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Contributions to the Chemistry of 3-Cyanoacetylhydrazono-2-indolinones and X-ray Structure of *Z*-3-Cyanoacetylhydrazono-2-indolinone Monohydrate

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ABSTRACT: *The tendency of acylhydrazones to undergo a spontaneous cyclization into 1,3,4-oxadiazolines has been investigated. Contrary to the literature data, an attempted transformation of isatin cyanoacetylhydrazone in solution generates stereoisomers and not the reported structural isomer oxadiazoline. A similar behavior of the corresponding l-methyl- and l-acetylisatin derivatives even under acetylation conditions has been found. The crystal structure of the Z isomer of 3-cyanoacetylhydrazono-2-indolinone monohydrate is reported. It contains strong intramolecular hydrogen bond between the hydrazone N—H and oxygen atom of the indolinone carbonyl, and in this way the Z isomer over the C=N bond is stabilized.* © 2009 Wiley Periodicals, Inc. Heteroatom Chem 20:183–193, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20531

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INTRODUCTION

It is always a challenging problem to verify the exact structure and electron distribution when several functional groups capable of conjugation (C=C, C=O, aromatic ring) are present in the same molecule. Cyclic *N,O*-acetals 3-acyl-1,3,4-oxadiazolines are 3-acyl derivatives of the cyclic isomers of aldehyde or ketone acylhydrazones and represent an interesting example for conjugation. They can be prepared by cycloaddition of 3,3-disubstituted diazirenes to diacyldiazenes [1–12], that of aldehydes to nitrilimines [13], or a ketene to a ketone acylhydrazone [14]. Other methods to prepare such compounds include $Pb(OAc)_4$ oxidation of aldazines [15], treating silver salt of acylhydrazones with acid chloride [16]. More conveniently, a reaction of (acyl)hydrazones with acid chlorides [10,11], as well as with acid anhydrides—either by itself or in the presence of a base and Lewis or protic acid, respectively [17–20]—also gives 3-acyl-1,3,4-oxadiazoline derivatives.

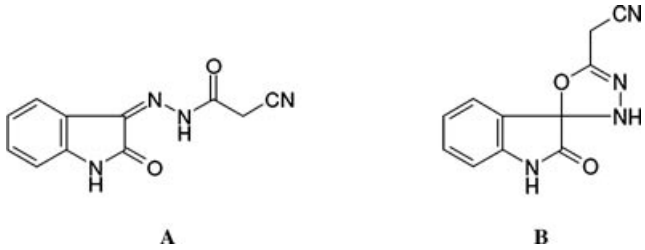
By considering the sulfur analogs, it is known that some of the thioacylhydrazones cyclize in the solution spontaneously into the isomeric 2,3-dihydro-1,3,4-thiadiazoles [21], probably due to the greater nucleophilicity of S in comparison to O. For 1,3,4-oxadiazolines, the presence of an acyl

group at position 3 is essential for the stabilization of the heterocycle. The 3-acyl-1,3,4-oxadiazolines are known to transform (sometimes reversibly) into the isomeric open-chain diacylhydrazones or substituent-isomeric 3-acyl-1,3,4-oxadiazolines [9–11,22,23] or to be transacylated [24] via an open-chain transitional azomethine imine form especially in polar solvents of high dielectric constant or under acetylating conditions.

Recently, a number of 1,3,4-oxadiazoline derivatives also with free *endo*cyclic NH group have been published [25–31] and the cyclic structure was suggested on the basis of IR and ^{1}H NMR spectral data. Ring-opening transformation into aldehyde acylhydrazones has also been observed [26] when 1,3,4-oxadiazoline derivatives were simply dissolved in dimethyl sulfoxide. According to our earlier experiences in the chemistry of oxadiazolines, ^{1}H NMR spectra are less informative and comprehensive. ^{13}C NMR investigations are needed for proving the cyclic structure of 2,2-disubstituted 1,3,4-oxadiazolines with free NH group, whereas the final proof for the structure determination could be a single crystal X-ray diffraction measurement. The tendency to cyclize even under acylating conditions depends on the electron distribution of the C=N and NH—C=O moieties of acylhydrazones and on steric factors, as well. Thus, in some cases, under acylating conditions acylhydrazones are transacylated rather than to cyclize into 3-acyloxadiazolines or transform into diacylhydrazones. Even the partial deacetylation of a diacetylhydrazone under acetylating conditions has been described [32].

Isatin aroylhydrazones have been reported to resist cyclization and gave acetylhydrazones via transacetylation [33] when they were treated with boiling Ac_2O for 1–36 h. Successful cyclization of both isatin aroyl- and acetylhydrazones into the corresponding 1,5′-disubstituted 3′-acetylspiro[oxindole-3,2′-[1,3,4]oxadiazolines] has been achieved [20] in Ac_2O in the presence of acid (trifluoroacetic acid, TFA) or base (pyridine, NaOAc) additives.

Keeping the above findings in mind, a recent report [34] on the cyclization of isatin cyanoacetylhydrazone **A** (2-cyano-*N*′-[(3*Z*)-2-oxo-1,2-dihydro-3*H*-indol-3-ylidene]-acetohydrazide) into the isomeric spiro[oxindole-3,2′-[1,3,4]oxadiazoline] **B** (2-oxo-1,2-dihydro-3′*H*-spiro[indole-3,2′ [1,3,4]oxadiazol]-5′-yl)acetonitrile) by boiling it in acetic acid for 2 h seemed to be a very unusual chemical reaction (see Scheme 1). Moreover, the product was claimed to be stable for subsequent transformations with HNO_2, aldehydes, AcOH/Zn, etc. Thus, we decided



SCHEME 1

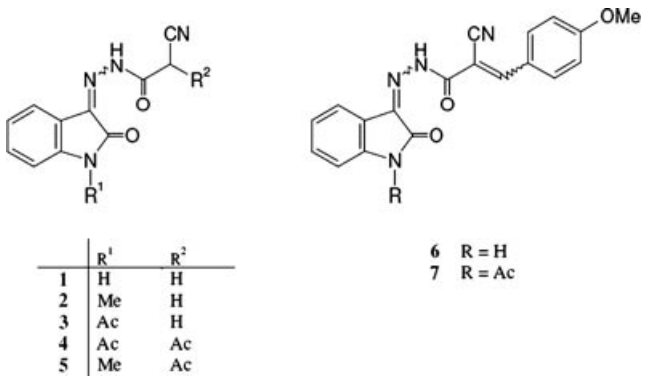
to repeat this questionable reaction converting **A** into **B** and check the structure of the product.

RESULTS AND DISCUSSION

In our work, compounds **1–5**, the isomers of lower R_f (thin layer chromatography, TLC), will be designated as **a**, those of higher ones as **b** (see Scheme 2).

