow solid.

Data of **7b**. M.p. 139–140° ($EtOH/H_2O$). R_f (toluene/AcOEt 5:1) 0.74. UV/VIS (cyclohexane): λ_{max} 373 (4.10), 332 (4.19), 275 (4.48), 223 (4.39); λ_{min} 345 (3.92), 323 (4.10), 241 (4.13), 216 (4.34). FL (cyclohexane): λ_{em} 475, 454. IR: 3062*w*, 2982*m*, 2935*m*, 2210*m* (C≡N), 1700v*s* (C=O), 1596*m*, 1564v*s*, 1531v*s*, 1492*m*, 1468*s*, 1454*m*, 1434*m*, 1404*w*, 1384*w*, 1373*w*, 1357*s*, 1310*w*, 1295*m*, 1254*m*, 1230*s*, 1197*m*, 1151*m*, 1120*m*, 1075*m*, 1036*w*, 1024*w*, 1010*m*, 924*w*, 866*m*, 812*w*, 780*w*, 749*s*, 708*m*, 697*m*, 686*w*, 674*w*, 635*w*, 515*w*, 468*w*, 446*w*. ^{1}H-NMR (300 MHz): 8.49 (*dm*, $^3J(5,6)=7.6$, H–C(5)); 7.93–7.89 (*m*, 2 arom. H); 7.71 (*dm*, $^3J(8,7)=7.3$, H–C(8)); 7.61 (*td*, $^3J(6,5)\approx{}^3J(6,7)=7.6$, $^4J(6,8)=1.4$, H–C(6)); 7.52 (*td*, $^3J(7,6)\approx{}^3J(7,8)=7.3$, $^4J(7,5)=0.9$, H–C(7)); 7.51–7.43 (*m*, 3 arom. H); 3.91 (*q*, $^3J=7.0$, 2 NCH_2Me); 1.41 (*t*, $^3J=7.0$, 2 NCH$_2$*Me*). ^{13}C-NMR (75 MHz, $CDCl_3$): 187.80 (C_q, CO); 160.67 (C_q); 159.37 (C_q); 158.39 (C_q); 138.41 (C_q); 136.64 (C_q); 135.64 (C_q); 133.90 (CH); 132.00 (CH); 130.35 (CH); 129.80 (2 CH); 127.59 (2 CH); 123.59 (CH); 123.37 (CH); 117.80 (C_q); 114.45 (C_q, CN); 81.81 (C_q); 45.08 (2 N*C*H$_2$Me); 13.73 (2 Me). EI-MS: 353 (33, $M^{+\bullet}$), 324 (100, $[M-Et]^+$), 310 (29), 281 (7), 252 (7), 72 (8, $C_4H_{10}N^+$). Anal. calc. for $C_{23}H_{19}N_3O$ (353.43): C 78.16, H 5.42, N 11.89; found: C 77.87, H 5.45, N 11.74.

2.4. *9-Oxo-3-(piperidin-1-yl)-1-(thien-2-yl)-9*H-*indeno[2,1-*c*]pyridine-4-carbonitrile* (**7c**). The procedure for the reaction with thiophen-2-carbaldehyde (0.6 mmol) was the same as described in *1.5* for PhCHO. The usual purification by CC (silica gel; hexane/Et_2O and then CH_2Cl_2) gave **7c** (111.5 mg, 60%). Yellow solid.

