Synthesis and structures of benzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-one derivatives

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A procedure was developed for the synthesis of derivatives of the new heterocyclic system, benzo[*cd*]furo[2,3-*f*]indole, based on the cyclodehydration of 6-acylmethyloxy-1-alkylbenzo[*cd*]indol-2(1*H*)-ones. Either 7- or 8-aryl derivatives of benzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-ones can be prepared depending on the reaction conditions. The molecular and crystal structures of 7- and 8-phenylbenzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-ones were established by X-ray diffraction.

Key words: benzo[*cd*]indol-2(1*H*)-one, benzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-one, cyclodehydration, X-ray diffraction.

Many benzo[*cd*]indol-2(1*H*)-one derivatives were found to be physiologically active compounds with a broad spectrum of action.[1—3] 6,7-Benzo derivatives of this heterocyclic system, which are involved as structural fragments in some alkaloids,[4—7] are of particular interest. At the same time, both synthetic and natural benzo[*cd*]indol-2(1*H*)-one derivatives containing the 6,7-fused heterocycle are virtually unknown. Earlier, we have synthesized 7,8-dihydrobenzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-ones as first representatives of the new heterocyclic system, benzo[*cd*]furo[2,3-*f*]indole, by the thermal or catalytic Claisen rearrangement of 1-alkyl-6-allyloxybenzo[*cd*]indol-2(1*H*)-ones.[8] It was of interest to develop an alternative procedure for the synthesis of derivatives of this heterocycle.

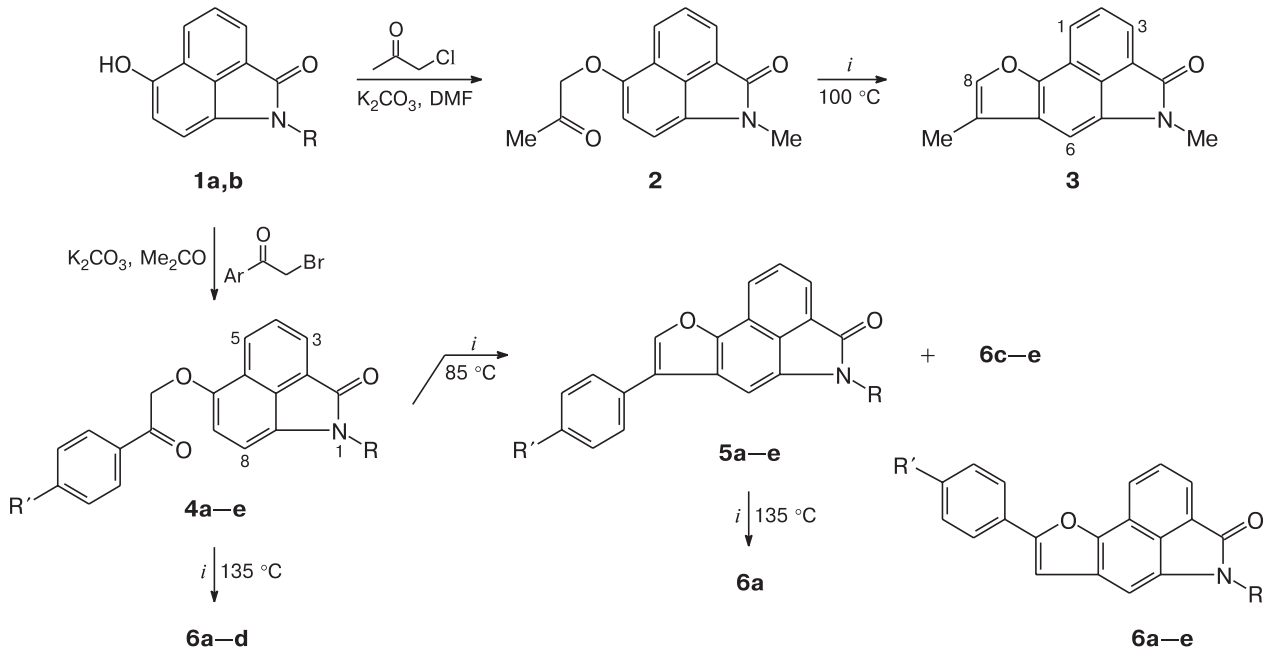
Among known methods for the construction of polynuclear heterocyclic systems, in particular, of benzo[*b*]furans, the cyclodehydration occupies an important place.[9] We used this method for the synthesis of keto esters **2** and **4a—e** starting from 1-alkyl-6-hydroxybenzo[*cd*]indol-2(1*H*)-ones **1a,b** (Scheme 1).