To perform a valid and comprehensive comparison, not only the reported [34] isatin 3-cyanoacetylhydrazone (**la**) but the analogous l-methyl and l-acetyl derivatives (**2a** and **3a**) were prepared too. To distinguish the isomeric acylhydrazone from the oxadiazoline structures, a detailed analysis of IR-, ^{1}H-, and ^{13}C NMR spectra was performed. As it was mentioned earlier for structure elucidation, the IR spectra of analogous 3-acylhydrazono-2-indolinones were found to be less informative [20], and because of the lack of an azomethine or O—C*H*R—N acetalic hydrogen also the ^{1}H NMR spectra are inferior than in the case of the corresponding aldehyde derivatives [35].

Cyanoacetylhydrazone **la**, mp 211–212°C [recrystallized from EtOH; [34] mp 230–232°C (from EtOH)], was synthesized according to the literature method [34] by condensing isatin (**10**) with cyanoacetohydrazide in EtOH. Compound **1b**, mp 205–206°C, was obtained as an AcOH solvate by



	R^1	R^2
1	H	H
2	Me	H
3	Ac	H
4	Ac	Ac
5	Me	Ac

SCHEME 2

treatment of **1a** with boiling AcOH. The paper in question reports [34] this method to transform cyanoacetylhydrazone **A** into spiro-oxadiazoline **B** ([34] mp 207–209°C). According to our results, compound **1b** could also be prepared in poor yield by condensing **10** with cyanoacetohydrazide in hot AcOH. Contrary to **1a**, isomer **1b** was found to form an AcOH and a pyridine solvate, as well. Moreover, a partial transformation **1a** → **1b** in hot $MeO(CH_2)_2OH$ (2-methoxyethanol) was observed (see the section Experimental). Similarly, 1-Me and 1-Ac analogs **2a** and **3a** were synthesized by condensing cyanoacetohydrazide with 1-methylisatin (**11**) in MeOH and 1-acetylisatin (**12**) in EtOAc, respectively. Transformations **a** → **b** could be effected by recrystallizing **2a** from $MeO(CH_2)_2OH$ or by treating **2a** with Ac_2O/TFA to give **2b**, as well as by heating **3a** in AcOH or more advantageously in Ac_2O/TFA (see the section Experimental). The condensation of **12** with cyanoacetohydrazide in warm AcOH afforded **3b** in poor yield.

Although the isomerization of cyanoacetylhydrazones **1–3** into spiro-oxadiazolines of type **B** was unsuccessful, cyclization of 3-acylhydrazono-2-indolinones into 1,5′-disubstituted 3′-acetylspiro-[oxindole-3,2′-[1,3,4]oxadiazolines] has been performed smoothly [20] under acetylating conditions by treatment with Ac_2O in the presence of acid or base additives. Nevertheless, the treatment with $Ac_2O/ZnCl_2$ at room temperature left both **1a** and **1b** unreacted (see the section Experimental). As mentioned above, even the Ac_2O/TFA couple was not suitable for spirocyclization into the corresponding 3-acetyl[1,3,4]-oxadiazolines as this agent generated merely **a** → **b** isomerizations with cyanoacetylhydrazones **1–3**. A treatment with Ac_2O/py or Ac_2O/NaOAc did not affect a spirocyclization of neither **1a, 1b**, or **2a**, instead by C-acetylation resulted in the formation of 2-cyanoacetoacetylhydrazones **4a,b** and **5a,b** (see the section Experimental).

For blocking the neighboring group effect of the CH_2 moiety, *p*-anisylidene derivative **6** was prepared and subjected to the transformation in question under acetylating conditions and this led to the formation of 1-acetyl derivative **7** instead of a spiro-oxadiazoline derivative.

Structures for compounds **1–7** were confirmed by ^{1}H NMR (Table 1), ^{13}C NMR (Table 2), and IR spectra (Table 3). On the basis of ^{1}H- and especially ^{13}C NMR spectral data, the presence of *C*=N signals at δ 140–145 and particularly the lack of a signal about δ 90–95 (see Table 2) characteristic [20] of the *N*,*O*-acetalic spiro C, we suggest products **b** to be the *Z* isomers of the corresponding compounds. To have the final structural evidence, monohydrate of **1b** was subjected to X-ray diffraction studies and was found to be the *Z* isomer of 3-cyanoacetylhydrazono-2-indolinone (Fig. 1) with a strong intramolecular hydrogen bond between N3—H3 and O1 (see below).

Unfortunately, several attempts to grow X-ray quality single crystals of **1a** remained unsuccessful. However, its structure tentatively assigned as the *E* isomer on the basis of NMR and IR data (see below). The appearance of isomers may be promoted also by the presence of the CH_2 moiety with C—H bonds loosened by the electron-withdrawing cyano group. This is reflected by the presence of two separate singlets of different intensities at δ 4.17–4.41 (see Table 1). FT-IR spectra gave additional information as in the spectrum (Nujol) of **1a**; the relative intensities of the bands at 1622 and 1606 cm^{-1} are different from those of **1b** at 1618 and 1606 cm^{-1} (NH bands). The ^{1}H NMR spectra (Table 1) of isomers **a** (i.e., lower R_f) of compounds **1–5** reveal that one of the H—Ar signals (H4) is downfield shifted (δ 8.11–8.38). This was attributed to the deshielding effect of the 3-hydrazono moieties with *E* stereostructure. The spectra of the 1-Ac compounds **3,4** show that an additional signal (H7) is downfield shifted. In the ^{1}H NMR spectra of the acetylation products **4** and **5**, the CH_2 signals are absent. However, because of the possibility for various chelated mesomeric or tautomeric forms [36–38] the signal of —C(O)—C*H*(CN)—C(O)—Me could not be unequivocally assigned. In the IR spectra of compounds **1–7**, the CN bands show diverse intensities (Table 3).

To further investigate the transformation **A** → **B** in question, benzohydrazide was made to react with diethyl acetylenedicarboxylate. This reaction could serve as a model for the reported [31] synthesis of 1,3,4-oxadiazolines with the free *endo*cyclic NH group. Such compounds are the products of the reaction of aroylhydrazines with acetylenedicarboxylic acid or -dimethyl ester. However, in our case the product turned out to be diethyl 1-benzoylhydrazonoethane-1,2-dicarboxylate (**8**) and not the 2,2,5-trisubstituted 1,3,4-oxadiazoline **13** (see Scheme 3). When **8** was treated with Ac_2O/py at room temperature (see the section Experimental) diethyl 1-(*N*-acetylbenzoylhydrazono)-3-butanone-1,2-dicarboxylate (**9**) could be prepared via N- and C-acetylation and not the 3-acetylated oxadiazoline **14** or its C-acetylated derivative.