Data of **7c**. M.p. 218–220° (cyclohexane). R_f (toluene/AcOEt 5:1) 0.83. UV/VIS (cyclohexane): λ_{max} 390 (4.22), 336 (4.38), 308 (4.27), 283 (4.41), 212 (4.40); λ_{min} 371 (4.18), 315 (4.20), 303 (4.26), 243 (4.01), 204 (4.36). FL (cyclohexane): λ_{em} 487, 463. IR: 3106*w*, 3082*w*, 3012*w*, 2988*w*, 2941*m*, 2932*m*, 2853*m*, 2208*m* (C≡N), 1691*s* (C=O), 1598*s*, 1572v*s*, 1524 (sh), 1516v*s*, 1492*s*, 1464*s*, 1449*s*, 1425*s*, 1395*m*, 1369*m*, 1341*w*, 1318*w*, 1286*m*, 1269*m*, 1258*m*, 1242*m*, 1208*s*, 1167*m*, 1161*m*, 1124*s*, 1086*w*, 1059*m*, 1024*m*, 957*w*, 868*m*, 860*m*, 854*m*, 839*w*, 809*w*, 763*s*, 722*s*, 684*w*, 618*w*, 546*w*, 476*w*. ^{1}H-NMR (300 MHz): 9.08 (*dd*, $^3J(3',4')=4.0$, $^4J(3',5')=1.1$, H–C(3′)); 8.39 (*dm*, $^3J(5,6)=7.5$, H–C(5)); 7.74 (*dm*, $^3J(8,7)=7.1$, H–C(8)); 7.59 (*td*, $^3J(6,5)\approx{}^3J(6,7)=7.5$, $^4J(6,8)=1.4$, H–C(6)); 7.55–7.50 (*m*, H–C(7), H–C(5′); 7.19 (*dd*, $^3J(4',3')=4.0$, $^3J(4',5')=5.1$, H–C(4′)); 3.96 (br. *s*, 2 NCH_2CH$_2$); 1.78 (br. *s*, 2 NCH$_2$CH_2CH$_2$, NCH$_2$CH$_2$CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 187.91 (C_q, CO); 160.77 (C_q); 159.91 (C_q); 151.47 (C_q); 143.48 (C_q); 138.09 (C_q); 135.52 (C_q); 133.90 (CH); 133.07 (CH); 132.11 (CH); 131.66 (CH); 128.67 (CH); 123.62 (CH); 123.21 (CH); 117.16 (C_q); 113.60 (C_q, CN); 83.98 (C_q); 49.52 (2 N*C*H$_2$CH$_2$); 26.02 (2 CH_2); 24.41 (CH_2). EI-MS: 371 (100, $M^{+\bullet}$), 342 (73), 328 (43), 316 (32), 315 (32), 303 (26), 288 (44, $[M-C_4H_3S]^+$), 260 (14), 233 (14), 188 (15), 175 (25), 133 (22), 131 (28), 101 (21), 89 (77), 87 (76), 84 (70, $C_5H_{10}N^+$), 75 (22), 73 (21), 59 (22), 57 (23), 56 (25). Anal. calc. for $C_{22}H_{17}N_3OS$ (371.46): C 71.14, H 4.61, N 11.31, S 8.63; found: C 71.10, H 4.58, N 11.33, S 8.72.

2.5. *9-Oxo-3-(piperidin-1-yl)-1-(pyridin-4-yl)-9*H-*indeno[2,1-*c*]pyridine-4-carbonitrile* (**7d**). 3-(Dicyanomethylidene)indan-1-one (97.1 mg, 0.5 mmol), freshly distilled pyridine-4-carbaldehyde (0.06 ml, 0.6 mmol), and piperidine (0.06 ml, 0.6 mmol) were reacted as described in *2.2*. A red solid, which did not dissolve again during the reaction and also not after the addition of chloranil, was precipitated. The purification of the crude product by CC (SiO_2; hexane/Et_2O 10:1), followed by recrystallization from cyclohexane (and a small amount of toluene), gave pure **7d** (47.5 mg, 26%). Yellow solid.

Data of **7d**. M.p. 195–197°. R_f (toluene/AcOEt 5:1) 0.18. UV/VIS (cyclohexane): λ_{max} 380 (4.10), 336 (4.10), 308 (4.16), 267 (4.45), 225 (4.43); λ_{min} 349 (3.93), 318 (4.01), 305 (4.15), 235 (4.23), 212 (4.26). FL (cyclohexane): λ_{em} 476, 459. IR: 3068*w*, 3033*w*, 3009*w*, 2940*m*, 2859*w*, 2208*w* (C≡N), 1706*s* (C=O),