Product **2** was synthesized from compound **1a**. The heating of compound **2** in polyphosphoric acid (PPA) at 100 °C for 8 h affords 5,7-dimethylbenzo[*cd*]furo[2,3-*f*]-indol-4(5*H*)-one (**3**) in 10% yield. The structure of the latter compound was confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum shows the following characteristic signals for the aromatic protons: a singlet at δ 6.94 (1 H, C(6)H), a quartet at δ 7.55 (1 H, C(8)H, $J_{H,H}$ = 1.5 Hz), a doublet of doublets at δ 7.76 (1 H, C(2)H, $J_{H,H}$ = 7.9 Hz), a doublet at δ 8.03 (1 H, C(3)H, $J_{H,H}$ = 7.9 Hz), and a doublet at δ 8.27 (1 H, C(1)H, $J_{H,H}$ = 7.9 Hz), which indicate that the cyclization proceeds at position 7 rather than at position 5 of the benzo[*cd*]indole moiety to give the five-membered furan ring. The use of sulfuric, orthophosphoric, trifluoromethanesulfonic, or Lewis acids for the condensation of keto ester **2** did not lead to an increase in the yield of the product because of resinification. On the contrary, the cyclodehydration of compounds containing the aryl group in the keto ester fragment with PPA proceeds more smoothly. For example, the cyclodehydration of compounds **4a—e** with PPA proceeds at 85 °C to give 5-methyl- and 5-butyl-7-arylbenzo[*cd*]furo[2,3-*f*]-indol-4(5*H*)-ones **5a—e** in higher yields (42—82%). It should be noted that the reaction giving products **5a,b** from compounds **4a,b** is regioselective and affords only 7-phenyl-substituted benzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-ones in 74 and 82% yields, respectively. Under these conditions, the reactions of compounds **4c—e** produce, in addition to 7-aryl-substituted benzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-ones, 8-aryl-substituted derivatives in low yields (~20%). However, this leads to a substantial decrease in the yield of the target products because it is difficult to separate these isomers by preparative methods (they have similar R_f and solubilities). In these cases, the ratios between the yields of the 7- and 8-isomers were determined by HPLC of the reaction mixtures. The use of the Lewis acid $BF_3 \cdot Et_2O$ (taken as the medium) for the condensation of **4e** did not give the expected result. According to the HPLC data, both isomers, **5e** and **6e**, were produced in equal amounts in 43.3 and 42.3% yields, respectively. The subsequent refluxing (10 h) did not lead to the formation of exclusively the 8-isomer. The heating of compound **4e** with a tenfold excess (w/w) of PPA at 85 °C for 3 h afforded a mixture of **5e** and **6e** (HPLC data) in 34.3 and 39.4% yields, respectively.

The cyclodehydration of compounds **4a—d** with PPA at 135 °C gave pure 8-arylbenzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-ones **6a—d** in good yields. However, we failed to

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 154—158, January, 2008.

Scheme 1



i. Polyphosphoric acid.

R = Me (**1a**), Bu^n (**1b**)
R = Me, R′ = H (**4a**—**6a**), Cl (**4c**—**6c**), OMe (**4e**—**6e**); R = Bu^n, R′ = H (**4b**—**6b**), Cl (**4d**—**6d**)

prepare compound **6e** from **4e** under these conditions; the reaction was accompanied by resinification of the mixture. Product **6e** was isolated as an impurity in the synthesis of compound **5e**. The heating of 7-aryl-substituted derivatives of arylbenzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-ones in the presence of polyphosphoric acid at 135 °C results in their transformation into the corresponding 8-isomers, as was exemplified by compound **5a**. Earlier, this transformation has been described for benzo[*b*]furan derivatives.[9]

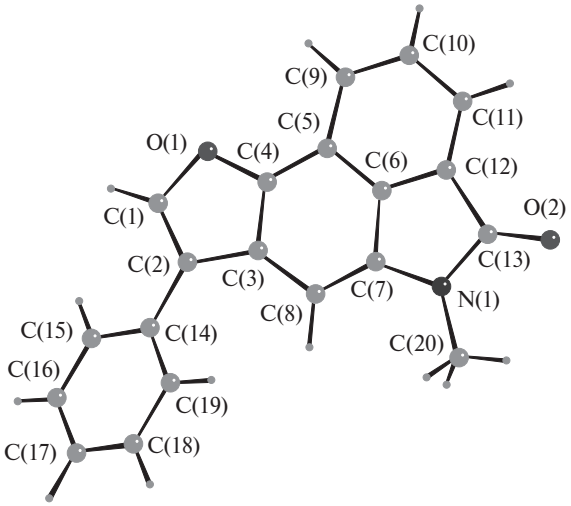


Fig. 1. Molecular structure of compound **5a**.