Bond length and bond angle data are in agreement with the expected values, clearly indicating partial conjugation along the molecule. In the hydrogen bond web, hydrogen atoms of N1—H1, N3—H3, O1w–H11, and O1w–H12 participate. O1 forms both intramolecular hydrogen bond with H3 and intermolecular one with H1 of the next molecule

TABLE 1 ^{1}H NMR Spectral Data of Acylhydrazones **1a–5b**[a]

Compound	*NH/OH*	*H-Ar*	*CH_2*	*NCH_3*	*CH_3—CO*
1a	[b]10.83 (1H)[d] 11.31 (1/3 H) 11.61 (2/3 H)	6.90[f] 7.04 7.40 8.11[i]	4.17 (2/3 H) 4.33 (1 1/3 H)		
1b	[b]11.27 (1H)[d] 11.92 (0.9H) 12.47 (0.1H) 12.61 (0.7H)[e] 13.00 (0.3H)[e]	6.92[f] 7.08[g] 7.37[g] 7.52[f]	4.18 (0.5H) 4.38 (1.5H)		1.90 (2.6H)[e] 2.31 (0.2H)[e]
2a	[b]11.55 (1H)[o]	7.09 (2H)[f,h] 7.48 8.13[i]	4.19 (0.5H) 4.33 (1.5H)	3.17	
2b	[b]12.55 (0.8H) 12.98 (0.2H)	7.08–7.18 (2H) 7.46–7.49 7.57–7.58[f]	4.21 (0.5H) 4.41 (1.5H)	3.20	
3a	[b]11.65 11.90	7.34[i] 7.56[g,j] 8.26[f,h] 8.29[i]	4.34[k]		2.62
3b	[b,l]12.29	7.32–7.35[g] 7.50–7.53[g] 7.71[f,m] 8.14[f,m,n]	4.37 (2H)[o]		2.62
4a	[b]11.13	7.30–7.33[g,p] 7.51–7.54[g,p] 8.24–8.26[f] 8.27–8.29[f]			2.31[o] 2.62
4b	[c]14.49	7.26–7.68 (4H)[q] 8.13–8.18[f,n]			2.15[o] 2.63
5a	[c]13.62 (0.8H) 14.07 (0.2H)	7.08–7.21 (2H) 7.41–7.49[g] 8.35–8.38[f,r]		3.20	2.13 (2.4H) 2.30 (0.6H)
5b	[c]4.18	7.10–7.17 (2H) 7.39–7.46[g] 7.55–7.58[f]		3.21	2.12 (0.6H) 2.24 (2.4H)

[a] In $[CD_3]_2SO$; the frequencies are indicated *before* the first column.
[b] 500 MHz.
[c] 200 MHz.
[d] H1.
[e] AcOH solvate.
[f] d-shaped m.
[g] t-shaped m.
[h] $J = 8$ Hz.
[i] s-shaped m.
[j] $J = \sim 7$ Hz.
[k] 2 br s (major/minor).
[l] At 320 K, because of the poor solubility.
[m] $J = \sim 10$ Hz.
[n] H7.
[o] br s.
[p] The signal of —C*H*(CN) is not noticeable.
[q] H4,5,6, and presumably —C*H*(CN)—.
[r] H4.

TABLE 2 ^{13}C NMR Spectral Data of Acylhydrazones **1a–4a**[a]

			Aromatic				
Compound	*C═O*	*C═N*	*═CR*	*═CH*	*—CN*	*CH_2*	*CH_3*
1a	164.1 167.9	144.0	115.0 137.5	110.7 121.7 126.2 132.9	115.7	25.8	
1b[b]	162.4 165.8 172.0[b]	142.7	119.3 135.5	111.3 120.9 122.7 132.0	115.5	23.9	21.0[b]
2a	162.8 167.9	145.0	114.3[c]	109.3 122.2 125.9 132.8	115.6	24.9	26.0[d]
2b	160.5 165.8	143.9	118.6 131.9	110.0 120.5 123.2 131.9	115.4	23.9	25.7[d]
3a	162.9[e] 168.2[e] 170.3	141.2	116.3[c]	116.2 124.8 125.6 132.7	115.6	25.0	26.5
3b	[f]160.6 169.7	140.5	[g]	116.2 120.2 125.2 131.6	115.0	~ 24[h]	26.0
4a	163.3 170.3[c] ~190.0[e]	140.7	116.5[c]	116.0 124.7 125.3 132.0	—[g,i]		26.5[c]
4b[j]							

[a]125 MHz, for solutions in DMSO-d_6, at 23°C if not otherwise stated *before* the first column.
[b]AcOH solvate.
[c]2C.
[d]*N-Me*.
[e]Weak.
[f] At 320 K, because of the poor solubility.
[g]Not observable.
[h]Barely observable.
[i]The IR(KBr) band, however, is observable at 2190 cm^{-1}.
[j]Because of the poor solubility, the spectrum of **4b** could not be registered.

TABLE 3 IR Spectral Data of Acylhydrazones **1a–5b**[a]

1a	(KBr):	3256 (s), 2262 (w), 1732 (s), 1654 (w), 1612 (s), 1560 (w), 1512 (m), 1472 (s/m), 1382 (m), 1344 (s)
	(Nujol):	3244 (w), 3162 (m), 2264 (w), 1732 (s), 1704 (s), 1622 (m), 1606 (s/m)
1b	(KBr):	3204 (s), 2264 (w/m), 1730 (s), 1698 (vs), 1618 (s), 1598 (m/s), 1490 (w), 1470 (s), 1452 (m/s), 1382 (m), 1350 (s)
	(Nujol)[b]:	3350 (w), 3162 (w), 2264 (w), 1704 (s), 1618 (m/s), 1606 (w), 1462 (s), 3162 (w), 2262 (w), 1726 (s), 1698 (s), 1694 (s), 1682 (sh), 1674 (sh), 1620 (m), 1598 (m)
2a	(KBr):	3268 (m), 2968 (w), 2932 (w), 2260 (w), 1724 (s), 1698 (s), 1606 (s), 1556 (vw), 1490 (m), 1472 (s)
2b	(KBr):	3218 (m), 2928 (w), 2262 (m), 1710 (s), 1678 (s), 1614 (s), 1560 (m)
3a	(KBr):	3244 (w), 2260 (w), 1768 (m/s), 1704 (s), 1654 (w), 1648 (w), 1636 (w), 1616 (m), 1600 (m)
3b	(KBr):	3218 (s), 3140 (m/w), 3058 (w), 2970 (m), 2924 (m), 2260 (m), 1772 (sh), 1708 (s), 1654 (w), 1648 (w), 1636 (w), 1606 (s)
4a	(KBr):	3252 (m), 2190 (w), 1756 (s), 1716 (s), 1704 (s), 1674 (m), 1604 (s), 1586 (m/s)
4b	(KBr):	3212 (w), 2216 (m), 1716 (s), 1648 (m/s), 1604 (s), 1578 (m), 1510 (s/vs), 1462 (s)
5a	(KBr):	3432 (br s), 2926 (w), 2220 (m), 1702 (s), 1644 (m), 1606 (s), 1518 (s), 1494 (m), 1466 (m/s)
5b	(KBr):	3438 (br s), 2930 (w), 2212 (m/s), 1696 (s), 1642 (m/s), 1614 (s), 1526 (s), 1492 (m/w), 1470 (s)

[a]Wave numbers (cm^{-1}).
[b]The product was kept at 100°C/0.5 Torr over P_4O_{10} to reach constant weight.