1596*m*, 1567v*s*, 1551*s*, 1529v*s*, 1506 (sh), 1488*s*, 1467*s*, 1453*s*, 1416*m*, 1366*m*, 1314*w*, 1293*m*, 1280*w*, 1256*s*, 1206*s*, 1165*w*, 1148*w*, 1123*m*, 1065*w*, 1028*w*, 1005*m*, 872*m*, 855*w*, 836*w*, 760*s*, 722*w*, 709*w*, 686*w*, 682*w*, 542*w*. ^{1}H-NMR (300 MHz): 8.76 (*dm*, $^3J = 4.5$, 2 arom. H); 8.43 (*dm*, $^3J(5,6) = 7.5$, H–C(5)); 7.78 (*dm*, $^3J = 4.5$, 2 arom. H); 7.73 (*dm*, $^3J(8,7) = 7.3$, H–C(8)); 7.64 (*td*, $^3J(6,5) \approx {}^3J(6,7) = 7.5$, $^4J(6,8) = 1.4$, H–C(6)); 7.55 (*td*, $^3J(7,6) \approx {}^3J(7,8) = 7.3$, $^4J(7,5) = 1.0$, H–C(7)); 4.00 (br. *s*, 2 NCH_2CH$_2$); 1.80 (br. *s*, 2 NCH$_2$CH_2CH$_2$, NCH$_2$CH$_2$CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 187.43 (C_q, CO); 160.57 (2 C_q); 156.42 (C_q); 149.52 (2 CH); 143.76 (C_q); 138.20 (C_q); 135.40 (C_q); 134.31 (CH); 132.48 (CH); 123.95 (CH); 123.69 (2 CH); 123.44 (CH); 116.82 (C_q); 115.60 (C_q, CN); 84.91 (C_q); 49.55 (2 NCH_2CH$_2$); 26.07 (2 CH$_2$); 24.31 (CH$_2$). EI-MS: 366 (100, $M^{+\bullet}$), 337 (81), 323 (44), 311 (30), 298 (21), 283 (46), 254 (20), 91 (51), 84 (57, $C_5H_{10}N^+$), 75 (18), 56 (17). Anal. calc. for $C_{23}H_{18}N_4O$ (366.42): C 75.39, H 4.95, N 15.29; found: C 75.45, H 4.97, N 15.17.

2.6. *9-Oxo-1-phenyl-3-(pyrrolidin-1-yl)-9*H*-indeno[2,1-*c*]pyridine-4-carbonitrile* (**7e**). The procedure as described in *2.2* was applied with pyrrolidine instead of piperidine to give **7e** (120.8 mg, 68%). Yellow solid.

Data of **7e**. M.p. 201–202° (cyclohexane/toluene). R_f (toluene/AcOEt 5:1) 0.71. UV/VIS (cyclohexane): λ_{max} 373 (4.13), 332 (4.20), 275 (4.50), 223 (4.40); λ_{min} 345 (3.93), 323 (4.10), 241 (4.15), 216 (4.34). FL (cyclohexane): λ_{em} 475, 452. IR: 3049*w*, 3000*w*, 2969*m*, 2870*m*, 2215*m* (C≡N), 1701v*s* (C=O), 1639*w*, 1594*s*, 1564v*s*, 1539v*s*, 1512v*s*, 1492v*s*, 1478*s*, 1457*s*, 1406*m*, 1346*m*, 1330*s*, 1316*m*, 1293*m*, 1281*m*, 1262*s*, 1240*s*, 1223*s*, 1200*s*, 1179*m*, 1149*m*, 1127*m*, 1088*w*, 1070*w*, 1044*w*, 1034*w*, 1022*w*, 1008*m*, 998*w*, 980*w*, 967*w*, 921*w*, 870*m*, 858*m*, 819*w*, 779*w*, 771*m*, 754*s*, 711*m*, 697*m*, 689*m*, 675*m*, 539*w*. ^{1}H-NMR (600 MHz): 8.39 (*dm*, $^3J(5,6) = 7.6$, H–C(5)); 7.93–7.90 (*m*, 2 arom. H); 7.69 (*dm*, $^3J(8,7) = 7.4$, H–C(8)); 7.57 (*td*, $^3J(6,5) \approx {}^3J(6,7) = 7.6$, $^4J(6,8) = 1.3$, H–C(6)); 7.50 (*td*, $^3J(7,6) \approx {}^3J(7,8) = 7.4$, $^4J(7,5) = 0.9$, H–C(7)); 7.51–7.43 (*m*, 3 arom. H); 3.98 (br. *s*, 2 NCH_2CH$_2$); 2.02 (br. *s*, 2 NCH$_2$CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 187.64 (C_q, CO); 160.13 (C_q); 159.76 (C_q); 157.22 (C_q); 138.21 (C_q); 136.63 (C_q); 135.69 (C_q); 133.84 (CH); 132.01 (CH); 130.37 (CH); 129.90 (2 CH); 127.53 (2 CH); 123.54 (CH); 123.23 (CH); 117.89 (C_q); 114.24 (C_q, CN); 82.25 (C_q); 49.80 (2 NCH_2CH$_2$); 25.32 (2 CH$_2$). CI-MS (NH_3): 352 (100, $[M+H]^+$). EI-MS: 351 (33, $M^{+\bullet}$), 322 (95), 296 (50), 154 (42), 128 (21), 84 (100), 70 (32, $C_4H_8N^+$). Anal. calc. for $C_{23}H_{17}N_3O$ (351.41): C 78.61, H 4.88, N 11.96; found: C 78.43, H 4.64, N 11.95.

