A Cyclic Vicinal Bis(tetraketone) and Structural Investigations of Formoins

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Investigations of simple formoins such as 2,5-bis(1,1-dimethyl-2-phenylethyl)-2,4-dihydroxyfuran-3(2*H*)-one (**17**), benzoylformoin (**18**), *p*-toluoylformoin (**19**), pivaloylformoin (**20**), and the 2,4-dihydroxy-2,5-bis(heterocycl-2-yl)furan-3-ones **21**–**23** (heterocycle = furan, thiophene, selenophene) by NMR spectroscopy in DMSO showed the dihydroxyfuranone skeleton and not an enediol structure. The formoin **17** was oxidized to the corresponding tetraketone **10**. The intermolecular double benzoin condensation of 1,4-bis(2,2-dimethyl-3,4-dioxobutyl)benzene (**27**) affords, in low yield, the bis(formoin) **29**, and this could be oxidized to provide 2,2,2′,2′,7,7,7′,7′-octamethyl[8.8]paracyclophan-3,3′,4,4′5,5′6,6′-octaone (**9**). The molecular structures of **17** and **29**, the monohydrate of **10** (**30**), and also the dihydrate of **9** (**31**) are reported.

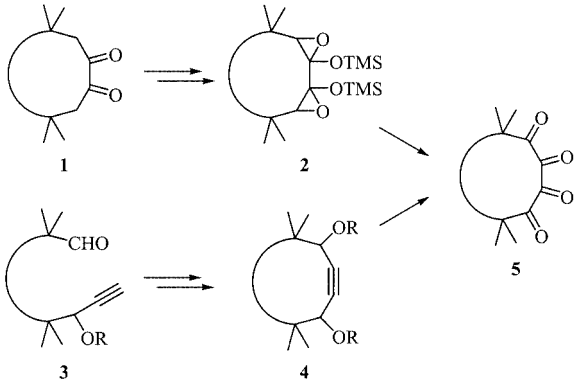
Introduction

Vicinal polyketones have been known since 1890, when Neuville and Pechmann reported the first syntheses of diphenyl triketone.[1] One year later, Abenius and Söderbaum described diphenyl tetraketone.[2] Since then the structures and spectroscopic properties of a considerable number of vicinal polyketones have been reported.[3,4] Common to all of them is their high electrophilicity, demonstrated by the formation of hydrates in the presence of water, and their electron acceptor properties, as attested to by their low reduction potentials.[4]

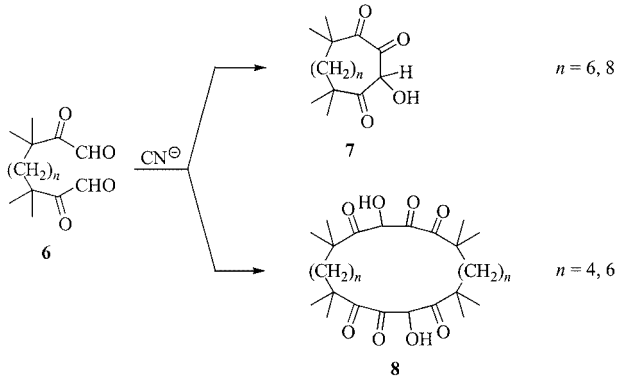
Cyclic vicinal tetraketones have been available since 1986,[5−8] by oxidation variously of cyclic formoins (in this paper we use the trivial name "formoin" because it comprises not only the cyclic form dihydroxyfurane (**D** in Scheme 4) but also the diketo-enediol form (**B** in Scheme 4).[5] of a butane-2,3-dione fragment **1**,[6,7] or of a 1,4-diprotected 1,4-dihydroxy-2-butyne moiety **4**.[8] The last two possibilities are shown schematically in Scheme 1.

An alternative procedure for the construction of cyclic tetraketones, the benzoin condensation of a bis(glyoxal) (e.g. **6**), yielded (for $n = 4$ and 6; Scheme 2) the corresponding bis(tetraketones) **8**[5] (Scheme 1).

We intended to explore this observation for the synthesis of cyclic bis(tetraketones) because they might exhibit interesting properties as ring systems with two acceptor centers by including electron-rich π-systems in their cavities. To explore the feasibility of this concept we started to synthesize a cyclic bis(tetraketone) in which two tetracarbonyl chains



Scheme 1



Scheme 2

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are separated by a rigid spacer. In this paper we report the synthesis of 2,2,2′,2′,7,7,7′,7′-octamethyl[8.8]paracyclophane-3,3′,4,4′,5,5′,6,6′-octaone (**9**). Furthermore, we pre-

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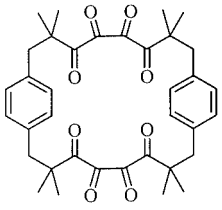
sent NMR spectroscopic data for formoins for the first time.