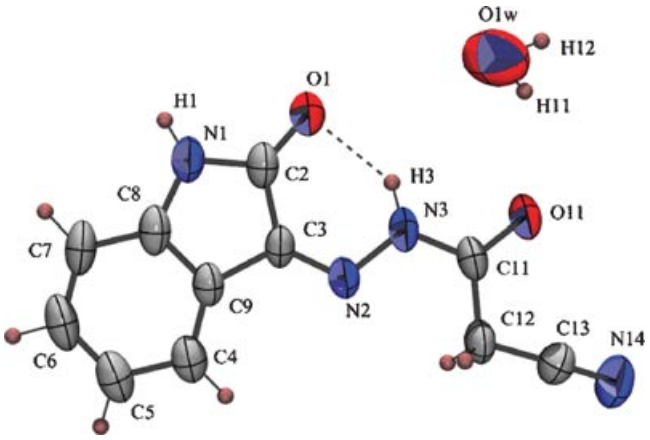


FIGURE 1 ORTEP view of **1b** monohydrate. Selected bond distances (Å): N1–C8 1.411(6); N1–C2 1.355(5); C2–O1 1.236(5); C2–C3 1.496(6); C3–N2 1.283(5); C3–C9 1.461(5); N2–N3 1.381(5); C11–N3 1.346(5); C11–O11 1.226(5); C11–C12 1.507(6); C13–N14 1.137(5). Torsion angles (°): C11–N3–N2–C3 173; N3–C11–C12–C13 177.

in the lattice. H11 is donated to O11, whereas H12 to oxygen atom of another solvate water molecule. Stacking interaction of the indolinone rings further stabilizes the layered structure.

In conclusion, the reported [34] spirocyclization of isatin cyanoacetylhydrazone (**A**) into oxadiazoline **B** is not a valid reaction and the real transformation was found to be an *E*/*Z* isomerization common [39–50] among (acyl)hydrazones. Even under acetylating conditions, no spirocyclization could be observed.

EXPERIMENTAL

Melting points (uncorrected): Kofler block. Solutions were concentrated under reduced pressure in a rotary evaporator (<50°C, bath). TLC: Kieselgel 60 F_{254} (Merck, Alurolle). IR (KBr disks and Nujol mull): Perkin-Elmer 16 PC-FT spectrophotometer. 200 MHz ^{1}H- and 50 MHz ^{13}C NMR: Bruker WP 200 SY, 500 MHz ^{1}H- and 125 MHz ^{13}C NMR: Bruker DRX 500 spectrometers; for recording the ^{13}C NMR spectra, *J*-echo techniques were used. MALDI-TOF MS: Bruker BIFLEX III (Brehmen, Germany) instrument, acceleration voltage 19 kV, reflection mode, nitrogen laser (337 nm), 50 μL solution of 2,5-dihydroxybenzoic acid (DHB) matrix (20 mg/mL MeOH) and 10 μL solution of the substance (5 mg/mL MeOH) were mixed and 0.5 μL of the mixture examined. Atomic emission Na determination: Varian SpectrAA 10 spectrometer (FES), at 589.0 nm, after HNO_3/H_2O_2 destruction.

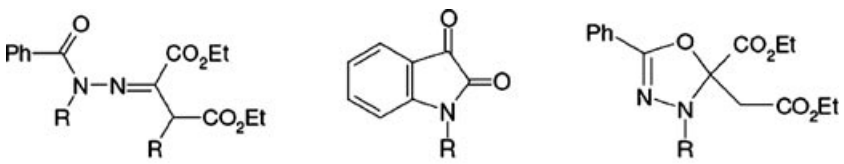
X-ray Data Collection and Reduction

Crystals of **1b** monohydrate were grown from AcOH by slow evaporation of the solution. A colorless prism crystal ($0.55 \times 0.45 \times 0.2$ mm) was fixed on a glass capillary using epoxy glue. Data were collected at 293(1) K, Bruker–Nonius MACH3 diffractometer, Mo Kα radiation $\lambda = 0.71073$ Å, ω motion, $\theta_{max} = 25.4°$. The structure was solved using the SIR-92 software [51] and refined on F^2 using SHELX-97 program, publication material was prepared with the WINGX-97 suite. Hydrogen atoms were fixed into geometric position except N—H and O—H that could be found at the difference electron density map.

Crystal data: formula $C_{11}H_8N_4O_2.H_2O$, M= 246.23, monoclinic, space group $P2_1/n$, $a = 4.7103(10)$ Å, $b = 27.057(2)$ Å, $c = 9.4354(10)$, $\beta = 101.33(1)°$, $V = 1179.1(3)$ Å^3, $Z = 4$, $\rho_{calc} = 1.387$, 2191 measured, 995 reflections were unique with $I > 2\sigma(I)$, decay: 2%, $R1 = 0.0792$ and $wR2 = 0.1797$ for all 2191 reflections and 117 parameters, GOF = 1.013. Residual electron density: 0.217/−0.202 e/Å^3.

*E and Z-3-Cyanoacetylhydrazono-2-indolinone (**1a** and **1b**)*

(a) A mixture of isatin (2.943 g, 20 mmol), powdered cyanoacetohydrazide (2.063 g, 20.4 mmol; 98%; Aldrich), and commercial anhydrous EtOH (50 mL) was boiled with stirring for 2.5 h and then cooled to give crude [3.676 g, 80.5%, mp 206–208°C, [34] 230–232°C (from EtOH)] or recrystallized **1a**, mp 211–212°C (from EtOH).



8 R = H
9 R = Ac

10 R = H
11 R = Me
12 R = Ac

13 R = H
14 R = Ac

SCHEME 3

The mother liquor of crude **1a** was concentrated, and the residue crystallized from 99%–100% AcOH to give **1b** (0.449 g, 7.8% as an AcOH solvate), mp 202–203°C.