2.7. *9-Oxo-1-[(*E*)-2-phenylethenyl]-3-(piperidin-1-yl)-9*H*-indeno[2,1-*c*]pyridine-4-carbonitrile* (**7f**). To a soln. of the indanone (194.2 mg, 1.00 mmol) in 1,4-dioxane (40 ml) were added successively freshly distilled cinnamaldehyde (0.16 ml, 1.2 mmol) and piperidine (0.12 ml, 1.2 mmol), and the mixture was stirred for 18 h at r.t. All volatile material was removed by evaporation in high vacuum without warming. The brown residue was separated by CC (silica gel; hexane/AcOEt 25:1, 10:1, 5:1, 2:1). The fluorescing yellow fractions were collected, and the solvents were removed in a rotatory evaporator at 30° *in vacuo*. The residue was dissolved in a small amount of CH_2Cl_2, and crystallization was induced by slow addition of cyclohexane and by evaporation to yield **7f** (46.7 mg, 12%). Yellow needles.

Data of **7f**. M.p. 225–227°. R_f (toluene/AcOEt 5:1) 0.79. UV/VIS (cyclohexane): λ_{max} 392 (4.27), 351 (4.47), 339 (4.48), 307 (4.41), 295 (4.41), 286 (4.40), 225 (4.37); λ_{min} 374 (4.24), 348 (4.46), 315 (4.31), 303 (4.39), 289 (4.40), 248 (4.17), 213 (4.29). FL (cyclohexane): λ_{em} 487, 462. IR: 3058*w*, 3024*w*, 2936*m*, 2850*m*, 2212*m* (C≡N), 1691v*s* (C=O), 1632*s*, 1593*m*, 1570v*s*, 1544v*s*, 1498*s*, 1466*s*, 1447*s*, 1407*m*, 1388*m*, 1366*m*, 1347*w*, 1322*m*, 1275*s*, 1260*m*, 1227*m*, 1214*s*, 1203*s*, 1175*w*, 1158*w*, 1132*m*, 1121*s*, 1087*w*, 1076*w*, 1028*m*, 1017*m*, 980*m*, 959*w*, 910*w*, 900*m*, 858*m*, 763*s*, 735*w*, 691*s*, 665*w*, 611*w*. ^{1}H-NMR (300 MHz): 8.29 (*dm*, $^3J(5,6) = 7.5$, H–C(5)); 8.19 (*d*, $^3J = 15.7$, H–C(1′)); 7.92 (*d*, $^3J = 15.7$, H–C(2′)); 7.70 (*dm*, $^3J(8,7) = 7.4$, H–C(8)); 7.68–7.65 (*m*, 2 arom. H); 7.56 (*td*, $^3J(6,5) \approx {}^3J(6,7) = 7.5$, $^4J(6,8) = 1.4$, H–C(6)); 7.49 (*td*, $^3J(7,6) \approx {}^3J(7,8) = 7.4$, $^4J(7,5) = 1.3$, H–C(7)); 7.43–7.34 (*m*, 3 arom. H); 3.93 (br. *s*, 2 NCH_2CH$_2$); 1.78 (br. *s*, 2 NCH$_2$CH_2CH$_2$, NCH$_2$CH$_2$CH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 189.20 (C_q, CO); 160.80 (C_q); 159.04 (C_q); 154.38 (C_q); 138.87 (CH); 138.55 (C_q); 136.04 (C_q); 135.91 (C_q); 133.90 (CH); 132.00 (CH); 129.37 (CH); 128.68 (2 CH); 128.15 (2 CH); 123.50 (CH); 123.34 (CH); 122.46 (CH); 117.18 (C_q); 115.10 (C_q, CN); 84.99 (C_q); 49.58 (2 NCH_2CH$_2$); 25.97 (2 CH$_2$); 24.46 (CH$_2$). EI-MS: 391 (100, $M^{+\bullet}$), 362 (74), 348 (41), 336 (26), 335 (25), 323 (18), 307 (21), 281 (26), 279 (20), 251 (15), 126 (16), 107 (10), 84 (48, $C_5H_{10}N^+$), 77 (11, $C_6H_5^+$), 56 (11). Anal. calc. for $C_{26}H_{21}N_3O$ (391.47): C 79.77, H 5.41, N 10.73; found: C 79.66, H 5.54, N 10.74.