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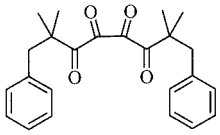

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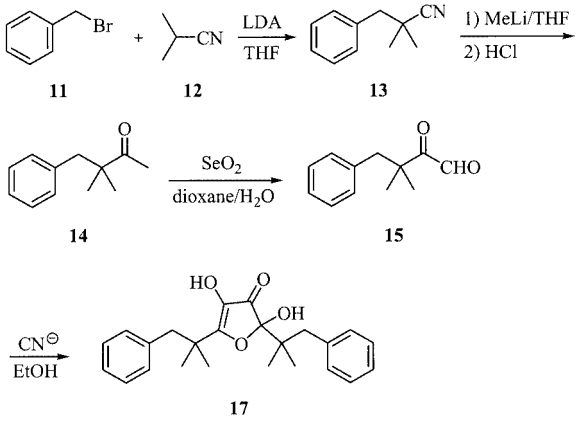
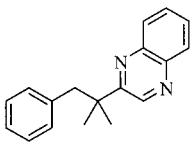
Synthesis and Structures of Formoins

As a model reaction we first tested the accessibility of 2,2,7,7-tetramethyl-1,8-diphenyloctane-3,4,5,6-tetraone (**10**) by a benzoin condensation. The synthesis of this tetraketone started with the preparation of 2,2-dimethyl-3-phenylpropionitrile (**13**) from benzyl bromide (**11**) and isobutyronitrile (**12**) as shown in Scheme 3, analogously to a literature procedure.[9] The ketone **14** was obtained by treatment of **13** with methyllithium and subsequent hydrolysis of the iminium salt.



Scheme 3

Oxidation of **14** with SeO_2 in dioxane/water yielded the desired glyoxal derivative **15**. The purified product was identified and characterized by treatment with 1 equiv. of *o*-phenylenediamine to yield the quinoxaline derivative **16**. The benzoin-type condensation of **15** to **17** was carried out with potassium cyanide in aqueous ethanol to afford the formoin in 67% yield.



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The structure of **17** in DMSO was derived from NMR spectroscopic data. To assign the signals in the ^{13}C NMR spectrum to the individual carbon atoms we used a heteronuclear multiple bond correlation (HMBC) procedure. The spectroscopic assignments were confirmed by the investigation of single crystals of **17** by X-ray diffraction, and the molecular structure of **17** is shown in Figure 1. No solvent molecules are included, while intramolecular hydrogen bonds are present between O2−H and O4 (197.5 pm) and O4−H and O3 (186.3 pm). The most relevant distances in the dihydroxyfuranone ring are given in Table 1. It is found that because of conjugation effects in the unsaturated fragment the formal C2−C3 single bond is shorter (141.5 pm) than would be expected, while the formal C1−C2 double bond (136.2 pm) and the formal C3−O3 double bond (123.4 pm) are longer than would be anticipated. The bond lengths are close to those reported for benzoylformoin (**18**),[10] the only formoin for which the molecular structure is reported in the literature. These investigations confirm that, both in the solid state and in solution (DMSO), **17** adopts the formoin structure.

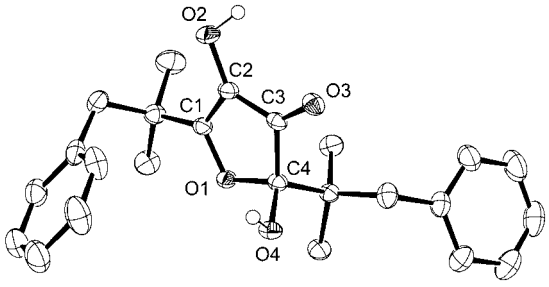
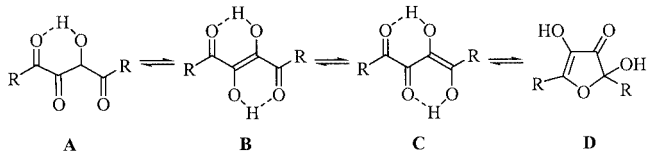


Figure 1. Molecular structure of **17** (50% ellipsoid probability, the hydrogen atoms at the carbon centers are omitted for the sake of clarity)

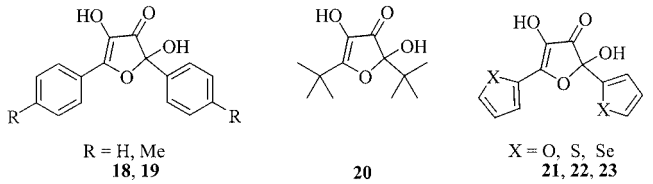
Table 1. Bond lengths of the dihydroxyfuranone moiety in **17** and **29**; for the numbering of the atoms of **17** and **29**, see Figures 1 and 2