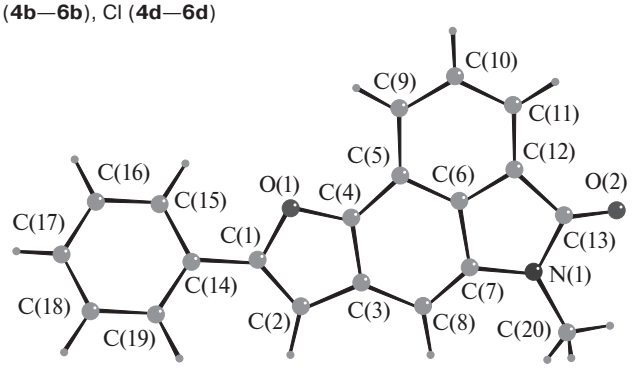


Fig. 2. Molecular structure of compound **6a**.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in compounds **5a** and **6a**

Parameter	**5a**	**6a**
Bond	*d*/Å	
C(1)—O(1)	1.370(6)	1.387(4)
C(4)—O(1)	1.368(5)	1.376(3)
C(7)—N(1)	1.401(5)	1.409(4)
C(13)—N(1)	1.401(6)	1.389(4)
C(20)—N(1)	1.430(6)	1.450(5)
C(13)—O(2)	1.213(5)	—
Angle	ω/deg	
C(2)—C(1)—O(1)	112.4(4)	—
C(3)—C(4)—O(1)	110.3(4)	—
C(6)—C(7)—N(1)	106.2(4)	—
C(1)—O(1)—C(4)	—	105.8(2)
C(7)—N(1)—C(13)	—	111.2(3)

Table 2. Characteristics of compounds **2—6**

Compound	Yield* (%)	M.p. /°C	Found / Calculated (%)			Molecular formula
			C	H	N (S)	
2	83	139—140	70.57 / 70.58	5.10 / 5.13	5.56 / 5.49	$C_{15}H_{13}NO_3$
3	10	162—163	76.01 / 75.94	4.66 / 4.67	5.96 / 5.90	$C_{15}H_{11}NO_2$
4a	69	167—168	75.75 / 75.70	4.76 / 4.76	4.53 / 4.41	$C_{20}H_{15}NO_3$
4b	62	142—143	76.88 / 76.86	5.81 / 5.89	3.97 / 3.90	$C_{20}H_{15}NO_3$
4c	45	179—180	68.28 / 68.29	3.97 / 4.01	3.99 / 3.98	$C_{23}H_{21}NO_3$
4d	78	144—145	70.20 / 70.14	5.08 / 5.12	3.77 / 3.56	$C_{20}H_{14}ClNO_3$
4e	72	198—199	72.45 / 72.61	5.00 / 4.93	4.09 / 4.03	$C_{21}H_{17}NO_4$
5a	74	170—171	80.21 / 80.25	4.46 / 4.38	4.76 / 4.68	$C_{20}H_{13}NO_2$
5b	82	134—135	80.92 / 80.92	5.61 / 5.61	4.10 / 4.10	$C_{23}H_{19}NO_2$
5c	55	270—271	71.95 / 71.97	3.67 / 3.62	4.26 / 4.20	$C_{20}H_{12}ClNO_2$
5d	42	154—155	73.63 / 73.50	4.85 / 4.83	9.40 / 9.43	$C_{23}H_{18}ClNO_2$
5e	58	161—162	76.78 / 76.58	4.56 / 4.59	4.26 / 4.25	$C_{21}H_{15}NO_3$
6a	63	175—176	80.27 / 80.25	4.47 / 4.38	4.81 / 4.68	$C_{20}H_{13}NO_2$
6b	78	116—117	80.47 / 80.92	5.71 / 5.61	4.11 / 4.10	$C_{23}H_{19}NO_2$
6c	42	246—247	71.90 / 71.97	3.60 / 3.62	4.36 / 4.20	$C_{20}H_{12}ClNO_2$
6d	42	140—141	73.53 / 73.50	4.91 / 4.83	3.79 / 3.73	$C_{23}H_{18}ClNO_2$
6e	15**	220—221	76.76 / 76.58	4.42 / 4.59	4.35 / 4.25	$C_{21}H_{15}NO_3$

* The yields of the compounds isolated preparatively.
** The compound was isolated as an impurity to **5e**.

