Crystal Structure of 3,3′-Ethanediylidenebis(1-ethylindoline-2-one): An Unexpected Byproduct in *N*-Ethylation of Isatin in Tetrahydrofurane

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The title compound 3,3′-ethanediylidenebis(1-ethylindoline-2-one) was isolated as a byproduct through the reaction of isatin and sodium hydride with iodoethane in tetrahydrofurane. It crystallizes in the space group $P2_1/c$ (#14) with the cell parameters a = 8.7451(9)Å, b = 15.1964(13)Å, c = 6.9425(6)Å, β = 113.561(2)°, Z = 2, and V = 845.70(14)Å^3. The 3,3′-ethanediylidenebis(indoline-2-one) core is planar, adopting an *s-trans* conformation with regard to the ethanediylidene moiety. The crystal structure is stabilized by intermolecular C=O···HC and N···HC hydrogen bonds as well as by π-π interactions.

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In the course of our study towards the synthesis of novel π-expanded compounds as potential precursors of functional dyes, we encountered the need to prepare *N*-alkylisatins (1-alkylindoline-2,3-dione). A variety of *N*-alkylation reactions of isatins are known, all of which are rather simple reactions at textbook levels. Thus, we carried out the reaction of isatin with iodoethane in the presence of sodium hydride in THF.[1] As expected, *N*-ethylisatin was obtained in 62% yield. In addition, crystalline red solids were isolated in only 2% yield as a byproduct, the structure of which was deduced to be 3,3′-ethanediylidenebis(1-ethylindoline-2-one) (**1**) on the basis of spectroscopic and analytical data. The formation of **1** is quite interesting, because the ethanediylidene unit is incorporated in its structural framework: we wonder where this C2 unit comes from. A possible precursor may be iodoethane. Thus, we carried out the reaction of *N*-ethylisatin with sodium hydride without iodoethane. The result, however, was the same as that of the reaction using iodoethane: **1** was again isolated in *ca*. 2% yield. We considered that there may still be some ambiguity in the structure of **1** deduced from spectroscopic data. Thus, to confirm the structure of **1**, a single-crystal X-ray diffraction analysis of the red needlelike crystals was performed, and the structure of **1** was indeed determined to be 3,3′-ethanediylidenebis(1-ethylindoline-2-one). The mother compound, 3,3′-ethanediylidenebis(indoline-2-one), has not been known so far, and its derivatives have been mentioned in only a few reports.[2,3,4]

1 was isolated as follows: *N*-ethylisatin and sodium hydride (in oil) in a 2:1 molar *ratio* were refluxed in freshly distilled anhydrous THF under a nitrogen atmosphere for 3 hours. After the usual workup using the saturated ammonium chloride solution with ice and extraction with chloroform, the product mixture was chromatographed on silica gel. Using dichloromethane as the eluent, we recovered most of the starting compound in the fractions eluted early, and a small amount of **1** was obtained in the fractions eluted late. This byproduct could be easily detected and isolated because of its characteristic red

Table 1 Crystal and experimental data

Chemical formula: $C_{22}H_{20}N_2O_2$
Formula weight = 344.41
T = 93 K
Crystal System: monoclinic Space Group: $P2_1/c$ (#14)
a = 8.7451(9)Å
b = 15.1964(13)Å β = 113.561(2)°
c = 6.9425(6)Å
V = 845.70(14)Å^3 Z = 2
D_x = 1.352 g/cm^3
Radiation: Mo K_α (λ = 0.71075 Å)
μ(Mo K_α) = 0.087 mm^{-1} F_{000} = 364.00
Crystal size = 0.900 × 0.070 × 0.070 mm^3
Crystal color: red
No. of reflections collected = 8124
No. of independent reflections = 1920
$2\theta_{max}$ = 54.9° with Mo K_α
Data/Restraints/Parameters = 8124/0/158
Goodness-of-fit on F^2 = 1.046
R indices [$I > 2.00\sigma(I)$]: $R1$ = 0.0434
R indices (all data): $R1$ = 0.0513, $wR2$ = 0.1188
$(\Delta/\sigma)_{max}$ = 0.000
$(\Delta\rho)_{max}$ = 0.23 e$^-$/Å^3 $(\Delta\rho)_{min}$ = 0.24 e$^-$/Å^3
Measurement: Rigaku R-AXIS RAPID
Program system: Rigaku CrystalStructure 4.0
Structure determination: SHELXL-97
CCDC deposition number: CCDC 1031855

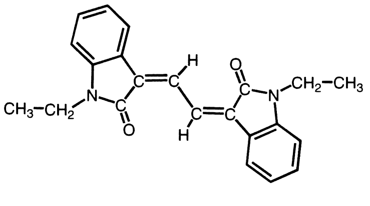

Fig. 1 Chemical structure of **1**.

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Table 2 Bond lengths (Å) and bond angles (°) for non-hydrogen atoms

Atoms	Length	Atoms	Angle
C1-C1^{i}	1.436(3)	C1^{i}-C1-C2	124.51(13)
O1-C9	1.223(2)	C1-C2-C9	126.92(15)
N1-C8	1.400(2)	C3-C2-C9	105.94(11)
N1-C9	1.383(2)	C2-C9-N1	106.09(13)
N1-C10	1.456(2)	C8-N1-C9	111.10(11)
C1-C2	1.354(2)	O1-C9-N1	124.28 (12)
C2-C3	1.456 (3)	C9-N1-C10	123.34(14)
C3-C8	1.403(2)		

Symmetry code: (i) –*x*+2; –*y*, –*z*+2.