(b) Compound **1a** (2.282 g, 10 mmol) was boiled in 99%–100% AcOH (25 mL) with stirring for 2.5 h to give **1b** (2.449 g, 84.9% as an AcOH solvate), mp 201–202°C [for compound **B**, [34] mp 207–209°C (from AcOH)]: TLC [$CHCl_3$/EtOAc (9:1), three-fold run] $R_f \sim 0.35$, whereas compound **1a** remained at the start point. Product **1b** (5.317 g), mp 205–206°C, when kept over P_4O_{10}/0.5 Torr at 100°C unto constant weight, sustained a decrease in weight 0.616 g (11.2%; calcd for 1 AcOH solvate, 20.8%), mp 204–205°C.

(c) Compound **1a** (1.500 g) was recrystallized from $MeO(CH_2)_2OH$ to give **1a** (0.270 g), mp 203–206°C, TLC [$CHCl_3$/EtOAc (9:1), three-fold run] R_f 0.0. The mother liquor was concentrated, and the residue triturated with MeOH to give **1b** (0.638 g), with R_f 0.35 and traces of **1a** with R_f 0.0; thus also in hot $MeO(CH_2)_2OH$ **1a** undergoes a transformation into **1b**. **1a,b**: For ^{1}H- and ^{13}C NMR, as well as IR spectral data, see Tables 1–3.

Pyridine-Solvate Formation of **1b**

Compound **1b**, previously having been kept at 100°C/0.5 Torr over P_4O_{10} to constant weight (0.1212 g) was stirred in pyridine (1.2 mL) for 30 min and then hexane (3.6 mL) was added. The solid was filtered off and washed with hexane to give a product (0.1564 g), mp 204–205°C, which on the basis of the increase in weight could be regarded as a 1:1 solvate but the ^{1}H- and ^{13}C NMR spectra revealed a **1b**•½py composition: ^{1}H NMR (500 MHz, 23°C, DMSO-d_6) δ: 4.21 (s, 0.5H) and 4.41 (s, 1.5H) (CH_2), 6.95 (d, 1H, H7), 7.10 (t, 1H, H6), 7.37–7.41 (m, 2H, H5 +½*py* H3.5), 7.54 (d, 1H, H4), 7.77–7.81 (t, 0.5H, ½*py* H4), 8.58 (d, 1H, ½*py* H2,6), 11.31 (s, 1H, H1), 12.64 (s, 0.75H), and 13.02 (s, 0.25H)(=*NNH*—). ^{13}C NMR (125 MHz, 23°C, DMSO-d_6) δ: 23.9 (*C*H_2), 111.3 (2C, aromatic =*C*H), 115.5 (*C*≡N), 119.3 (aromatic =*C*R), 120.8, 122.6 (2C), 123.9, and 132.0 (2C)(aromatic =*C*H), 135.5 (aromatic =*C*R), 136.1 (aromatic =*C*H), 142.7 (*C*=NNH—), 149.6 (aromatic =*C*H), 162.4, and 165.8 (2 *C*=O). Under similar conditions, a solvate formation of compounds **1a** or **2b** could not be observed.

*3-Cyanoacetylhydrazono-1-methyl-2-indolinone (***2a** *and* **2b***)*

A mixture of powdered 1-methylisatin (**11**, 1.661 g, 10 mmol), powdered cyanoacetohydrazide (1.031 g, 10.2 mmol; 98%; Aldrich), and MeOH (30 mL) was stirred at 50°C (bath) for 6 h. The solid was filtered off at ~30°C to give TLC [$CHCl_3$/EtOAc (9:1), three-fold run] homogeneous (R_f 0.14) crude **2a** (1.856 g; 76.6%), mp 205–206°C, which when recrystallized from $MeO(CH_2)_2OH$ transformed into TLC (as mentioned above) homogeneous (R_f 0.74) **2b**, mp 215–217°C. The mother liquor of crude **2a** was concentrated, and the residue triturated with water in the cold to give an amorphous solid (0.458 g; 18.9%) consisting (TLC as mentioned above) of **2a, 2b**, and some **11**. For ^{1}H- and ^{13}C NMR, as well as IR spectral data of **2a,b**, see Tables 1–3. **2b**: Anal. Calcd for $C_{12}H_{10}N_4O_2$ (242.23): C, 59.50; H, 4.16; N, 23.13. Found: C, 59.38; H, 4.24; N, 23.08.

*1-Acetyl-3-cyanoacetylhydrazono-2-indolinone (***3a** *and* **3b***)*

(a) A mixture of 1-acetylisatin [20] (**12**, 5.675 g, 30 mmol), powdered cyanoacetohydrazide (3.032 g, 30 mmol; 98%; Aldrich), and EtOAc (100 mL) was stirred at 60°C (bath) for 22 h. The solid was filtered off in the cold to give crude (4.248 g, 52.4%, mp 195–197°C) or recrystallized **3a**, mp 220–223°C (from DMF). **3a**: For ^{1}H- and ^{13}C NMR, as well as IR spectral data, see Tables 1–3. Anal. Calcd for $C_{13}H_{10}N_4O_3$ (270.24): C, 57.77; H, 3.73; N, 20.73. Found: C, 57.70; H, 3.76; N, 20.80.

(b) A mixture of powdered **12** [20] (2.838 g, 15 mmol), powdered cyanoacetohydrazide (1.547 g, 15.3 mmol; 98%; Aldrich), and AcOH (15 mL, 99%–100%) was stirred at 58°C (bath) for 18 h, and then cooled to give crude **3b** (0.707 g, 17.4%), mp 218–220°C. A solution of the crude product in hot $CHCl_3$ was treated with charcoal and was concentrated to a smaller volume, and hexane was added to give TLC homogeneous [$CHCl_3$/EtOAc (9:1); R_f 0.49] **3b**, mp 232–233°C.

(c) A solution of pure **3a** (0.540 g) in 99–100% AcOH (20 mL) was boiled with stirring for 2 h and then concentrated. The residue was processed as in (b) to give pure isomer **3b** (0.174 g; 32%), mp 232°C.

(d) A mixture of Ac_2O (60 mL, 640 mmol), TFA (98%, 2 mL, 26 mmol), and pure **3a** (2.702 g, 10 mmol) was stirred at 70°C (bath) for 24 h and then concentrated. The deep freezed residue was triturated with commercial anhydrous EtOH (10 mL), and after being kept at room temperature for 1 h hexane (10 mL) was added in portions to afford TLC (see above in (b))

homogeneous pure isomer **3b** (1.850 g; 68.5%), mp 232–233°C. **3b**: For ^{1}H- and ^{13}C NMR, as well as IR spectral data, see Tables 1–3.