	17	**29**
O1−C1	135.1	135.9
O1−C4	146.7	147.7
O2−C2	135.8	136.3
O3−C3	123.4	123.5
O4−C4	138.8	138.6
C1−C2	136.2	135.5
C2−C3	141.5	142.0
C3−C4	154.1	153.0

Since the systematic investigation of the tautomerism of formoins by Miyagi and Goto[11,12] and by Horner and Maurer[13] it has been known that formoins exist in solution and in the solid state either in the symmetric enediol (**B**) or the cyclic (**D**) form. (Scheme 4). This assignment was based solely on IR and UV experiments, NMR spectroscopic data not being available at that time. In this paper we therefore present NMR spectroscopic data for benzoylformoin (**18**), 4,4′-dimethylbenzoylformoin (**19**), pivaloylformoin (**20**), and the three formoins **21**−**23** with heterocyclic 6π-systems.

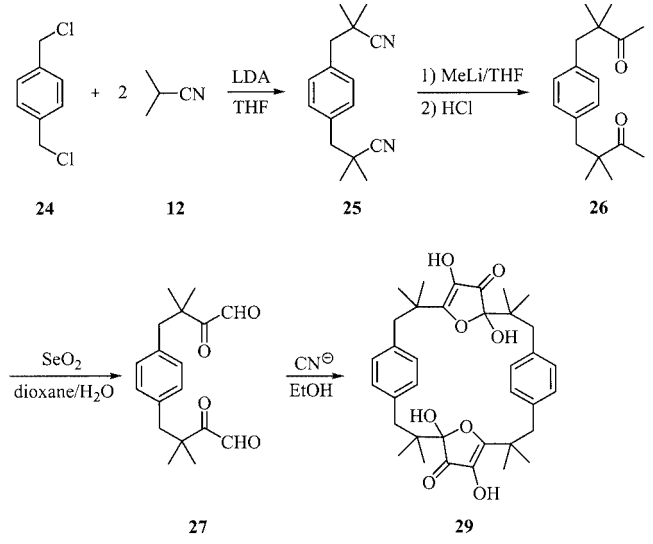


Scheme 4



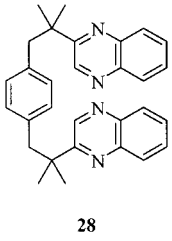
The NMR spectroscopic data for all six examples show that the formoin structure **D** prevails in DMSO. When **19** was dissolved in chloroform, the tautomer **B** was the only isomer detectable in solution. The solubilities of the formoins **20**−**23** in chloroform were too low for NMR investigations.

The high yield of **17** in the benzoin condensation of **15** encouraged us to use this procedure to prepare the cyclic bis(tetraketone) **9**. The starting point of our synthesis was 1,4-bis(2-cyano-2-methylpropyl)benzene (**25**), described in the literature previously.[9] The bis(glyoxal) derivative **27** was obtained analogously to **15** by selenium dioxide oxidation of **26** (Scheme 5).



Scheme 5

The purification of **27** was achieved by vacuum distillation, it being ensured that the distilled product was efficiently cooled to avoid oligomerization. The purified product was identified and characterized as the bis(quinoxaline) derivative **28**. To achieve cyclization, a dilute solution of **27** in ethanol was stirred with potassium cyanide, dissolved in ethanol/water, to afford the desired bis(formoin) **29** in low yield. The purification of **29** also caused problems. The viscous yellow residue obtained after removal of the solvent was triturated with dichloromethane, and recrystallization of the resulting solid from methanol yielded crystals only after a prolonged period of time. The quality of the crystals allowed an X-ray structure determination (Figure 2).



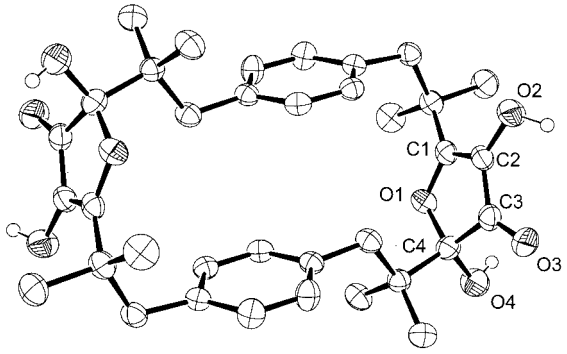
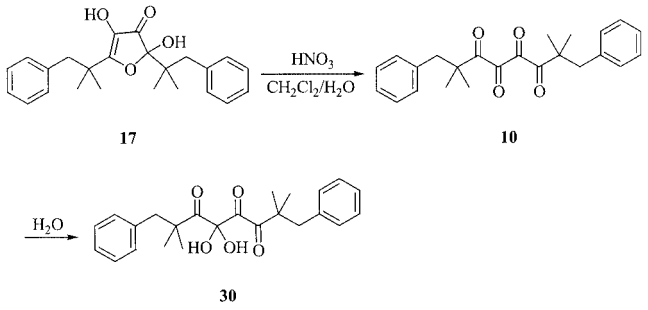