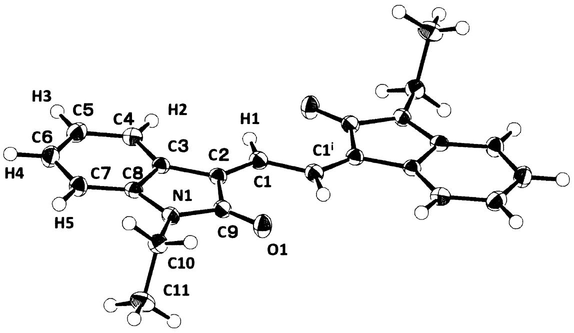

Fig. 2 ORTEP structure of **1**, drawn with 50% probability ellipsoids, and with hydrogen atoms shown as circles of arbitrary radius. Symmetry code: (i) –*x*+2; –*y*, –*z*+2.

color on the column. **1**, comprising red needles of mp 259-261°C. The spectral and analytical data are deposited as Supplementary material.

Single crystals of **1** suited for X-ray diffraction analysis were isolated by the slow evaporation of an acetonitrile solution of **1**. All of the hydrogen atoms were found by deference Fourier synthesis and refined isotropically. Fig. 1 shows the chemical structure of **1**. The crystallographic data and experimental details are listed in Table 1. The selected bond lengths and angles are given in Table 2. Figure 2 shows an ORTEP diagram of **1** with thermal ellipsoids drawn at 50% probability.

The two indoline-2-one moieties, including the exocyclic C=C double bond and the methylene unit of the *N*-ethyl substituent, are coplanar with each other. Thus, the molecular structure of **1** is centrosymmetric. Only two methyl groups are out of plane with a C8–N1–C10–C11 torsion angle of 87.21° and a N1–C10–C11 angle of 113.03°. With respect to the exocyclic C1=C2 double bond geometry, the central C1–C1^{i} bond (symmetry code: (i) –*x*+2; –*y*, –*z*+2) is directed to the carbonyl side of the indolinone core, and the ethanediylidene moiety adopts an *s-trans* conformation. The exocyclic C1=C2 bond length is 1.354 Å, being intermediate between the lengths of the C(sp^2)=C(sp^2) bond in the conjugated (1.397 Å) and unconjugated (1.321 Å) systems,[5] indicating the enhanced delocalization of π-electrons over the two indoline-2-one rings. In accord with this, the central C1–C1^{i} bond is rather shortened to 1.436 Å as compared with similar moieties in the conjugated systems. The C2–C9 and N1–C9 bond lengths are 1.502 Å and 1.383 Å, respectively, the former being smaller than the corresponding bond length (1.516 Å) in 1,1′-dimethyl[$\Delta^{2,2'}$-biindoline]-2,2′-dione (**2**),[6] which would be the most appropriate compound to refer to, whereas the latter being larger than the C–N bond length (1.366 Å) of **2**. The length of the carbonyl O1=C9 double bond (1.223 Å) is larger than the standard value for the carbonyl group (1.192 Å), but is almost the same as that in **2** and other isatine derivatives.[7] These characteristics of the structure of **1** suggest that the conjugation of the carbonyl group in **1** is highly expanded to the ethanediylidene moiety, but rather diminished in the π-delocalization as an amide unit.

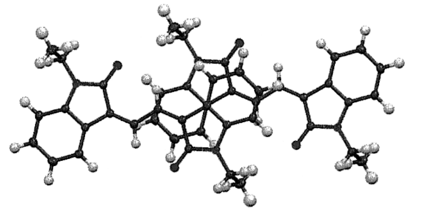

Fig. 4 Overlap of the neighboring **1** molecules in crystals.

A view of the packing arrangement of the molecules in the unit cell is shown in Fig. 3S-a (supporting information). The molecules are linked in infinite *zigzag* chains along the *b*-axis by hydrogen bonding between nitrogen N1 as a H-acceptor and hydrogen H5 at C7 of the benzene ring (N1···H5(C7); 2.573 Å). The *zigzag* chains are aligned side by side using short contacts of the carbonyl oxygen with hydrogen H3 at the indoline-2-one ring periphery (O1···H3(C5); 2.566 Å) (Fig. 3S-a). As a result, molecular belts extending along the *a*-axis are formed (Fig. 3S-b). The belt stacks in parallel by an offset type π-π interaction with a mutual shift for a half of the indoline-2-one ring (Fig. 4). The shortest distance in this overlap is observed between the C3···C3^{ii} atoms (3.330 Å. Symmetry code: (ii) –*x*+2, –*y*, –*z*+1).

With respect to the mechanism of the formation of **1**, further investigation is required. At this stage, however, we assume that the solvent, *i.e.*, THF, participates as the source of the C2 unit of the unexpected byproduct **1**. This is suggested by reports that THF affords the ethylene unit in its reaction with metal hydride.[8,9,10] In the case of **1**, presumably, THF reacts with sodium hydride to produce a radical anion of THF via electron transfer, followed by fission to a C2 fragment. The detailed mechanistic investigation will be reported in due course.

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