*1-Acetyl-3-(2-cyanoacetoacetylhydrazono)-2-indolinone (**4a**)*

A mixture of **1a** (1.141 g, 5 mmol), anhydrous pyridine (12 mL), and Ac_2O (12 mL) was stirred at room temperature for 24 h. The solid was filtered off, washed with Ac_2O and hexane to give crude pyridine salt of **4a** (1.231 g), mp 198–202°C. **4a**•(~0.65 py): ^{1}H NMR (500 MHz, 23°C, DMSO-d_6) δ: 2.15 (s, 3H, *Ac*), 2.63 (s, 3H, *Ac*), 7.39–7.42 (t, 1H) and 7.50–7.53 (t, 1H H5.6), 8.06–8.08 (t, ~1.3H, *py* H3,5), 8.30–8.32 (d, 1H, H4?), 8.49–8.50 (d, 1H, H7?), 8.58–8.61 (t, ~0.65H, *py* H4), 8.94–8.95 (d, ~1.3H, *py* H2,6), 13.87 (br s, 1H, *NH*). The mother liquor of the crude product was concentrated, and the residue was triturated with commercial anhydrous EtOH (2 mL) in the cold to give a solid (0.147 g), which was treated with charcoal in hot $CHCl_3$ and the solution concentrated. The residue was boiled in EtOAc to give pure **4a** (0.051 g), mp 191–192°C. For ^{1}H- and ^{13}C NMR, as well as IR spectral data, see Tables 1–3. Anal. Calcd for $C_{15}H_{12}N_4O_4$ (312.28): C, 57.69; H, 3.87; N, 17.94. Found: C, 57.59; H, 3.89; N, 17.88.

*1-Acetyl-3-(2-cyanoacetoacetylhydrazono)-2-indolinone (**4b**)*

A mixture of Ac_2O (16 mL, 170 mmol), anhydrous NaOAc (0.50 g, ~6 mmol), and **1b** (0.577 g, ~2 mmol, AcOH solvate) was stirred at 91–92°C (bath) for 2 h, and then concentrated. The cold residue was triturated with water (~50 mL), and the undissolved was filtered off, washed with water and hexane and dried in a vacuum desiccator to give crude Na-salt of **4b** (0.528 g; 79%), mp >360°C. Anal. Calcd for $C_{15}H_{11}N_4O_4Na$ (334.27): Na, 6.88. Found: Na, 6.04.

The aqueous mother liquor was acidified by addition of 2 N HCl (4 mL, 8 mmol), the precipitate was filtered off as a powder, washed with water and hexane to give **4b** (0.073 g; ~11.7%), mp 223°C. For ^{1}H NMR and IR spectral data, see Tables 1–3. Anal. Calcd for $C_{15}H_{12}N_4O_4$ (312.28): C, 57.69; H, 3.87; N, 17.94. Found: C, 57.76; H, 3.86; N, 17.99.

*3-(2-Cyanoacetoacetylhydrazono)-1-methyl-2-indolinone (**5a**)*

A mixture of **2a** (1.211 g, 5 mmol), Ac_2O (15 mL, 159 mmol), and anhydrous pyridine (7 mL, 87 mmol) was stirred at room temperature for 29 h. The solid was filtered off, washed with Ac_2O and hexane to give a pyridine salt of **5a** (1.411 g, 77.7%), mp 153–155°C, well soluble in cold water. **5a**•py: ^{1}H NMR (200 MHz, 23°C, DMSO-d_6) δ: 2.13 (s, 3H, CH_3–CO), 3.19 (s, 3H, *NMe*), 7.09–7.22 (m, ~2.2H), 7.39–7.49 (m, ~1.2H), 8.01–8.08 (m, 2H), 8.36–8.40 (d, 1H), 8.51–8.61 (m, 1H), and 8.92–8.96 (m, 2H), altogether 9.4H (9 *H-Ar* and probably the C(O)—C*H*(CN)—C(O)—CH_3). IR (KBr, cm^{-1}): 3416 (vw), 3066 (w), 2194 (s), 1720 (s), 1610 (s), 1562 (m), 1488 (s), 1468 (m), 1418 (m), 1378 (vs).

A solution of **5a**•py (0.1817 g, 0.5 mmol) in water (5 mL) was filtered and acidified by addition of 1N HCl (0.6 mL, 0.6 mmol). The yellow powder precipitate was filtered off, washed with water, 2-PrOH/hexane (1:2), and hexane to give **5a** (0.1384 g; 97.4%), mp 132–133°C. For ^{1}H NMR and IR spectral data, see Tables 1 and 3. Anal. Calcd for $C_{14}H_{12}N_4O_3$ (284.27): C, 59.15; H, 4.26; N, 19.71. Found: C, 59.04; H, 4.28; N, 19.64.

*3-(2-Cyanoacetoacetylhydrazono)-1-methyl-2-indolinone (**5b**)*

A mixture of powdered **2b** (1.453 g, 6 mmol), Ac_2O (20 mL), and anhydrous pyridine (15 mL) was stirred at room temperature for 24 h. The solid was filtered off, washed with Ac_2O and hexane to give crude **5b**•py salt (1.744 g; 80%), mp 179–180°C. **5b**•py: ^{1}H NMR (200 MHz, 23°C, DMSO-d_6) δ: 2.10 (s, 3H, *Ac*), 3.21 (s, 3H, *NMe*), 7.05–7.12 (t, 2H), and 7.33–7.49 (m, 2H H4-Ar), 7.93–8.00 (t, 2H, *py* H3.5), 8.43–8.51 (t, 1H, *py* H4), 8.88–8.90 (d, 2H, *py* H2.6), 14.52 (br s, 1H, *NH*). IR (KBr, cm^{-1}): 3436 (br s), 3062 (m), 2930 (w), 2200 (s), 1688 (s), 1614 (s), 1604 (sh), 1556 (m), 1484 (s), 1470 (s), 1380 (m).

A solution of **5b**•py (0.1817 g, 0.5 mmol) in water (25 mL, at ~40°C) was filtered and in the cold acidified by addition of 1 N HCl (0.6 mL, 0.6 mmol). The yellow precipitate was filtered off, washed with water and hexane to give **5b** (0.1231 g; 86.6%), mp 189°C. For ^{1}H NMR and IR spectral data, see Tables 1 and 3. Anal. Calcd for $C_{14}H_{12}N_4O_3$ (284.27): C, 59.15; H, 4.26; N, 19.71. Found: C, 59.02; H, 4.25; N, 19.77.

