

# An X-Ray Crystal and Molecular Structure Determination of a Benzo[1,2-*b*:4,5-*b'*]bisbenzofuran Derivative Formed by Base-induced Condensation of 3(2*H*)-Benzofuranone

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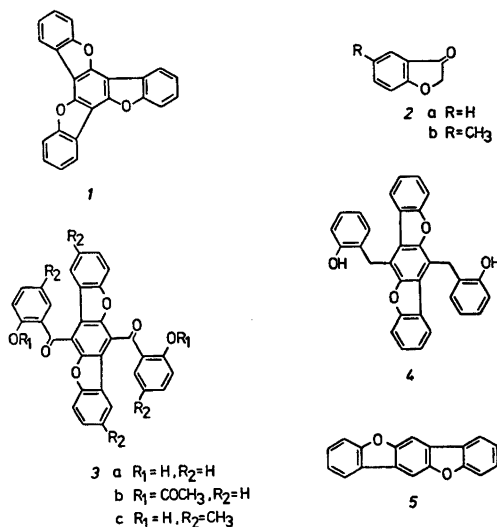
A base-induced condensation product from 3(2*H*)-benzofuranone is shown to be the tetrameric compound **3a** and not the trimeric compound **1** earlier proposed. The condensation product was studied by X-ray diffraction analysis and the structure was solved by direct methods. Refinements by least-squares methods, based on 1167 reflections with  $I > 1.5 \sigma(I)$  gave a final  $R$  of 0.071 and a  $R_w$  of 0.075.

3(2*H*)-Benzofuranone undergoes oligomerization under acidic or basic conditions yielding dimeric,<sup>1,2</sup> trimeric,<sup>3</sup> and tetrameric<sup>3</sup> condensation products. When refluxed in pyridine 3(2*H*)-benzofuranone (**2a**) furnishes an insoluble oligomeric product in 1% yield. Chatterjea proposed the trimeric structure **1** for this compound.<sup>3</sup> However, we have found that the compound is tetrameric (the composition was shown to be  $C_{32}H_{18}O_6$ , high resolution mass spectrum).<sup>3</sup>

The yield of this tetrameric compound was substantially increased (to 15%) upon addition of a catalytic amount of piperidine (1%) to the reaction mixture, whereas if analytically pure pyridine (*i.e.*, free of piperidine) is used only traces of the product are obtained. These results clearly indicate that a base-induced condensation has taken place.

Due to its very low solubility, further characterization of the condensation product was difficult. The IR spectrum showed no characteristic peaks and the UV spectrum gave no

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structural information other than the presence of a more conjugated system than that of the monomer. No NMR spectrum could be recorded. However, some information could be obtained from two derivatives (a diacetate and a  $LiAlH_4$ -reduction product with the composition  $C_{32}H_{22}O_4$ ).

Some attempts to prepare further derivatives failed. Thus all the following reagents failed to react with the condensation product:  $(CH_3)_2SO_4$  in combination with aqueous NaOH or monoglyme containing  $K_2CO_3$ ,  $K_3Fe(CN)_6$  in NaOH solution, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in dioxane or xylene,  $H_2O_2$  in HOAc and  $Br_2$  in HOAc.

It is clear, that the available data were insufficient for certain conclusions about the structure. Therefore, the condensation product was subjected to X-ray diffraction analysis, which provided conclusive evidence for the structure **3a** (6,12-disalicyloylbenzo[1,2-*b*:4,5-*b'*]bisbenzofuran). From these results it follows that the diacetate must have the structure **3b** and the  $\text{LiAlH}_4$ -reduction product must have the structure **4**.

When treated with strong alkali (90 % NaOH in  $\text{H}_2\text{O}$ , 210–230 °C) compound **3a** splits off the salicyloyl groups, furnishing the known<sup>4,5</sup> compound benzo[1,2-*b*:4,5-*b'*]bisbenzofuran (**5**). When subjected to the treatment described for 3(2*H*)-benzofuranone (**2a**) the methyl substituted homologue **2b** gave, as expected, the analogous tetrameric condensation product **3c** (17 %).

## EXPERIMENTAL

### Preparative part

Melting points under 360 °C were determined on a micro hot stage melting point apparatus and are uncorrected. Melting points above 360 °C were determined using a Perkin Elmer DSC-2 Differential Scanning Calorimeter calibrated from 231.9 °C (m.p. of tin) to 419.4 °C (m.p. of zinc). IR spectra were recorded with a Perkin Elmer 257 infrared spectrophotometer, the spectra being determined on KBr discs. Mass spectra were recorded with an Atlas SM 1 instrument or an LKB 9000 instrument. UV spectra were recorded with a Hitachi 200 spectrophotometer.