3. *Crystal-Structure Determinations of* **4′**, **5′**, *and* **7a**[6]). The data collection and refinement parameters for each compound are summarized in *Table 5*. All measurements were conducted at low-temp. on a *Rigaku AFC5R* diffractometer using graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å) and a 12-kW rotating anode generator. The intensities were collected using $\omega/2\theta$ scans, and three standard reflections measured after every 150 reflections showed negligible variation in intensity. The intensities

Table 5. *Crystallographic Data for Compounds* **4′**, **5′**, *and* **7a**

		4′	**5′**	**7a**
Crystallized from		EtOH	AcOEt	cyclohexane/toluene
Empirical formula		$C_{35}H_{35}N_3O \cdot EtOH$	$C_{35}H_{33}N_3O$	$C_{24}H_{19}N_3O$
Formula weight [g mol^{-1}]		559.75	511.66	365.43
Crystal color, habit		red, prism	orange, prism	yellow, prism
Crystal dimensions [mm]		$0.40 \times 0.45 \times 0.50$	$0.25 \times 0.40 \times 0.50$	$0.18 \times 0.25 \times 0.32$
Temp. [K]		173(1)	173(1)	173(1)
Crystal system		monoclinic	monoclinic	triclinic
Space group		$P2_1/c$	$P2_1/n$	$\bar{P}1$
Z		4	4	2
Reflections for cell determination		25	25	25
2θ Range for cell determination [°]		35 – 40	32 – 38	37 – 40
Unit cell parameters	a [Å]	18.213(3)	12.791(1)	10.186(2)
	b [Å]	12.531(2)	11.707(2)	11.771(2)
	c [Å]	14.348(2)	18.352(3)	8.881(2)
	α [°]	90	90	94.00 (1)
	β [°]	100.49(1)	98.31(1)	111.05(1)
	γ [°]	90	90	68.06(1)
	V [Å^3]	3219.9(8)	2719.1(6)	919.2(3)
$F(000)$		1200	1088	384
D_x [g cm^{-3}]		1.155	1.250	1.320
μ(MoK_α) [mm^{-1}]		0.0714	0.0756	0.0824
Scan type		$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
$2\theta_{(max)}$ [°]		55	55	55
Total reflections measured		8038	6831	4459
Symmetry-independent reflections		7398	6236	4221
R_{int}		0.022	0.031	0.024
Reflections with $I > 2\sigma(I)$		4580	4078	2647
Reflections used in refinement		7398	6236	4221
Parameters refined; restraints		421; 57	357	254
Final $R(F)$ [$I > 2\sigma(I)$ reflections]		0.0618	0.0503	0.0483
$wR(F^2)$ (all data)		0.1956	0.1368	0.1300
Weighting parameters[a]) [a; b]		0.0981; 0.704	0.0516; 0.5839	0.0506; 0.1601
Goodness-of-fit		1.045	1.023	1.010
Secondary extinction coefficient		0.0032(9)	–	0.005(2)
Final Δ_{max}/σ		0.002	0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]		0.64; −0.48	0.25; −0.24	0.26; −0.22

[a]) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$.

6) CCDC-663490 – 663492 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

were corrected for *Lorentz* and polarization effects, but not for absorption, and equivalent reflections were merged. Each structure was solved by direct methods using SHELXS86 [21] or SIR92 [22], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. For **4′**, in addition to the expected org. substrate, the asymmetric unit also contains a disordered EtOH molecule. Two sets of overlapping positions were defined for the atoms of the EtOH molecule, and the site occupation factor of the major conformation was refined to 0.761(6). Similarity restraints were applied to the chemically equivalent bond lengths and angles involving all disordered atoms, while neighboring atoms within and between each conformation of the disordered EtOH molecule were restrained to have similar atomic displacement parameters. The amine H-atom in **4′** was placed in the position indicated by a difference electron-density map, and its position was allowed to refine together with an isotropic displacement parameter. All of the other H-atoms in each structure were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent atom (1.5 U_{eq} for the Me groups). The refinement of each structure was carried out on F^2 by using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied in the cases of **4′** and **7a**. Neutral atom scattering factors for non-H-atoms were taken from [23a] and the scattering factors for H-atoms from [24]. Anomalous dispersion effects were included in F_c [25]; the values for f' and f'' were taken from [23b]. The values of the mass attenuation coefficients are those of [23c]. All calculations were performed using the SHELXL97 program [26] and the crystallographic diagrams were drawn using ORTEPII [27].