Figure 2. Molecular structure of **29** (50% ellipsoid probability, the hydrogen atoms at the carbon centers are omitted for the sake of clarity)

It was found that in the solid state the molecule crystallizes with four molecules of methanol, two of which are disordered. Each of the other two methanol molecules forms two hydrogen bonds to **29**, one between O3 and the hydroxy proton of the methanol (182.4 pm) and the other between O2−H and the oxygen atom of the methanol (173.7 pm). From Figure 2 it can be seen that **29** adopts the bis(formoin) form. The bond lengths obtained for the dihydroxyfuranone part are very similar to those in **17** (Table 1). Because of the very low solubility of **29** in the usual solvents, we were unable to obtain ^{1}H and ^{13}C NMR spectroscopic data. A low solubility in common solvents was also reported for a macrocyclic hexaketone monohydrate with a hemiketal structure.[14]

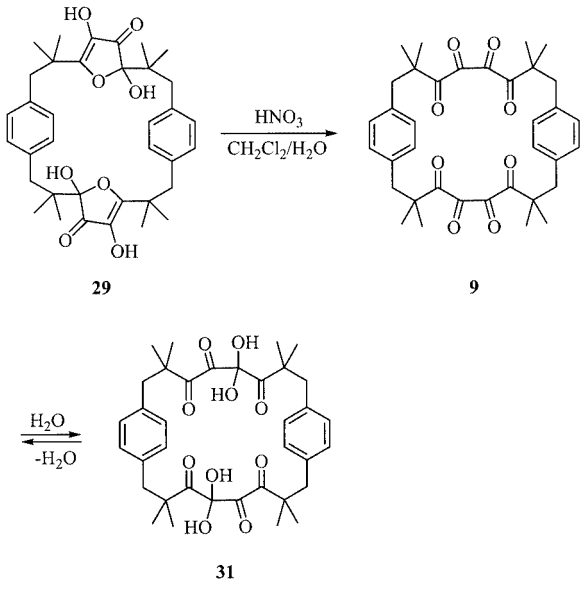
Synthesis of 9 and 10

For the oxidation of **17** to **10** we suspended the formoin in dichloromethane and added concd. nitric acid. During a few minutes of stirring a red color appeared. The product was purified by chromatography and yielded a red liquid with the expected spectroscopic data. The hydrate of **10** was obtained by addition of water to a solution of **10** in acetone (Scheme 6).



Scheme 6

The monohydrate **30** crystallized from the acetone solution at −30 °C to yield yellow crystals. An X-ray structure determination of **30** confirmed the structure (Figure 3, Table 2). An intramolecular hydrogen bond exists between O3−H and O1 (212.1 pm), two intermolecular hydrogen bonds are between O2−H and the acetone's carbonyl group (195.3 pm) and O3−H and O4 of a neighboring molecule of **30** (214.0 pm). In a manner similar to that used for the oxidation of **17**, we were able to oxidize **29** to the corresponding bis(tetraketone) **9** (Scheme 7). To purify the deep-red crude material the solvent was removed and the residue was dissolved in acetone. After addition of a small amount of water, the color changed from red to yellow. After storage of the solution at −20 °C for several months, light-yellow crystals of the dihydrate **31** were isolated. We were unable to record the ^{1}H and ^{13}C NMR spectra, due to the low solubility of **31** in the usual solvents. However, the crystalline material was used to carry out diffraction studies on **31**. These studies reveal an unsymmetrical structure of the bis(hydrate) **31**, which includes two molecules of acetone hydrogen-bonded to hydroxy groups with distances of 188.3 pm to H−O2 and 183.2 pm to H−O7, respectively. The carbonyl groups of the diketone moiety form a torsion



Scheme 7

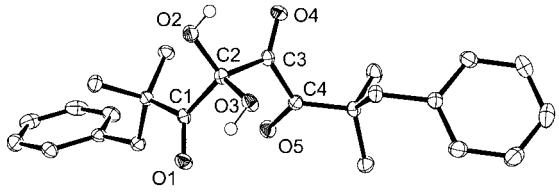


Figure 3. Molecular structure of **30** (50% ellipsoid probability, the hydrogen atoms at the carbon centers are omitted for the sake of clarity)