3(2*H*)-Benzofuranone (**2a**) and 5-methyl-3(2*H*)-benzofuranone (**2b**) were prepared according to literature procedures.<sup>6</sup>

6,12-Disalicyloylbenzo[1,2-*b*:4,5-*b'*]bisbenzofuran (**3a**). 3(2*H*)-Benzofuranone (5.0 g) was refluxed in pyridine (25 ml) containing piperidine (0.25 ml) for 72 h. When left in the freezer for 2 days a precipitate formed, which was collected and dried. Yield 0.7 g (15 %). Yellow crystals, m.p. 393–395 °C (diglyme). The compound can be sublimed. IR: 1620 (CO), 1571, 1511, 1482, 1471, 1449, 1350, 1323, 1310, 1278, 1242, 1195, 1144, 1081, 980, 809, 745, and 721  $\text{cm}^{-1}$ . UV[dioxane (log  $\epsilon$ ): 224 (4.64), 265 (4.34), 295 (4.24), and 355 (4.26) nm. High resolution MS gave  $M^+ = 498.1103$  (calculated 498.1103 for  $\text{C}_{28}\text{H}_{18}\text{O}_6$ ). MS[m/e (% rel.int.)]: 499 (22), 498 (M, 61), 379 (12), 378 (51), 377 (100), 259 (16), 258 (70), 121 (49), 93 (18), and 65 (22). Only peaks stronger than 10 % of the base peak are listed.

6,12-Bis(2-hydroxy-5-methylbenzoyl)-2,8-dimethylbenzo[1,2-*b*:4,5-*b'*]bisbenzofuran (**3c**). 5-

methyl-3(2*H*)-benzofuranone (5.0 g) was reacted under the same conditions as described for the preparation of compound **3a**. Yield 0.8 g (17 %). Yellow crystals, m.p. 379–383 °C (diglyme). IR: 1630 (CO), 1610, 1588, 1479, 1348, 1323, 1300, 1282, 1248, 1239, 1218, 1208, 1199, 1158, 1080, 983, 830, 800, and 793  $\text{cm}^{-1}$ . UV[dioxane(log  $\epsilon$ ): 227 (4.76), 268 (4.47), 301 (4.35), and 364 (4.38) nm.

High resolution MS gave  $M^+ = 554.1730$  (calculated 554.1729 for  $\text{C}_{38}\text{H}_{28}\text{O}_6$ ). MS [m/e (% rel.int.)]: 555 (30), 554 (M, 71), 421 (18), 420 (62), 419 (91), 287 (23), 286 (100), 285 (16), 223 (14), 135 (16), 77 (11), and 58 (14). Only peaks stronger than 10 % of the base peak are listed.

6,12-Bis(2-acetoxybenzoyl)-benzo[1,2-*b*:4,5-*b'*]bisbenzofuran (**3b**). Compound **3a** (0.10 g) was refluxed in acetic anhydride (10 ml) containing pyridine (0.1 ml) for 3 h. The light yellow product formed was collected and dried. Yields 0.09 g (77 %). M.p. 279–282 °C ( $\text{CH}_2\text{CN}$ ). IR: 1769 (CO), 1670 (CO), 1603, 1451, 1340, 1329, 1204, 1187, 1090, 992, 913, 762, 752, and 748  $\text{cm}^{-1}$ . MS[m/e (% rel.int.)]: 583 (14), 582 (M, 38), 540 (21), 498 (18), 379 (11), 378 (44), 377 (100), 258 (41), 121 (55), 60 (12), 45 (16), and 43 (49). Only peaks stronger than 10 % of the base peak are listed.

6,12-Bis(2-hydroxybenzoyl)-benzo[1,2-*b*:4,5-*b'*]bisbenzofuran (**4**). Compound **3a** (1.0 g, 2 mmol) and lithium aluminium hydride (5.0 g, 130 mmol) in diglyme (125 ml) was heated to 100 °C with stirring for 4 h. After cooling, ethyl acetate was added, followed by water, and then the solid formed was collected. This solid was extracted (Soxhlet) with ether for 4 days. Ether was evaporated and the white solid obtained was recrystallized from acetonitrile. Yield 0.3 g (32 %). M.p. 300–305 °C. If the compound is sublimed (290 °C/10 mmHg) the m.p. is raised to 318–323 °C. IR: 3575 (OH), 1585, 1489, 1454, 1407, 1342, 1246, 1230, 1201, 1183, 1167, 1092, 1080, 983, 766, 752, and 745  $\text{cm}^{-1}$ . MS[m/e (% rel.int.)]: 472, (8), 471 (46), 470 (M, 100), 377 (6), 365 (20), 364 (78), 363 (28), 361 (11), 345 (7), 271 (22), 259 (18), 258 (100), 198 (14), 107 (27), and 77 (7). Only peaks stronger than 5 % of the base peak are listed.