Table 3. Spectroscopic characteristics of compounds **2—6** in dichloromethane

Compound	λ_{max}/nm ($\varepsilon \cdot 10^{-4}$/L mol^{-1} cm^{-1})
2	265 (3.43), 283 (1.83), 311(0.33), 326 (0.37), 393 (0.81)
3	282 (3.31), 341 (0.19), 359 (0.23), 388 (0.19)
4a	254 (2.19), 283 (0.99), 326 (0.19), 340 (0.18), 396(0.42)
4b	253 (2.17), 284 (0.95), 399 (0.39)
4c	260 (3.27), 396 (0.4)
4d	260 (3.49), 326 (0.33), 397 (0.52)
4e	265 (2.68), 282 (2.39), 399 (0.37)
5a	227 (7.79), 284 (2.98), 360 (0.27)
5b	287 (3.13), 362 (0.38)
5c	257 (2.48) 286 (3.62) 380 (0.30)
5d	256 (2.45) 287(3.57) 362 (0.29)
5e	269 (2.56) 362 (0.27)
6a	308 (5.02) 321 (5.31)
6b	308 (6.00) 322 (6.35) 351 (0.6)
6c	312 (5.57) 325 (6.01)
6d	312 (5.95) 322 (6.35) 353 (0.85)
6e	313 (3.78) 327(4.03)

The molecular and crystal structures of compounds **5a** and **6a** were studied by X-ray diffraction and are shown in Figs 1 and 2, respectively. Selected geometric parameters are listed in Table 1.

In both molecules, the main cyclic O(1)N(1)C(1)—C(13) group is approximately planar (the maximum deviations of the atoms from the mean plane are 0.026 and 0.039 Å for **5a** and **6a**, respectively). The N(1) atom has a trigonal-planar configuration (the sum of the bond angles at this atom in both molecules is 359.9°). The bond-length distribution in this system is indicative of a substantial electron density delocalization.[10,11] The benzene ring C(14)—C(19) is twisted with respect to the central plane by only 14.7° in compound **6a**; in compound **5a**, the twisting is substantially larger (by 29.5°). In the crystals, molecules **5a** and **6a** are packed to form infinite stacks.

To summarize, the cyclodehydration of 1-alkyl-6-(2-oxo-2-arylethoxy)- or 1-alkyl-6-(2-oxo-2-alkylethoxy)benzo[*cd*]indol-2(1*H*)-ones can be used for the synthesis of functionalized benzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-one derivatives.

Experimental

The ^{1}H NMR spectra of solutions were recorded on a Varian VXR-300 instrument (300 MHz) with $SiMe_4$ as the internal standard. The electronic absorption spectra were measured on a Shimadzu UV-3100 spectrophotometer at a concentration of $1 \cdot 10^{-5}$ mol L^{-1}. The HPLC analysis was carried out on a Hitachi LiChrograph high-pressure liquid chromatograph equipped with a 250½4.6 mm column and a LiChrosorb RP 18 column; acetonitrile—water (80 : 20) was used as the mobile phase, the flow rate was 1.0 mL min^{-1}; the analytical wavelength λ = 295 nm; the temperature was 24 °C, the volume of the samples was 20 μL. The chromatograms were processed and the chromatographic characteristics of the compounds were calculated on a Multispektr 3-1 integrating device (Scientific and Production Company "Analitika"). The yields, melting points, elemental analysis data, electronic absorption spectra, and ^{1}H NMR spectra of compounds **1—6** are given in Tables 2—4. Compounds **1a,b** were synthesized according to procedures described earlier.[8,12]

1-Methyl-6-(2-oxopropoxy)benzo[*cd*]indol-2(1*H*)-one (2). Calcined potassium carbonate (48.3 g, 350 mmol) was added with stirring to a solution of compound **1a** (14 g, 70 mmol) in anhydrous DMF (280 mL) warmed to 40 °C. Then chloroacetone (6.1 mL, 7.12 g, 77 mmol) was added dropwise for 30 min. The reaction mixture was stirred for 3 h. The precipitate was filtered off, washed on a filter with hot acetone (2×100 mL), and concentrated to 1/3 of the initial volume. The precipitate of **2** was filtered off, the filtrate