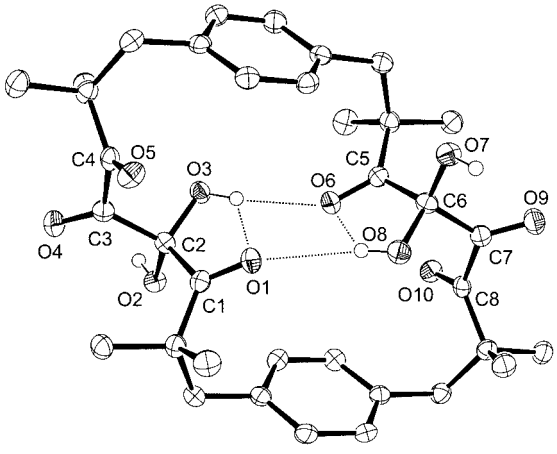


Figure 4. Molecular structure of **31** (acetone) (50% ellipsoid probability, the hydrogen atoms at the carbon centers are omitted for the sake of clarity); the dotted lines indicate the intramolecular hydrogen bonds

Table 2. Bond lengths of the tetracarbonyl hydrate moiety in **30** and **31**; for the numbering of the atoms of **30**, see Figure 3

	30	**31** (acetonitrile)
O1−C1	120.6	120.8
O2−C2	137.9	139.0
O3−C2	140.0	140.2
O4−C3	120.1	120.4
O5−C4	120.8	121.1
C1−C2	156.1	156.4
C2−C3	154.4	154.5
C3−C4	153.5	153.2

Table 3. Bond lengths of the tetracarbonyl hydrate moiety in **31**; for the numbering of the atoms of **31**, see Figure 4

31 (acetone)			
O1−C1	121.2	O6−C5	121.3
O2−C2	139.2	O7−C6	138.9
O3−C2	140.3	O8−C6	141.1
O4−C3	120.6	O9−C7	120.8
O5−C4	121.0	O10−C9	121.1
C1−C2	156.2	C5−C6	156.0
C2−C3	155.1	C6−C7	154.8
C3−C4	153.0	C7−C8	153.0

angle of approximately 120°. Furthermore, following intramolecular hydrogen bonds exist: O3−H···O1···O6 and O8−H···O1···O6 (Figure 4, Table 3). The bond lengths of the transannular hydrogen bonds are 215.5 pm (O3−H···O6) and 242.2 pm (O8−H···O1), and the angle between the planes of the phenyl rings amounts to 3.5°. Bis(hydrate) **31** was also crystallized from acetonitrile at room temp. to give a symmetrical molecular structure without the inclusion of any solvent molecules within the structure. The distance of the transannular hydrogen bond here is 227.7 pm. The bis(tetraketone) **9** was obtained by warming of bis(hydrate) **31** in vacuo. The analytical data are given in the Exp. Sect.

Conclusion

Our experiments on formoins have elucidated their structures in solution and in the solid state by providing NMR spectroscopic data for eight formoins and crystal data for two. Although we achieved our goal, the synthesis of **9**, the yield of the last step was too low to produce enough material for further studies indicated in the introduction. A stepwise approach seems desirable. The low solubilities of the formoins and hydrates in the usual solvents turned out to be a disadvantage that appears difficult to avoid.

Experimental Section

General Remarks: THF was dried by distillation under argon from sodium benzophenone ketyl. All glyoxal derivatives were freshly distilled before use. Commercially available reagents were used as supplied, without further purification. Column chromatography was performed on Macherey & Nagel silica gel (40−63 mesh). Unless otherwise noted, organic extracts were dried with anhydrous Na_2SO_4. All melting points are uncorrected. The NMR spectra were measured with a Bruker WH 300 or Avance 500 spectrometer (^{1}H NMR at 300 or 500 MHz and ^{13}C at 75 or 125 MHz) with use of the solvent signal as internal standard (δ). The mass spectra refer to data from a JEOL JMS-700 instrument. IR spectra were recorded with a Bruker Vector 22 FT-IR spectrometer. UV/Vis absorption data were recorded with a Hewlett−Packard HP 8452A Diode Array spectrometer. Elemental analyses: Microanalytical Laboratory of the University of Heidelberg. The following substances were prepared by literature procedures: 2-acetylselenophene,[15] furan-2-ylglyoxal,[16] thiophen-2-ylglyoxal,[17] benzoylformoin (**18**),[18] *p*-tolylglyoxal,[19] *tert*-butylglyoxal,[20] pivaloylformoin (**20**),[11] and 1,4-bis(2,2-dimethyl-3-oxobutyl)benzene (**26**).[9]