Benzo[1,2-*b*:4,5-*b'*]bisbenzofuran (**5**). Compound **3a** (95 mg) was heated in NaOH (5.0 g) and water (0.5 ml) at 225 °C for 48 h in a flask equipped with a glass-tube as condenser. White crystals of benzo[1,2-*b*:4,5-*b'*]bisbenzofuran sublimed into the tube. Yield 41 mg (84 %); m.p. 269–270 °C (lit. m.p. 265.5–266.5 °C,<sup>4</sup> 267–268 °C<sup>5</sup>). IR: 1471, 1437, 1229, 1221, 1145, 868, 855, 807, 752, 742, and 690  $\text{cm}^{-1}$ . UV[dioxane(log  $\epsilon$ ): 217 (4.61), 261 (4.28), 311 (4.65), 327 (4.77), and 338 (4.49) nm. MS[m/e (% rel.int.)]: 259 (19), 258 (M, 100), 229 (8), 202 (4), 201 (3), 200 (6), 129 (16), 114.5 (3), 101 (3), 100 (4), and 88 (4). Only peaks stronger than 2 % of the base peak are listed.

A sample<sup>4</sup> kindly provided by Dr. N. E. Stjernström was identical with our product.

### X-Ray part

*Preparation of crystals.* Sublimation (280 °C/10 mmHg) of compound 3a gave yellow plates. A prismatic crystal with the approximate dimensions of about 0.2 × 0.2 × 0.08 mm was chosen for the X-ray investigation.

*X-Ray data collection.* The intensity data were collected at room temperature on a computer-controlled four-circle diffractometer of type Syntex P2<sub>1</sub>, equipped with a scintillation counter. Graphite-monochromatized MoK $\alpha$ -radiation ( $\lambda = 0.71069$  Å) was used.

The unit cell parameters were determined as a least-squares refinement based on the scattering angles of 13 centred reflections. An orthorhombic unit cell was found with the crystal data:  $a = 7.144(4)$ ,  $b = 14.359(9)$ ,  $c = 21.88(3)$  Å,  $V = 2344(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.48$  g cm<sup>-3</sup>, and  $D_m = 1.5$  g cm<sup>-3</sup>.

The  $\omega$ -scan mode was used for the intensity data collection with different scan speeds, the minimum scan speed being 0.49° min<sup>-1</sup>. Background counts were taken for half the scanning time on either side of the peak. The intensity,  $I$ , and its standard deviation,  $\sigma(I)$ , were calculated as previously.<sup>7</sup> All intensities were corrected for Lorentz and polarization effects and converted to  $|F_o|$  by means of a data reduction program. Of the 1980 possible independent reflections for  $2\theta < 50^\circ$ , 1167 had intensities larger than 1.5  $\sigma(I)$  and were considered observed. After every 64th reflection the intensities of two check reflections were measured. Their intensities varied within  $\pm 6\%$  during data collection and showed no trend. No absorption correction was performed ( $\mu(\text{MoK}\alpha) = 1.1$  cm<sup>-1</sup>).

*Computer programs.* The program system supplied by Syntex (XTL version 2)<sup>8</sup> for a NOVA 24K computer with a disk memory unit, was used for most of the calculations. In addition the program TORSO<sup>9</sup> was used for some torsion angles calculations and the crystal structure illustrations were drawn by the thermal-ellipsoid plot program ORTEP 2.<sup>10</sup>

## STRUCTURE DETERMINATION AND REFINEMENTS

*Determination of the structure.* Systematic extinctions showed that the crystal belonged to the orthorhombic space group  $Pbca$  (No. 61) and the centrosymmetry was also supported by the statistical distribution of the normalized structure factors. Since this space group has eight-fold general positions and the unit cell contains only four molecules, the molecule must maintain a centre of symmetry.