REFERENCES

[1] A. A. S. Briquet, P. Uebelhart, H.-J. Hansen, *Helv. Chim. Acta* **1996**, *79*, 2282.
[2] S. El Houar, H.-J. Hansen, *Helv. Chim. Acta* **1997**, *80*, 253; S. Maillefer-El Houar, P. Uebelhart, H.-J. Hansen, *Helv. Chim. Acta*, to be submitted.
[3] P. Ott, H.-J. Hansen, *Helv. Chim. Acta* **2001**, *84*, 2670.
[4] T. Landmesser, H.-J. Hansen, *Helv. Chim. Acta*, to be submitted.
[5] K. A. Bello, L. Cheng, J. Griffiths, *J. Chem. Soc., Perkin Trans. 2* **1987**, 815.
[6] P. P. Fu, R. G. Harvey, *Chem. Rev.* **1978**, *78*, 317.
[7] J.-J. Godfroid, *Bull. Soc. Chim. Fr., Ser. 5*, **1964**, 2953; J. V. Crivello, J. L. Lee, *Macromolecules* **1981**, *14*, 1141.
[8] R. C. Fuson, J. J. Miller, *J. Am. Chem. Soc.* **1957**, *79*, 3477.
[9] C. Mayor, C. Wentrup, *J. Am. Chem. Soc.* **1975**, *97*, 7467.
[10] D. Lin-Vien, N. B. Colthup, W. G. Fateley, J. G. Grasselli, 'The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules', Academic Press, Inc., San Diego, 1991, p. 341.
[11] J. F. Ireland, in 'Advances in Physical Organic Chemistry', Eds. V. Gold, D. Bethell, Academic Press, Ltd., London, 1975, Vol. 12, p. 131.
[12] ' Handbook of Chemistry and Physics', 70th edn., CRC Press, Inc., 1989, p. D-161.
[13] A. Huth, R. Schmiechen, I. Motoc, I. Beetz, A. Breitkopf, E. Frost, I. Schumann, K. Thielert, *Arch. Pharm.* **1988**, *321*, 297.
[14] M.-J. Shiao, K.-H. Liu, P.-Y. Lin, *Heterocycles* **1993**, *36*, 507.
[15] H. Fischer-Colbrie, H. Aigner, H. Junek, *Monatsh. Chem.* **1975**, *106*, 743.
[16] N. S. Kozlov, V. D. Pak, Z. Z. Nugumanov, *Khim. Geterotsikl. Soedin (Engl. Transl.)* **1970**, *6*, 179; N. S. Kozlov, K. N. Gusak, *Dokl. Chem. (Engl. Transl.)* **1990**, *314*, 300.
[17] H. Junek, M. Klade, H. Sterk, *Monatsh. Chem.* **1989**, *120*, 781.
[18] H. Boutome, H. Hartmann, *Monatsh. Chem.* **1997**, *128*, 71.
[19] M. Mishriky, F. A. Asaad, Y. A. Ibrahim, A. S. Girgis, *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 35.
[20] H. Hellmann, K. Seegmüller, *Chem. Ber.* **1958**, *91*, 2420.
[21] G. M. Sheldrick, SHELXS86, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
[22] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, SIR92, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[23] a) E. N. Maslen, A. G. Fox, M. A. O'Keefe, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 6.1.1.1, pp. 477 – 486; b) D. C. Creagh, W. J. McAuley, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.6.8, pp. 219 – 222; c) D. C. Creagh, J. H. Hubbell, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992, Vol. C, Table 4.2.4.3, pp. 200 – 206.
[24] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175.
[25] J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.* **1964**, *17*, 781.
[26] G. M. Sheldrick, SHELX97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, 1997.
[27] C. K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.

Received November 26, 2007