2,2-Dimethyl-3-phenylpropionitrile (13): Isobutyronitrile (**12**, 5.60 g, 81 mmol) was added at 0−5 °C to a solution of LDA, prepared from diisopropylamine (8.70 g, 86 mmol) and *n*-butyllithium (1.6 M, 55 mL, 88 mmol) in dry THF (700 mL). After 30 min of stirring, a solution of benzyl bromide (**11**; 10.50 g, 60 mmol) in THF (10 mL) was added at the same temperature. The mixture was stirred for 2 h, treated with 10% hydrochloric acid, and concentrated. The residue was extracted with ethyl acetate, and the organic layer was washed successively with aqueous $NaHCO_3$ and brine and dried, and the solvents were evaporated in vacuo. The pure compound crystallized from a pale yellow oil as colorless crystals to give **13** (8.38 g, 52.6 mmol, 88%), m.p. 56 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.34 (s, 6 H, CH_3), 2.80 (s, 2 H, CH_2), 7. 25−7. 33 (m, 5 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.6 (CH_3), 33.6 [$C(CH_3)_2$], 46.8 (CH_2), 124.9 (CN), 127.4 (CH_{ar}), 128.5 (CH_{ar}), 130.3 (CH_{ar}), 135.8 (C_{ar}) ppm. MS (positive EI): *m/z* = 159 $[M]^+$, 91 $[C_7H_7]^+$, 77 $[C_6H_5]^+$, 65 $[C_5H_5]^+$. IR (KBr): $\tilde{\nu}$ = 3028, 2230, 1450, 761, 706 cm^{-1}. $C_{11}H_{13}N$ (159.23): calcd. C 82.97, H 8.23, N 8.80; found C 82.68, H 8.16, N 8.78.

3,3-Dimethyl-4-phenylbutan-2-one (14): A solution of methyllithium in diethyl ether (1.6 M, 50 mL, 80 mmol) was added at −40 °C to a solution of the nitrile **13** (4.50 g, 28.3 mol) in dry THF (700 mL). After the mixture had been stirred at 0−5 °C for 2 h, hydrochloric acid (10%) was added. The mixture was stirred at ambient temperature overnight and extracted with ethyl acetate. The organic extract was washed successively with aqueous $Na_2S_2O_3$, aqueous $NaHCO_3$, and brine, and was then dried and concentrated in vacuo. The residual liquid was purified by column chromatography on silica gel [elution with petroleum ether (boiling range 30−40 °C) and then dichloromethane] to give **14** (4.54 g, 25.8 mmol, 91%) as a colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.11 (s, 6 H, CH_3), 2.10 [s, 3 H, $C(O)CH_3$], 2.80 (s, 2 H, CH_2), 7.07−7.09 (m, 2 H, Ar-H), 7.23−7.24 (m, 3 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.4 (CH_3), 26.2 [$C(O)CH_3$], 45.4 (CH_2), 48.7 [$C(CH_3)_2$], 126.5 (CH_{ar}), 128.1 (CH_{ar}), 130.4 (CH_{ar}), 137.9 (C_{ar}), 214.0 (C=O) ppm. MS (positive EI): *m/z* = 176 $[M]^+$, 161 $[M - CH_3]^+$, 133 $[M - COCH_3]^+$, 105 $[C_8H_9]^+$, 91 $[C_7H_7]^+$, 65 $[C_5H_5]^+$. $C_{12}H_{16}O$ (176.25): calcd. C 81.77, H 9.15; found C 81.51, H 9.14.

3,3-Dimethyl-2-oxo-4-phenylbutyraldehyde (15): Selenium(IV) oxide (20.80 g, 187 mmol) was dissolved in a solution of dioxane (24 mL) and water (8 mL) at 50−60 °C. The ketone **14** (30.00 g, 170 mmol) was added in one portion, and the mixture was heated at reflux for 4 d. After the system had cooled to ambient temperature, benzene was added, and the solution was filtered through a short column of Celite 545 to remove formed precipitates. After evaporation of the solvents, the resulting yellow liquid was purified by distillation in vacuo. Yield 71% (22.96 g, 121 mmol). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.14 (s, 6 H, CH_3), 2.94 (s, 2 H, CH_2), 6.94−6.96 (m, 2 H, Ar−H), 7.11−7.17 (m, 3 H, Ar-H), 9.19 (s, 1 H, CHO) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 23.5 (CH_3), 44.6 (CH_2), 47.0 (C), 127.0 (CH_{ar}), 128.4 (CH_{ar}), 130.5 (CH_{ar}), 136.5 (C_{ar}), 189.5 (CHO), 203.4 (C=O) ppm. $C_{12}H_{14}O_2$ (190.24): calcd. C 75.76, H 7.42; found C 75.47, H 7.49. **15** was also characterized as the quinoxaline derivative **16**.

