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Dedicated to Professor Ivan Petrov on the occasion of his 80th birthday

THE CRYSTAL STRUCTURE OF *N*-ETHYLISATIN

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The crystals of *N*-ethylindoline-2,3-dione are triclinic, space group $P\bar{1}$, with a = 8.321(12), b = 9.233(14), c = 12.145(16) Å, α = 72.519(10), β = 88.251(10), γ = 88.454(10) °, V = 889(2) Å^3 and Z = 4. The two crystallographically inequivalent molecules are π–π stacked over each other at 3.5 Å. The 2,3-dione single C–C bond is long at 1.553(7) and 1.539(7) Å.

Key words: crystal structure; *N*-ethylisatin; overlong bonds; π–π interactions

INTRODUCTION

The molecule of isatin (2,3-indolinedione) presents a classical example of an overlong endocyclic C(sp^2)–C(sp^2) bond, a feature that accounts for its ready hydrolysis in acidic and basic media. Several determinations of the crystal structure [1–4] confirmed the 2,3-dione carbon–carbon bond at 1.56 Å, significantly longer than the characteristic value 1.48 Å. The feature was prescribed to repulsion of the unshared electron pairs of the gem-carbonyl oxygen atoms [4], and to the joint action of dipole-dipole and intermolecular interactions [2]. In a recent theoretical study of substituted isatins [5], we predicted small (within the typical standard deviations from X-ray analysis) alteration of the anomalous bond by ring substituents: strong electron-donors are expected to shorten, while accepting groups would stretch the anomalous bond further. The short distance may be additionally altered by the action of cooperative intermolecular interactions through the amido and ketone functionalities. Being interested in limiting intramolecular parameters and hypervalent bonds in small heterocycles, we have prepared and studied by experimental and theoretical methods a series of ring- and *N*-substituted isatins. In the present communication, the crystal structure of *N*-ethylisatin is described and compared with structural data of related compounds retrieved from the Cambridge Structural Database (CSD).

EXPERIMENTAL

N-ethylisatin was prepared and purified according to a previously described method [6]. Diffraction data were collected from a red 0.40×0.40×0.20 mm^3 specimen with the MarResearch image plate diffractometer. Relevant crystallographic details are listed in Table 1. The data, incorrected for absorption effects, were processed with the XDS software [7]. The structure was solved with direct methods (SHELXS-97 [8]) and refined to R = 8.69 % on F^2 with SHELXL-97 [9]. The ben-

zene ring was fitted to a regular hexagon with C–C = 1.39 Å. The hydrogen atoms were set as riding bodies to the respective heavy atoms in the refinement. The structure is represented as an ORTEP plot in the illustrations [10].

Table 1

Crystallographic data and refinement conditions

Empirical formula	$C_{10}H_9NO_2$
Formula weight	175.18
Temperature / K	298 (2)
Radiation / Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a / Å	8.321 (12)
b / Å	9.233 (14)
c / Å	12.145 (16)
α / °	72.519 (10)
β / °	88.251 (10)
γ / °	88.454 (10)
V / Å^3	889 (2)
Z	4
D_x ,calculated/ Mg m^{-3}	1.308
Absorp. coeff. / mm^{-1}	0.092
F(000)	368
Crystal size / mm^3	0.40×0.40×0.20
Crystal color	Red
θ range for data collection / °	2.31 – 25.86
Limiting indices	$0 \leftarrow h \leftarrow 10$ $-11 \leftarrow k \leftarrow 11$ $-14 \leftarrow l \leftarrow 14$
Reflections total / > 2σ	3010/1646
Absorption correction	None
Refinement method	Full-matrix least squares on F^2
Weighting scheme	$W = 1/[\sigma^2(Fo^2) + (0.1494P)^2 + 0.1932P$, where $P = (Fo^2+2Fc^2) / 3$
Data/Restrains/Parameters	3010 / 0 / 211
GOF on F^2	1.081
Final R indices [$I > 2\sigma(I)$]	$R = 0.0869$ $wR = 0.2416$
R indices (all data)	$R = 0.1601$ $wR = 0.2785$

RESULTS AND DISCUSSION

The crystal structure of *N*-ethylisatin is shown in Figs. 1 and 2; Table 2 contains the intramolecular parameters. In Table 3, the distances of the dicarbonyl group in isatin and substituted isatins retrieved from the CSD [11] are listed.