Table 4. ^{1}H NMR spectra of compounds **2—6** in $CDCl_3$

Compound	δ (*J*/Hz)
2 *	2.26 (s, 3 H, SCH_3); 3.40 (s, 3 H, NCH_3); 4.97 (s, 2 H, OSH_2); 6.79 (d, 1 H, S(8)H, $^3J_{H,H}$ = 7.8); 6.98 (d, 1 H, S(7)H, $^3J_{H,H}$ = 7.8); 7.80 (dd, 1 H, S(4)H, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 8.1); 8.06 (d, 1 H, S(3)H, $^3J_{H,H}$ = 7.2); 8.27 (d, 1 H, S(5)H, $^3J_{H,H}$ = 8.1)
3	2.33 (s, 3 H, S(7)CH_3); 3.48 (s, 3 H, NCH_3); 6.94 (s, 1 H, S(6)H); 7.55 (q, 1 H, S(8)H, $^3J_{H,H}$ = 1.5); 7.76 (dd, 1 H, S(2)H, $^3J_{H,H}$ = 7.9); 8.03 (d, 1 H, S(3)H, $^3J_{H,H}$ = 7.9); 8.27 (d, 1 H, S(1)H, $^3J_{H,H}$ = 7.9)
4a	3.40 (s, 3 H, NCH_3); 5.42 (s, 2 H, OSH_2); 6.65 (d, 1 H, S(8)H, $^3J_{H,H}$ = 7.80); 6.70 (d, 1 H, S(7)H, $^3J_{H,H}$ = 7.80); 7.49—7.54 (m, 2 H, H_{Ar}); 7.61—7.67 (m, 1 H, H_{Ar}); 7.71 (dd, 1 H, S(4)H, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 8.1); 8.03—8.10 (m, 3 H, H_{Ar} + S(3)H); 8.32 (d, 1 H, S(5)H, $^3J_{H,H}$ = 8.1)
4b	0.95 (t, 3 H, $N(SH_2)_3S\underline{H}_3$, $^3J_{H,H}$ = 7.5); 1.37—1.50, 1.71—1.80 (both m, 2 H each, SH_2); 3.88 (t, 2 H, NCH_2, $^3J_{H,H}$ = 7.5); 5.42 (s, 2 H, OSH_2); 6.64 (d, 1 H, S(8)H, $^3J_{H,H}$ = 7.8); 6.72 (d, 1 H, S(7)H, $^3J_{H,H}$ = 7.8); 7.48—7.54 (m, 2 H, H_{Ar}); 7.61—7.68 (m, 1 H, H_{Ar}); 7.71 (dd, 1 H, S(4)H, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 8.1); 8.03—8.11 (m, 3 H, H_{Ar} + S(3)H); 8.32 (d, 1 H, S(5)H, $^3J_{H,H}$ = 8.1)
4c	3.41 (s, 3 H, NCH_3); 5.36 (s, 2 H, OSH_2); 6.67 (d, 1 H, S(8)H, $^3J_{H,H}$ = 7.8); 6.71 (d, 1 H, S(7)H, $^3J_{H,H}$ = 7.80); 7.47—7.51 (m, 2 H, H_{Ar}); 7.72 (dd, 1 H, S(4)H, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 8.1); 8.00—8.03 (m, 2 H, H_{Ar}); 8.09 (d, 1 H, S(3)H, $^3J_{H,H}$ = 8.1); 8.29 (d, 1 H, S(5)H, $^3J_{H,H}$ = 8.1)
4d *	0.90 (t, 3 H, $N(SH_2)_3S\underline{H}_3$, $^3J_{H,H}$ = 7.5); 1.30—1.40, 1.60—1.70 (both m, 2 H each, SH_2); 3.86 (t, 2 H, NCH_2, $^3J_{H,H}$ = 7.5); 5.75 (s, 2 H, OSH_2); 6.92 (d, 1 H, S(8)H, $^3J_{H,H}$ = 7.8); 7.03 (d, 1 H, S(7)H, $^3J_{H,H}$ = 7.8); 7.63—7.70 (m, 2 H, H_{Ar}); 7.80 (dd, 1 H, S(4)H, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 8.1); 8.05—8.11 (m, 3 H, H_{Ar} + S(3)H); 8.30 (d, 1 H, S(5)H, $^3J_{H,H}$ = 8.1)
4e	3.41 (s, 3 H, NCH_3); 3.90 (s, 3 H, OCH_3); 5.37 (s, 2 H, OSH_2); 6.67 (d, 1 H, S(8)H, $^3J_{H,H}$ = 7.80); 6.70 (d, 1 H, S(7)H, $^3J_{H,H}$ = 7.8); 6.96—7.00 (m, 2 H, H_{Ar}); 7.72 (dd, 1 H, S(4)H, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 8.1); 8.03—8.09 (m, 3 H, H_{Ar} + S(3)H); 8.33 (d, 1 H, S(5)H, $^3J_{H,H}$ = 8.1)
5a	3.47 (s, 3 H, NCH_3); 7.17 (s, 1 H, S(6)H); 7.42—7.48 (m, 1 H, H_{Ar}); 7.52—7.57, 7.64—7.67 (both m, 2 H each, H_{Ar}); 7.81 (dd, 1 H, S(2)H, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 8.1); 7.88 (s, 1 H, S(8)H); 8.06 (d, 1 H, S(3)H, $^3J_{H,H}$ = 7.2); 8.32 (d, 1 H, S(1)H, $^3J_{H,H}$ = 8.1)