2-(1,1-Dimethyl-2-phenylethyl)quinoxaline (16): A solution of 1,2-phenylenediamine (1.24 g, 11.5 mmol) in ethanol (16 mL) was added to a solution of freshly distilled **15** (1.04 g, 5.5 mmol) in dioxane (8 mL). After stirring at 80 °C for 5 h, the mixture was allowed to cool to ambient temperature, and the solvents were removed in vacuo. Purification by column chromatography on silica gel (elution with petroleum ether/diethyl ether, 4:1) afforded the quinoxaline **16** as a colorless liquid in 79% yield (1.14 g, 4.35 mmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.54 (s, 6 H, CH_3), 3.16 (s, 2 H, CH_2), 6.88−6.90 (m, 2 H, Ar−H), 7.14−7.16 (m, 3 H, Ar-H), 7.70−7.77 (m, 2 H, Ar-H), 8.08−8.11 (m, 2 H, Ar-H), 8.79 (s, 1 H, NCH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.1 (CH_3), 41.5 [$C(CH_3)_2$], 49.1 (CH_2), 126.3 (CH_{ar}), 127.9 (CH_{ar}), 129.0 (CH_{ar}), 129.1 (CH_{ar}), 129.4 (CH_{ar}), 129.7 (CH_{ar}), 130.4 (CH_{ar}), 138.2 (C_{ar}), 140.8 (C_{ar}), 141.7 (C_{ar}), 143.7 (N=CH), 162.4 (C=N) ppm. HRMS (positive EI): calcd. for $C_{18}H_{18}N_2$ $[M]^+$ 262.1470; found 262.1461 (−0.9 mmu). MS (positive EI): *m/z* = 262 $[M]^+$, 247 $[M - CH_3]^+$, 171 $[M - C_7H_7]^+$, 129 $[C_8H_5N_2]^+$, 91 $[C_7H_7]^+$,

77 $[C_6H_5]^+$, 65 $[C_5H_5]^+$. IR (film): $\tilde{\nu}$ = 2967, 1552, 1489, 1459, 1087, 757, 703 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 236 (4.48), 296 (3.63), 308 (3.79), 320 (3.83) nm. $C_{18}H_{18}N_2$ (262.35): calcd. C 82.41, H 6.92, N 10.68; found C 82.21, H 6.92, N 10.57.

2,5-Bis(1,1-dimethyl-2-phenylethyl)-2,4-dihydroxyfuran-3(2*H*)-one (17): A solution of KCN (175 mg, 2.7 mmol) in aqueous ethanol (50%, 3 mL) was added to a solution of freshly distilled glyoxal derivative **15** (4.65 g, 24.4 mmol) in ethanol (15 mL). After the mixture had been cooled in ice and stirred for 15 min, the pale yellow solid that precipitated was collected by filtration. Recrystallization from ethanol gave **17** in 67% yield (3.10 g, 8.1 mmol) as colorless crystals, m.p. 146−149 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 0.72 (s, 6 H, CH_3), 1.18 (s, 3 H, CH_3), 1.21 (s, 3 H, CH_3), 2.59 (d, ^2J = 12.9 Hz, 1 H, CH_2), 2.78 (d, ^2J = 12.9 Hz, 1 H, CH_2), 2.80 (d, ^2J = 13.0 Hz, 1 H, CH_2), 3.10 (d, ^2J = 13.0 Hz, 1 H, CH_2), 7.02−7.04 (m, 2 H, Ar-H), 7.12−7.26 (m, 8 H, Ar-H), 7.45 (s, 1 H, OH), 8.23 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 20.0 (2 CH_3), 23.6 (CH_3), 25.4 (CH_3), 38.9 [$C(CH_3)_2$], 40.3 (CH_2), 40.9 [$C(CH_3)_2$], 44.0 (CH_2), 103.2 (C), 125.8 (CH_{ar}), 126.2 (CH_{ar}), 127.6 (CH_{ar}), 127.8 (CH_{ar}), 130.4 (CH_{ar}), 130.8 (CH_{ar}), 132.5 (=C−OH), 137.6 (C_{ar}), 137.9 (C_{ar}), 176.6 (=C−O−),197.2 (C=O) ppm. HRMS (positive EI): calcd. for $C_{24}H_{28}O_4$ $[M]^+$ 380.1988; found 380.1979 (−0.9 mmu). MS (positive EI): *m*/*z* = 380 $[M]^+$, 289 $[M - C_7H_7]^+$, 271, 219, 191, 161, 157, 133, $[C_{10}H_{13}]^+$, 105 $[C_8H_9]^+$, 91 $[C_7H_7]^+$. IR (KBr): $\tilde{\nu}$ = 3420, 2977, 1682, 1587, 1077, 703. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 312 (3.88) nm. $C_{24}H_{28}O_4$ (380.48): calcd. C 75.76, H 7.42; found C 75.65, H 7.41.