*3-(4-Methoxybenzylidenecyanoacetylhydrazono)-2-indolinone (**6**)*

(a) A mixture of **1a** (9.128 g, 40 mmol), anisaldehyde (5.990 g, 43 mmol; 98%), commercial anhydrous EtOH (160 mL), and Et_3N (12 drops) was boiled with stirring for 3 h. The solid was filtered off in the cold, washed with EtOH and hexane to give crude (8.045 g, 58.1%, mp 274–277°C) or recrystallized **6**, mp 277–278°C (from DMF).

(b) A mixture of **1b** (3.195 g, ~14 mmol, previously kept at 100°C/0.5 Torr over P_4O_{10} for several hours), anisaldehyde (2.06 g, 14.8 mmol; 98%), commercial anhydrous EtOH (50 mL), and Et_3N (10 drops) was boiled with stirring for 3 h, as described above, to give crude (4.217 g. 87%, mp 281–282°C) or recrystallized **6**, mp 286–287°C (from DMF), identical (^{1}H NMR, IR) with that obtained from **1a** as described in (a)). **6**: ^{1}H NMR (200 MHz, 23°C, DMSO-d_6) δ: 3.89 (s, 3H, OCH_3), 6.95–7.63 (m, 6H, H4,5,6,7 and H3.5-Ph), 8.14 (d-shaped m, 2H, H2.6-Ph), 8.44 (s, 1H, −C(CN)=C*H*−), 11.35 (s, 1H, H1), 13.86 (br s, 1H, =N−N*H*). ^{13}C NMR (50 MHz, 23°C, DMSO-d_6) δ: 55.8 (O*C*H$_3$), 98.5 (−*C*(CN)=CH−), 116.3 (*C*≡N), 119.6 and 124.3 (2-2 aromatic =*C*R), 115.0 (2C), 121.2, 122.7, 132.2, 133.5 (2C) (altogether eight aromatic =*C*H), 142.9 (*C*=N−N), 153.8 (−C(CN)=*C*H−), 162.8 (*C*=O), 163.6 (*C*=O). IR (KBr, cm^{-1}): 3224 (m/w), 2204 (m/w), 1712 (s/m), 1676 (s), 1622 (s/m), 1602 (w), 1572 (s/m), 1562 (s/m), 1510 (s), 1466 (s), 1170 (vs). Anal. Calcd for $C_{19}H_{14}N_4O_3$ (346.33): C, 65.89; H, 4.07; N, 16.18. Found: C, 65.80; H, 4.10; N, 16.21.

Attempted Transformation of **1a,b** *by Treatment with* $Ac_2O/ZnCl_2$

To a solution of anhydrous $ZnCl_2$ (0.20 g, ~1.4 mmol) in Ac_2O (5 mL, 53 mmol) was added **1a** (0.2282 g, 1 mmol). The mixture was stirred at room temperature for 53 h, and then the solid was filtered off, washed with Ac_2O, water, and hexane to give a product (0.1858 g, 81.4%, mp 199–201°C) TLC [$CHCl_3$/MeOH (9:1)] identical with the substrate **1a**.

An exactly the same treatment of the AcOH-solvate **1b** (0.2882 g, ~1 mmol) afforded a product (0.1910 g, ~66%) TLC [$CHCl_3$/EtOAc (9:1), three-fold run] identical with the substrate **1b**.

Attempted Acetylation/Spirocyclization of Acylhydrazones **1a,b, 2a, 3a**, *and* **6** *by Treatment with* Ac_2O/TFA

(a) A mixture of Ac_2O (12 mL, 127 mmol), TFA (0.4 mL, 5 mmol; >98%), and **1a** (0.456 g, 2 mmol) was stirred at 70°C (bath) for 24 h and then concentrated. The residue was triturated with water in the cold to give a solid. A solution of the crude product in hot EtOAc was treated with fuller's earth and charcoal and concentrated. Recrystallization form EtOAc afforded **1b** (0.206 g; 45%), mp 199–200°C.

(b) A mixture of Ac_2O (25 mL, 265 mmol), TFA (1 mL, 13 mmol), and **1b** (1.000 g, ~ 4.4 mmol, as an AcOH-solvate) was stirred at 70°C (bath) for 22 h and then processed as described in (a)). A solution of the crude product (0.821 g) in hot $CHCl_3$ (170 mL) was treated with fuller's earth and charcoal and concentrated. Recrystallization from EtOAc yielded **1b** (0.354 g. ~35%), mp 200°C. The products obtained in (a) and (b) are identical (IR, TLC [$CHCl_3$/EtOAc (9:1), four-fold run]) with compound **1b** prepared from isatin (**10**) and cyanoacetohydrazide in AcOH or that obtained by recrystallization of **1a** from AcOH (see above).

(c) A mixture of Ac_2O (3 mL, 32 mmol), TFA (0.1 mL, 1.3 mmol; >98%), and **2a** (0.121 g, 0.5 mmol) was stirred at 70°C (bath) for 24 h, and then concentrated. The residue was triturated with anhydrous EtOH (1 mL) and, after being kept at room temperature for 0.5 h, hexane (1 mL) was added to give TLC [$CHCl_3$/EtOAc (9:1)] homogeneous **2b** (0.090 g; 74.4%), mp 220–221°C, identical (TLC, ^{1}H NMR) with the product obtained by condensing l-methylisatin (**11**) with cyanoacetohydrazide in EtOH followed by recrystallization from 2-methoxyethanol (see above).

(d) A mixture of Ac_2O (3 mL, 32 mmol), TFA (0.1 mL, 1.3 mmol; >98%), and **3a** (0.135 g, 0.5 mmol) was stirred at 70°C (bath) for 24 h, and then concentrated and processed as in described (c) to give TLC [$CHCl_3$/EtOAc (9:1)] homogeneous **3b** (0.093 g; 69%), mp 232–233°C, identical (TLC) with the product obtained by condensing 1-acetylisatin (**12**) with cyanoacetohydrazide in hot AcOH or by recrystallizing **3a** from AcOH (see above).

(e) A mixture of Ac_2O (3 mL, 32 mmol), TFA (0.1 mL, 1.3 mmol; >98%), and anisylidene derivative **6** (0.173 g, 0.5 mmol) was stirred at 70°C (bath) for 24 h. The solid was filtered off in the cold, washed with Ac_2O and hexane to give TLC homogeneous product (0.163 g; 94%), mp 283–285°C, identical (mp, TLC, IR, ^{1}H NMR) with **6** obtained from **1a** or **1b** (see above). Thus, in (a)–(e) neither acetylation nor spirocyclization of the substrates **1a,b, 2a, 3a**, and **6** occurred, but **1a, 2a**, and **3a** were transformed into the corresponding modifications **b** of higher R_f values.