5b	0.96 (t, 3 H, $N(SH_2)_3S\underline{H}_3$, $^3J_{H,H}$ = 7.5); 1.38—1.51, 1.77—1.83 (both m, 2 H each, SH_2); 3.96 (t, 2 H, NCH_2, $^3J_{H,H}$ = 7.5); 7.18 (s, 1 H, S(6)H); 7.43—7.49 (m, 1 H, H_{Ar}); 7.51—7.57, 7.61—7.68 (both m, 2 H each, H_{Ar}); 7.82 (dd, 1 H, S(2)H, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 8.1); 7.88 (s, 1 H, S(8)H); 8.07 (d, 1 H, S(3)H, $^3J_{H,H}$ = 7.2); 8.34 (d, 1 H, S(1)H, $^3J_{H,H}$ = 8.1)
5c	3.46 (s, 3 H, NCH_3); 7.08 (s, 1 H, S(6)H); 7.49—7.61 (m, 4 H, H_{Ar}); 7.81 (dd, 1 H, S(2)H, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 8.1); 7.87 (s, 1 H, S(8)H); 8.06 (d, 1 H, S(3)H, $^3J_{H,H}$ = 7.2); 8.31 (d, 1 H, S(1)H, $^3J_{H,H}$ = 8.1)
5d	0.96 (t, 3 H, $N(SH_2)_3S\underline{H}_3$, $^3J_{H,H}$ = 7.3); 1.42—1.48, 1.75—1.82 (both m, 2 H each, SH_2); 3.95 (t, 2 H, NCH_2, $^3J_{H,H}$ = 7.3); 7.08 (s, 1 H, S(6)H); 7.47—7.60 (m, 4 H, H_{Ar}); 7.81 (dd, 1 H, S(2)H, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 8.1); 7.86 (s, 1 H, S(8)H); 8.06 (d, 1 H, S(3)H, $^3J_{H,H}$ = 7.2); 8.32 (d, 1 H, S(1)H, $^3J_{H,H}$ = 8.1)
5e	3.47 (s, 3 H, NCH_3); 3.90 (s, 3 H, OCH_3); 7.06—7.09 (m, 2 H, H_{Ar}); 7.14 (s, 1 H, S(6)H); 7.56—7.59 (m, 2 H, H_{Ar}); 7.81 (dd, 1 H, S(2)H, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 8.1); 7.82 (s, 1 H, S(8)H); 8.06 (d, 1 H, S(3)H, $^3J_{H,H}$ = 7.2); 8.32 (d, 1 H, S(1)H, $^3J_{H,H}$ = 8.1)
6a	3.46 (s, 3 H, NCH_3); 6.99 (s, 1 H, S(7)H); 7.13 (s, 1 H, S(6)H); 7.35—7.40 (m, 1 H, H_{Ar}); 7.46—7.51 (m, 2 H, H_{Ar}); 7.78 (dd, 1 H, S(2)H, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 8.1); 7.89—7.92 (m, 2 H, H_{Ar}); 8.03 (d, 1 H, S(3)H, $^3J_{H,H}$ = 7.2); 8.32 (d, 1 H, S(1)H, $^3J_{H,H}$ = 8.1)
6b	0.97 (t, 3 H, $N(SH_2)_3S\underline{H}_3$, $^3J_{H,H}$ = 7.5); 1.39—1.52, 1.79—1.84 (both m, 2 H each, SH_2); 3.92 (t, 2 H, NCH_2, $^3J_{H,H}$ = 7.3); 6.98 (s, 1 H, S(7)H); 7.10 (s, 1 H, S(6)H); 7.33—7.38 (m, 1 H, H_{Ar}); 7.44—7.49 (m, 2 H, H_{Ar}); 7.77 (dd, 1 H, S(2)H, $^3J_{H,H}$ = 7.2, $^3J_{H,H}$ = 8.1); 7.87—7.91 (m, 2 H, H_{Ar}); 8.01 (d, 1 H, S(3)H, $^3J_{H,H}$ = 7.2); 8.30 (d, 1 H, S(1)H, $^3J_{H,H}$ = 8.1)
6c	3.46 (s, 3 H, NCH_3); 6.97 (s, 1 H, S(7)H); 7.11 (s, 1 H, S(6)H); 7.42—7.46 (m, 2 H, H_{Ar}); 7.76—7.83 (m, 3 H, H_{Ar} + S(2)H); 8.03 (d, 1 H, S(3)H, $^3J_{H,H}$ = 7.2); 8.30 (d, 1 H, S(1)H, $^3J_{H,H}$ = 8.1)
6d	0.98 (t, 3 H, $N(SH_2)_3S\underline{H}_3$, $^3J_{H,H}$ = 7.5); 1.42—1.48, 1.75—1.82 (both m, 2 H each, SH_2); 3.96 (t, 2 H, NCH_2, $^3J_{H,H}$ = 7.5); 7.02 (s, 1 H, S(7)H); 7.13 (s, 1 H, S(6)H); 7.43—7.47 (m, 2 H, H_{Ar}); 7.79—7.85 (m, 3 H, H_{Ar} + S(2)H); 8.05 (d, 1 H, S(3)H, $^3J_{H,H}$ = 7.2); 8.34 (d, 1 H, S(1)H, $^3J_{H,H}$ = 8.1)
6e	3.46 (s, 3 H, NCH_3); 3.88 (s, 3 H, OCH_3); 6.98 (s, 1 H, S(7)H); 7.00 (s, 1 H, S(6)H); 6.98—7.02 (m, 2 H, H_{Ar}); 7.76—7.83 (m, 3 H, H_{Ar} + S(2)H); 8.01 (d, 1 H, S(3)H, $^3J_{H,H}$ = 7.2); 8.31 (d, 1 H, S(1)H, $^3J_{H,H}$ = 8.1)