The structure was solved by direct methods, using the program MULTAN.<sup>11</sup> This gave the initial atomic parameters of all non-hydrogen atoms, which were refined by least-squares methods utilizing isotropic temperature factors to give  $R = 0.135$  and  $R_w = 0.149$ .

The conventional  $R$ -value is defined as  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ , and  $R_w = (\sum w_i ||F_o| - |F_c||^2 / \sum w_i |F_o|^2)^{1/2}$  is a weighted  $R$ -value. Subsequent Fourier difference synthesis gave the initial positions of the hydrogen atoms. Least-squares refinements of all atoms (hydrogen atoms with isotropic, non-hydrogen atoms with anisotropic temperature factors) gave a final  $R = 0.071$  and  $R_w = 0.075$  for the 1167 used reflections.

The rather high  $R$ -values are due to a large number of reflections with low intensities, and this could possibly have been improved by employing a lower scan speed, lower than the minimum of 0.49° min<sup>-1</sup>.

*Scattering factors and refinement conditions.* The scattering factors used for all non-hydrogen atoms were calculated from analytical expressions for the neutral atoms.<sup>12</sup> For the hydrogen atoms the spherical form factors proposed by Stewart *et al.* were used.<sup>13</sup>

The least-squares refinements were based on the minimization of  $\sum w_i ||F_o| - |F_c||^2$ . The weighting scheme used was  $w(s) = 1 / (\sigma^2(F_o) + (0.04F_o)^2)$  and a cut-off limit of  $F_o > 3.0 \sigma(F_o)$ . A total number of 208 parameters was varied in the final refinements. The ratios of the shifts in the last cycle to the standard deviation were less than 1%.

The final fractional atomic positional parameters are given in Table 1. Lists of the observed and calculated structure factors and the anisotropic thermal parameters for the non-hydrogen atoms are available from BE on request.

## RESULTS AND DISCUSSION OF THE STRUCTURE

A stereoscopic view of the molecule and the numbering of the atoms are given in Fig. 1.

The individual benzene and furan rings are planar within experimental error. Least-squares planes fitted to the individual rings in the benzo[1,2-*b*:4,5-*b'*]bisbenzofuran system make an angle of 4.4° between the adjacent benzene planes, in accordance with other investigations of similar ring systems.<sup>14-16</sup> Even though the

Table 1. Final fractional atomic positional parameters and isotropic thermal parameters ( $\text{\AA}^2$ ) for the hydrogen atoms (estimated standard deviations in parentheses).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
C1	-0.3942(7)	-0.1088(3)	0.5308(2)	
C2	-0.5601(8)	-0.1506(4)	0.5462(3)	
C3	-0.6696(8)	-0.1807(4)	0.4983(3)	
C4	-0.6135(8)	-0.1680(4)	0.4385(3)	
C5	-0.4455(8)	-0.1260(3)	0.4239(2)	
C6	-0.3298(7)	-0.0954(3)	0.4716(2)	
C7	-0.1527(7)	-0.0487(3)	0.4767(2)	
C8	-0.1254(7)	-0.0346(3)	0.5393(2)	
C9	0.0219(7)	0.0135(3)	0.5648(2)	
C10	0.0370(7)	0.0375(3)	0.6313(2)	
C11	0.0492(7)	-0.0340(3)	0.6776(2)	
C12	0.0600(7)	-0.1282(3)	0.6627(2)	
C13	0.0741(9)	-0.1953(4)	0.7062(2)	
C14	0.0780(9)	-0.1693(4)	0.7671(2)	
C15	0.0691(8)	-0.0773(4)	0.7835(2)	
C16	0.0551(7)	-0.0089(4)	0.7395(2)	
O1	-0.2707(4)	-0.0717(2)	0.5729(1)	
O2	0.0412(6)	0.1220(3)	0.6443(1)	
O3	0.0498(7)	0.0802(3)	0.7581(2)	
H(C2)	-0.5998(56)	-0.1659(27)	0.5865(18)	2.4(9)
H(C3)	-0.8047(71)	-0.2061(30)	0.5061(20)	4.1(11)
H(C4)	-0.6931(61)	-0.1862(28)	0.4067(19)	2.9(10)
H(C5)	-0.3984(57)	-0.1191(29)	0.3791(21)	3.3(10)
H(C12)	0.0501(55)	-0.1467(28)	0.6204(20)	2.4(9)
H(C13)	0.0722(67)	-0.2619(38)	0.6964(20)	4.5(12)
H(C14)	0.0812(73)	-0.2159(37)	0.8006(24)	6.0(14)
H(C15)	0.0819(60)	-0.0574(28)	0.8262(21)	3.2(10)
H(O3)	0.0548(94)	0.1174(44)	0.7206(32)	9.2(20)

standard deviation in this dihedral angle is large ( $5.1^\circ$ ), the non-planar structure was shown to be significant by torsion angles calculations, cf. Table 2.