*1-Acetyl-3-(4-methoxybenzylidenecyanoacetylhydrazono)-2-indolinone (***7***)*

(a) A mixture of crude compound **6** (0.200 g, ~0.57 mmol, prepared from **1a**), Ac_2O (2 mL), and anhydrous pyridine (2 mL) was stirred at

50–52°C (bath) for 21 h and then concentrated. The residue was triturated with water in the cold to give a TLC [$CHCl_3$/EtOAc (95:5)] multicomponent solid (0.258 g) which when extracted with hot $CHCl_3$ (5 mL) left undissolved compound **7** (0.050 g; 23%), mp 254–255°C.

(b) A mixture of crude compound **6** (0.693 g, 2 mmol, prepared from **1b**), Ac_2O (4 mL), and anhydrous pyridine (4 mL) was stirred at 70°C (bath) for 6 h and then was kept at room temperature for 2 days. The solid was filtered off, washed with Ac_2O and hexane to give crude **7** (0.607 g; 78%), which when extracted with hot AcOH (46 mL) left undissolved **7** (0.364 g; 47%), mp 258°C. From the mother liquor separated out recrystallized **7** (0.195 g; 25%), mp 264–265°C.

(c) A mixture of Ac_2O (14 mL), anhydrous NaOAc (0.60 g, 7.2 mmol), and crude **6** (0.693 g, 2 mmol, prepared from **1b**) was heated with stirring at 110°C (bath) for 7 h, and then was kept at room temperature for 1 day. The solid was filtered off, washed with Ac_2O, hexane, and several times with water to afford undissolved crude (0.674 g, 86.8%, mp 258–259°C) or recrystallized **7**, mp 260–261°C (from MePh/EtOAc). The products obtained in (a)–(c) are identical (TLC [MePh/EtOAc (8:2)], IR, and ^{1}H NMR). **7**: ^{1}H NMR (200 MHz, 23°C, DMSO-d_6/$CDCl_3$ (8:2)) δ: 2.67 (s, 3H, 1-*Ac*), 3.90 (s, 3H, OCH_3), 7.16–7.20 (d, 2H, H3,5-*Ph*), 7.36–7.40 (t, 1H, H-*Ar*), 7.51–7.55 (t, 1H, H-*Ar*), 7.76–7.80 (d, 1H, H-*Ar*), 8.13–8.22 (m, 2H, H2,6-*Ph*), 8.48 (s, 1H, —(CN)=C*H*—), 13.40 (s, 1H, *NH*). IR (KBr, cm^{-1}): 3434 (br), 2212 (w/m), 1718 (s), 1696 (s), 1606 (m), 1578 (vs), 1562 (m), 1514 (vs), 1460 (m/s). Anal. Calcd for $C_{21}H_{16}N_4O_4$ (388.37): C, 64.94; H, 4.15; N, 14.43. Found: C, 65.04; H, 4.20; N, 14.36.

*Diethyl 1-benzoylhydrazonoethane-1,2-dicarboxylate (**8**)*

A mixture of benzohydrazide (2.723 g, 20 mmol), anhydrous MeOH (50 mL), and diethyl acetylenedicarboxylate (3.582 g, 20 mmol; 98%; Fluka) was boiled with stirring for 2 h and then cooled to give **8** (0.890 g, 14.5%), mp 142–143°C. The mother liquor was concentrated to give a second crop of **8** (4.010 g; 65.4%). **8**: ^{1}H NMR (200 MHz, 23°C, $CDCl_3$) δ: 1.23–1.30 and 1.33–1.40 (each t, 3H; 2 CH_2CH_3), 3.86 (s, 2H, CH_2CO_2Et), 4.15–4.26 and 4.29–4.40 (each q, 2H; 2 CH_2CH_3), 7.95–7.99 (d shaped m, 2H, H2,6-*Ph*), 11.14 (br s, 1H, N*H*). ^{13}C NMR (50 MHz, 23°C, $CDCl_3$) δ: 13.9 and 14.0 (2 CH_2CH_3), 33.4 (CH_2CO_2Et), 62.4 (CH_2CH_3, 2C), 128.5 (C3,4,5-Ph), 132.1 (C1-Ph), 132.5 (C2,6-Ph), 163.9 (EtO—*C*=O, 2C), 168.8 (Ph—*C*=O). IR (KBr, cm^{-1}): 3190 (m), 3016 (w), 2986 (w), 2936 (w), 1746 (s), 1716 (s), 1668 (s), 1626 (w), 1598 (w), 1580 (w), 1542 (m). MALDI-TOF MS *m/z* 307.142 $[M + H]^+$, 329.114 $[M + Na]^+$, 345.066 $[M + K]^+$. Anal. Calcd for $C_{15}H_{18}N_2O_5$ (306.31): C, 58.81; H, 5.92; N, 9.15. Found: C, 58.88; H, 5.96; N, 9.09.

*Diethyl 1-(N-Acetylbenzoylhydrazono)-3-butanone-1,2-dicarboxylate (**9**)*

A mixture of benzoylhydrazone **8** (0.429 g, 1.4 mmol), Ac_2O (4 mL, 42 mmol), and anhydrous pyridine (3 mL, 37 mmol) was stirred until dissolution was complete (~3 min) and was kept at room temperature for 65 h and then concentrated. The residue was triturated with water in the cold. A solution of the doughy product in $CHCl_3$ was dried ($MgSO_4$), treated with fuller's earth and charcoal and then concentrated. The amorphous residue was dried in a vacuum desiccator to give a TLC [$CHCl_3$/EtOAc (95:5)] almost homogeneous glassy product (**9**, 0.545 g, 99.7%). **9**: ^{1}H NMR (200 MHz, 23°C, $CDCl_3$) δ: 1.11–1.24 (m, 6H, 2 CH_2CH_3), 2.08 and 2.36 (each s, 3H; 2 Ac), 4.01–4.21 (m, 4H, 2 CH_2CH_3), 5.63 (s, 1H, —C*H*(Ac)—CO_2Et), 7.32–7.59 (m, 5H, *Ph*). ^{13}C NMR (50 MHz, 23°C, $CDCl_3$) δ: 13.2 and 13.6 (2 CH_2CH_3), 20.9 and 23.4 (2 CH_3—C=O), 60.7 and 62.0 (2 CH_2CH_3), 107.1 (br low signal, detectable only with bb decoupling, —*C*H(Ac)—CO_2Et), 127.9–128.2 C3,4,5-Ph), 132.4 (C1-Ph), 132.7 (2C, C2,6-Ph), 143.2 (N—N=*C*), 161.7, 163.8, 169.2, 169.4, and 171.0 (5 *C*=O). MALDI-TOF MS *m/z* 413.180 $[M + Na]^+$, 429.129 $[M + K]^+$. $C_{19}H_{22}N_2O_7$ (390.39).

SUPPLEMENTARY DATA

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre. Deposition number CCDC-625194. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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