* For solutions in DMSO-d_6.

Table 5. Crystallographic parameters and the X-ray data collection and refinement statistics

Compound	**5a**	**6a**
a/Å	11.1406(16)	8.760(5)
b/Å	7.3930(11)	10.866(9)
c/Å	34.494(5)	16.013(12)
α/deg	90	90
β/deg	90	104.83(6)
γ/deg	90	90
V/Å^3	2841.0	1473.4
Z	8	4
d_{calc}/g cm^{-3}	1.4	1.35
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/C$
μ/cm^{-1}	0.091	0.876
F(000)	1248	624
Crystal dimensions/mm	0.21×0.11×0.43	0.19×0.40×0.52
Diffractometer	«Bruker Smart ApexII»	«Enraf Nonius CAD4»
Radiation	Mo-Kα	Mo-Kα
Index range	$-14 \le h \le 8$, $-9 \le k \le 7$, $-34 \le l \le 43$	$0 \ge h \ge 10$, $0 \ge k \ge 12$, $-19 \ge l \ge 18$
θ_{max}/deg	26.55	24.97
Number of reflections:		
measured	8372	2931
independent	2935	2587
used in refinement with $I \ge 3\sigma(I)$	1448	1118
R_{merge}	0.034	0.032
$R_1(F)$	0.038	0.037
$R_w(F)$	0.038	0.04
GOOF	1.125	1.194
Residual electron density/e Å^{-3}, max/min	0.16/−0.17	0.13/−0.15

was concentrated, and the residue was recrystallized from benzene. The total yield was 14.8 g.

5,7-Dimethylbenzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-one (3). Polyphosphoric acid (38 g) was added to compound **2** (2.55 g, 10 mmol). The reaction mixture was stirred at 100 °C for 8 h and cooled. Then ice water (250 mL) was added. The precipitate was filtered off and washed with water to neutral pH. The residue was chromatographed on a silica gel column (Silica gel Merck 60) using chloroform as the eluent.