The salicyloyl unit makes an angle of  $118^\circ$  with the central benzene plane. The molecule has strong intra-molecular hydrogen bonds be-

tween the hydroxyl hydrogen atoms, H(O3), and the carbonyl oxygen atoms, O2, ( $1.67(7)$  \AA).

The ring system created by the hydrogen bond through atoms O2, C10, C11, C16, and O3 is significantly non-planar. The deviations from the least-squares plane are listed in Table 3. The O-H-O angle seems to be remarkably

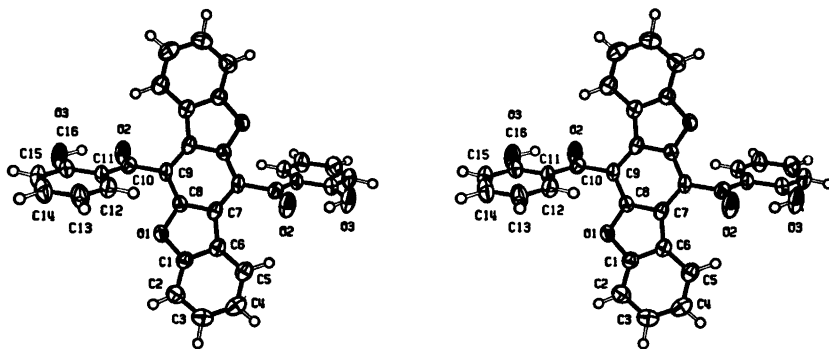


Fig. 1. A stereoscopic view of the molecule 3a. All non-hydrogen atoms are represented by 50 % probability thermal ellipsoids. The hydrogen atoms have for clarity been given a *B*-value of  $1 \text{\AA}^2$ .

Table 2. Torsion angles differing significantly from 0° and 180° in the benzo[1,2-b:4,5-b']bis-benzofuran system (estimated standard deviations in parentheses). An index 2 on the atom figure denotes a centrosymmetrical related atom toward the basic set.

Bond	Angle	Atoms involved
C6-C7	-177.5(7)	C1-C6-C7-C9 <sub>2</sub>
C6-C7	-1.9(5)	C1-C6-C7-C8
C6-C7	176.5(7)	C5-C6-C7-C8
C7-C9 <sub>2</sub>	174.3(7)	C6-C7-C9 <sub>2</sub> -C8 <sub>2</sub>
C7-C8	-175.5(6)	C6-C7-C8-C9
C7-C8	1.8(5)	C6-C7-C8-O1
C7-C8	178.2(6)	C9 <sub>2</sub> -C7-C8-O1
C9-C8	-177.9(7)	C7 <sub>2</sub> -C9-C8-O1
C8-O1	176.4(6)	C9-C8-O1-C1
C1-C2	177.6(8)	O1-C1-C2-C3
C1-C6	-177.3(6)	O1-C1-C6-C5

small, 149(6)°, albeit the standard deviation of this figure is high.

A three-dimensional Fourier difference map for the environment of O2 and O3 showed a unique position of the hydroxyl hydrogen. This means, as expected, that the other possible tautomeric form of this keto-enol system plays no role in the solid state.

All other bond distances and bond angles are within the expected range. The standard deviations in the C-C, C-O, and C-H distances (Å) are 0.006-0.009, 0.005-0.007, and 0.04-0.07, respectively.

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The X-ray investigation was made by BE and DR as an exercise in a graduate course,

Table 3. Deviations (Å) from the least-squares plane fitted to atoms O2, C10, C11, C16, and O3 (estimated standard deviations in parentheses).

Atom	Deviation
O2	0.014 (4)
C10	-0.029 (5)
C11	0.008 (5)
C16	0.015 (5)
O3	-0.013 (5)
H(O3)	0.060 (68)

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conducted by Professor I. Grenthe and Dr. G. Johansson at the Department of Inorganic Chemistry of this Institute. We gratefully acknowledge them and their colleagues for valuable teaching, advice and interest in this X-ray investigation. We also wish to thank Dr. A.-M. Pilotti, University of Stockholm, for valuable help with the torsion angles calculations.

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