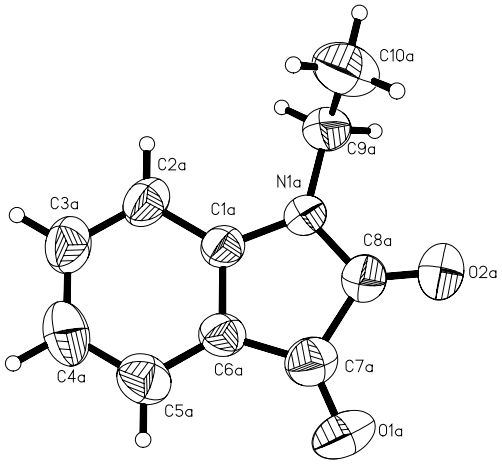

Fig. 1. ORTEP plot of one of the molecules of *N*-ethylisatin with the atom labeling scheme. The atoms are drawn at 50 % probability, hydrogens are represented as spheres of arbitrary radii

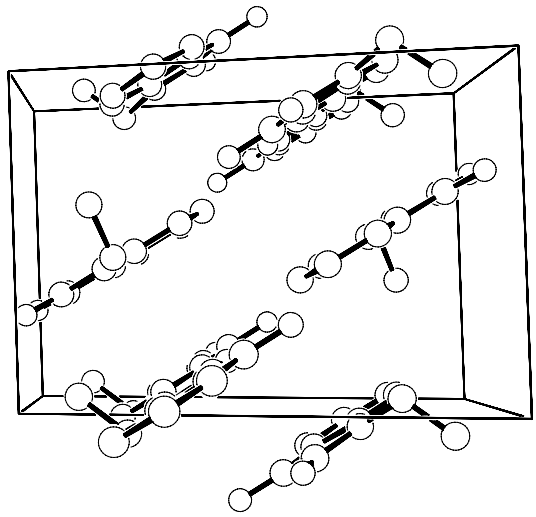

Fig. 2. Perspective view on the molecular packing of *N*-ethylisatin in the unit cell normal to the *ac* plane

The centrosymmetric structure consists of pairs of parallel independent molecules oriented in the direction of the *a*—*c* diagonal of the unit cell and π–π stacked over each other at 3.5 Å (Fig. 2).

Table 2

Intramolecular distances (Å) and angles (°)

O1a–C7a	1.229(5)
O2a–C8a	1.211(5)
N1a–C8a	1.357(5)
N1a–C1a	1.392(4)
N1a–C9a	1.467(5)
C6a–C7a	1.440(5)
C7a–C8a	1.553(7)
C9a–C10a	1.493(7)
O1b–C7b	1.221(5)
O2b–C8b	1.207(5)
N1b–C8b	1.370(6)
N1b–C1b	1.396(4)
N1b–C9b	1.465(6)
C6b–C7b	1.437(5)
C7b–C8b	1.539(7)
C9b–C10b	1.484(7)
C8a–N1a–C1a	110.9(3)
C8a–N1a–C9a	123.2(3)
C1a–N1a–C9a	125.8(3)
C2a–C1a–N1a	128.4(2)
C6a–C1a–N1a	111.6(2)
C5a–C6a–C7a	133.5(2)
C1a–C6a–C7a	106.5(2)
O1a–C7a–C6a	130.3(4)
O1a–C7a–C8a	123.8(4)
C6a–C7a–C8a	105.8(3)
O2a–C8a–N1a	127.1(4)
O2a–C8a–C7a	127.7(4)
N1a–C8a–C7a	105.1(3)
N1a–C9a–C10a	112.0(4)
C8b–N1b–C1b	110.1(3)
C8b–N1b–C9b	123.3(3)
C1b–N1b–C9b	126.3(3)
C2b–C1b–N1b	128.5(2)
C6b–C1b–N1b	111.5(2)
C5b–C6b–C7b	133.1(2)
C1b–C6b–C7b	106.9(3)
O1b–C7b–C6b	130.2(4)
O1b–C7b–C8b	123.9(4)
C6b–C7b–C8b	105.9(3)
O2b–C8b–N1b	127.1(4)
O2b–C8b–C7b	127.2(4)
N1b–C8b–C7b	105.6(3)
N1b–C9b–C10b	113.4(4)

Table 3

Distances (Å)[a] of the 2,3-dione part in isatin and some substituted isatins

Refcode[b]	C7–C8	C8–O2	C7–O1	Reference
ISATIN01	1.5606(21)	1.2204(19)	1.2135(19)	[2]
ISATIN02	1.562(3)			
	1.220(3)	1.211(3)		[3]
ISATIN03	1.555(3)	1.220(3)	1.213(3)	[4]
N-ethylisatin	1.553(7)	1.211(5)	1.229(5)	this work
	1.539(7)	1.207(5)	1.221(5)	
FOHHUF	1.548	1.205	1.203	[13]
	1.568	1.174	1.217	
FOHJER	1.552	1.194	1.193	[13]
LINDOB	1.542(6)	1.196(5)	1.209(5)	[14]
NAQRAY	1.577(6)	1.219(5)	1.224(5)	[15]
NAWBOC	1.598	1.229	1.218	[16]
	1.554	1.249	1.182	
PAQLEY	1.565	1.221(4)	1.206(4)	[17]
	1.567	1.218(4)	1.205(4)	
POBBIR	1.544	1.219	1.212	[18]
TARGEY	1.538(2)	1.196(2)	1.207(2)	[19]
WOCGOK	1.554(4)	1.222(3)	1.211(3)	[20]
ZZZPRC02	1.549	1.220	1.211	[21]
	1.541	1.219	1.213	

[a] Only the standard deviations that were available to us from the respective primary publications are listed.