Synthesis of compounds 4a—e (general procedure). The corresponding bromoacetophenone (20 mmol) and calcined potassium carbonate (13.8 g, 100 mmol) were added to a solution of compound **1** (20 mmol) in DMF (20 mL). The reaction mixture was stirred at 60 °C for 2 h, water (200 mL) was added, and the precipitate was filtered off and washed with water. The product was dried and recrystallized from an acetonitrile—DMF mixture. **1-Methyl-6-(2-oxo-2-phenylethoxy)benzo[*cd*]indol-2(1*H*)-one (4a)**, **1-butyl-6-(2-oxo-2-phenylethoxy)benzo[*cd*]indol-2(1*H*)-one (4b)**, **6-[2-(4-chlorophenyl)-2-oxoethoxy]-1-methylbenzo[*cd*]indol-2(1*H*)-one (4c)**, **1-butyl-6-[2-(4-chlorophenyl)-2-oxoethoxy]benzo[*cd*]indol-2(1*H*)-one (4d)**, and **6-[2-(4-methoxyphenyl)-2-oxoethoxy]-1-methylbenzo[*cd*]indol-2(1*H*)-one (4e)** were prepared.

Synthesis of compounds 5a—e (general procedure). Polyphosphoric acid (tenfold excess, w/w) was added to benzo[*cd*]indol-2(1*H*)-one derivatives **4a—e**. The reaction mixture was stirred at 85 °C for 3 h and cooled. Then a tenfold excess of ice water was added. The precipitate was filtered off and washed with water to neutral pH. The products were purified by chromatography or crystallization. **5-Methyl-7-phenylbenzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-one (5a)** (recrystallized from EtOH), **5-butyl-7-phenylbenzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-one (5b)** (purified by chromatography on a column with Silica gel Merck 100 using chloroform as the eluent), **7-(4-chlorophenyl)-5-methylbenzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-one (5c)** (purified by chromatography on a column with aluminium oxide Merck 90 using chloroform as the eluent), **5-butyl-7-(4-chlorophenyl)benzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-one (5d)** (recrystallized from toluene), and **7-(4-methoxyphenyl)-5-methylbenzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-one (5e)** (purified by chromatography on a column with Merck 90 using a benzene—ethyl acetate mixture as the eluent) were obtained.

Synthesis of compounds 6a—d (general procedure). Polyphosphoric acid (15-fold excess, w/w) was added to benzo[*cd*]indol-2(1*H*)-one derivatives **4a—d**. The reaction mixture was stirred at 135 °C for 3 h and cooled. Then a 15-fold excess of ice water was added. The precipitate was filtered off and washed with water to neutral pH. The product was purified by recrystallization or chromatography. **5-Methyl-8-phenylbenzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-one (6a)** (recrystallized from ethanol with an additive of activated carbon) and **5-butyl-8-phenylbenzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-one (6b)** (purified by chromatography on a column with aluminium oxide Merck 90 using chloroform as the eluent) were obtained. In the case of product **6c**, the reaction mixture was heated for 10 h, treated with water, and extracted with chloroform. The extract was dried with sodium sulfate and concentrated. **8-(4-Chlorophenyl)-5-methylbenzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-one (6c)** was purified by chromatography on a column with aluminium oxide Merck 90 using a benzene—ethyl acetate mixture as the eluent. **5-Butyl-8-(4-chlorophenyl)benzo[*cd*]furo[2,3-*f*]indol-4(5*H*)-one (6d)** was purified by chromatography on a column with aluminium oxide Merck 90 using chloroform as the eluent.

Synthesis of compound 6a from 5a. Polyphosphoric acid (45 g) was added to compound **5a** (2.99 g, 10 mmol). The reaction mixture was stirred at 135 °C for 3 h and cooled. Then ice water (300 mL) was added. The precipitate was filtered off and washed with water to neutral pH. The product was chromatographed on a column with Silica gel Merck 100 using chloroform as the eluent.

X-ray diffraction study of compounds 5a and 6a. Crystals were grown by crystallization from DMF. Principal crystallographic parameters for compounds **5a** and **6a** and the X-ray data collection and refinement statistics are given in Table 5. Both structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters using the CRYSTALS program package.[13] All hydrogen atoms were located in difference electron density maps and refined with fixed positional and thermal parameters. The Chebyshev weighting scheme[14] was used in the refinement. The complete X-ray structural data for compounds **5a** and **6a** were deposited with the Cambridge Structural Database (CCDC 631876 and 632375, respectively).

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Received October 8, 2007;
in revised form December 3, 2007