[b] ISATIN01, ISATIN02, ISATIN03: isatin; FOHHUF: 1,1′-oxalylbisisatin; FOHJER: 10α-(2',3'-Dioxo-2',3'-dihydroindol-1'-yl)-3,3-dimethyl-2H-(1,3)oxazino(3,2-α)indole-2,4, 10(3H,10αH)-trione; LINDOB: 1-chloroacetylindole-2,3 (2H,3H) -dione (alternative name: 1-α-chloro-acetylisatin); NAQRAY: (2,3-dioxoindolinyl-N)-triphenylphosphine-gold(I); NAWBOC: 4,6-Dibenzyloxy-1H-indole-2,3-dione methanol solvate; PAQLEY: *cis*-bis((2,3-dihydro-2,3-dioxoindolyl)triphenylphosphine)-platinum(II) (alternative name: *cis*-bis (isatin-triphenylphosphine)-platinum(II)); POBBIR: (2.2)-*p*-benzeno-(4,7)-1,5-dimethylisatinophane; TARGEY: 1-acetylindole-2,3-dione; WOCGOK: 5-fluoroindoline-2,3-dione (alternative name: 5-fluoro-2,3-indolinedione); ZZZPRC02: *N*-methylisatin.

The isatin moiety is planar with the ethyl chain bent 92.4(5) and 89.4(5) ° from the plane. The smaller angles at C9, 112.0(4) ° and 113.4(4) ° in the two molecules, are close to sp^3. In one of the molecules (b), the long isatin bond is shortened by the *N*-substitution (1.539(7) Å); experimental un-

certainty precludes comparison in the other molecule. In the crystal of the parent compound isatin, strong N–H···O hydrogen bonds stretch the amide carbonyl group within the centrosymmetric dimmers (Table 3). The *N*-substitution blocks the nitrogen donor for hydrogen formation in the ethyl product and the amide carbonyl bond (C8–O2) subsequently becomes shorter than the ketone one (C7–O1) in both molecules. It is apparent from Table 3 that the length order of carbonyl groups in isatins *N*-substituted with simple organic groups depends on the substituent. The electron-donating groups $–CH_3$ (CSD refcode: ZZZPRC02) and $–CH_2CH_3$ (the title compound) stretch the amide C–O bond more than the ketone one, while the electron-deficient –COCl (LINDOB) and $–COCH_3$ (TARGEY) would do the opposite. The substitution at the nitrogen, therefore, affects the length of the vicinal carbonyl groups, as we have theoretically shown on a series of *N*-substituted analogues of saccharin (sulfobenzimide) as a model compound [12]. Except for strong electron-donors (e.g., the nitro group), on the other hand, the ring substitution has a negligible effect on the carbonyl group length [5]. The inductive effect of the substituent is one apparent reason to account for the color difference and the shift of the optical absorption maximum of solid *N*-ethylisatin (dark red) compared to *N*-methylisatin (orange-red). An additional reason might be the difference in the charge-transfer energy within the stacks of the planar part of the molecules. Unlike the planar *N*-methyl compound, energy levels of isatin are modified in the *N*-ethyl derivative by the steric bulk of the non-coplanar substituent that hinders face-to-face approach of the molecules.

Structures containing more than one structurally independent molecule or different polymorphs of the same compound allow some assessment of crystal lattice forces effect on the intramolecular parameters. In both cases, the same molecule is embedded in different crystalline environments and its geometry would reflect the magnitude of these effects. In cases of isatins with more complex groups (FOHHUF) or with unsubstituted imino group available for stronger intermolecular bonds (NAWBOC), interaction with the crystalline environment may exceed the substituent effects (Table 3). The large experimental uncertainty precludes the analysis of the C–O bond lengths in the case of *N*-ethylisatin. The difference in the length of the anomalous bond C7–C8 is in the range of 0.00–0.028 Å, within the interval of 0.2–0.3 Å [12] is typical for the flexibility of the bonds in organic crystals due to the solid environment.

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Supplementary material: The atomic coordinates for the structure are deposited at the Cambridge Crystallographic Data Centre as CCDC 182705. The supplementary material can be obtained, free of charge, on application to the Cambridge Crystallographic Data Centre (e-mail: deposit@ccdc.cam.ac.uk). The listings of the structure factors are available from the last author up to one year after this publication has appeared.

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Р е з и м е

КРИСТАЛНА СТРУКТУРА НА *N*-ЕТИЛИЗАТИН

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Клучни зборови: кристална структура; *N*-етилизатин; долги врски; π–π интеракции

Синтетизиран е *N*-етилизатин (*N*-етилиндолин-2,3-дион) и определена е неговата кристална структура на собна температура. Соединението кристализира во просторната група $P\bar{1}$ од триклиничниот систем со параметри на елементарната ќелија a = 8.321(12), b = 9.233(14), c = 12.145(16) Å, α = 72.519(10), β = 88.251(10), γ = 88.454(10) °, V = 889(2) Å^3 и Z = 4. Двете кристалографски нееквивалентни молекули во структурата се поврзани со π–π интеракции на растојание од 3,5 Å. Двете C–C врски од 2,3-дионскиот фрагмент се очекувано подолги [(1.553(7) и 1.539(7) Å] од вообичаените C–C врски.