2,2,7,7-Tetramethyl-1,8-diphenyloctane-3,4,5,6-tetraone (10): Concd. nitric acid (6 mL) was added dropwise to a stirred, ice-cooled suspension of the formoin **17** (570 mg, 1.5 mmol) in dichloromethane (28 mL) and water (3.5 mL). After a few minutes, the mixture turned red and became homogeneous. The layers were separated and the organic layer was dried with $MgSO_4$. The crude product was purified by flash chromatography on silica gel (elution with petroleum ether/acetone, 1:1) to give the red tetraketone **10** (471 mg, 1.2 mmol, 83%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 1.27 (s, 12 H, CH_3), 3.06 (s, 4 H, CH_2), 7.08−7.14 (m, 4 H, Ar-H), 7.22−7.30 (m, 6 H, Ar-H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 22.8 (CH_3), 44.1 (CH_2), 47.1 [$C(CH_3)_2$], 126.8 (CH_{ar}), 128.2 (CH_{ar}), 130.6 (CH_{ar}), 136.6 (C_{ar}), 188.4 (C=O), 204.0 (C=O) ppm. MS (positive CI): *m*/*z* = 379 $[M + H]^+$, 351 $[M + H - CO]^+$, 133 $[C_{10}H_{13}]^+$. IR (CD_2Cl_2): $\tilde{\nu}$ = 2974, 1737, 1701, 703 cm^{-1}. UV/Vis (CD_2Cl_2): $\lambda_{max.}$ (log ε) = 254 (1443), 260 (1278), 266 (1065), 278 (793), 390 (91), 526 (106) nm. $C_{24}H_{26}O_4$ (378.46): calcd. C 76.17, H 6.92; found C 75.98, H 6.88.

5,5-Dihydroxy-2,2,7,7-tetramethyl-1,8-diphenyloctane-3,4,6-trione (30): The red tetraketone **10** was dissolved in a minimal amount of acetone, and 2−4 drops of water were added. Crystals of the yellow hydrate **30** were formed at −25 °C over several months. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 0.99 (s, 6 H, CH_3), 1.08 (s, 6 H, CH_3), 2.84 (s, 2 H, CH_2), 2.95 (s, 2 H, CH_2), 7.00−7.05 (m, 4 H, Ar-H), 7.18−7.23 (m, 6 H, Ar-H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 23.7 (CH_3), 24.2 (CH_3), 45.1 (CH_2), 45.4 (CH_2), 47.3 [$C(CH_3)_2$], 47.8 [$C(CH_3)_2$], 96.6 [$C(OH)_2$], 127.1 (CH_{ar}), 127.4 (CH_{ar}), 128.6 (CH_{ar}), 128.7 (CH_{ar}), 130.9 (CH_{ar}), 131.5 (CH_{ar}), 137.5 (C_{ar}), 137.7 (C_{ar}), 193.9 (C=O), 208.7 (s, C=O), 209.6 (s, C=O) ppm. MS (positive FAB): *m*/*z* = 419 $[M + Na]^+$, 397 $[M + H]^+$, 379 $[M + H - H_2O]^+$,361 $[M + H - 2\ H_2O]^+$.

1,4-Bis(2-cyano-2-methylpropyl)benzene (25): Isobutyronitrile (**12**; 3.08 g, 44.6 mmol) was added at 0−5 °C to a solution of LDA, prepared from diisopropylamine (4.32 g, 42.7 mmol) and *n*-butyllithium (1.6 M, 30 mL, 48.0 mmol) in dry THF (400 mL). After the mixture had been stirred for 30 min, a solution of 1,4-bis(chloromethyl)benzene (**24**; 2.58 g, 14.7 mmol) in THF (10 mL) was added at the same temperature. The mixture was stirred for 2 h, treated with 10% hydrochloric acid, and concentrated. The residue was extracted with ethyl acetate, and the organic layer was washed successively with aqueous $NaHCO_3$ and brine and then dried, and the solvents were evaporated in vacuo. Purification by column chromatography on silica gel (elution with dichloromethane) afforded the bis(nitrile) **25** (3.34 g, 13.8 mmol, 95%) as colorless crystals, m.p 187−189 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 12 H, CH_3), 2.81 (s, 4 H, CH_2), 7.25 (s, 4 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.2 (CH_3), 34.2 (C−CN), 47.0 (CH_2), 125.4 (CN), 130.9 (CH_{ar}), 135.5 (C_{ar}) ppm. MS (positive EI): *m*/*z* = 240 $[M]^+$, 172 $[M - C(CH_3)_2CN]^+$, 104 $[C_8H_8]^+$. IR (KBr): $\tilde{\nu}$ = 2980, 2933, 2231, 1458, 1369, 842 cm^{-1}. $C_{16}H_{20}N_2$ (240.35): calcd. C 79.96, H 8.39, N 11.66; found C 79.90, H 8.43, N 11.55.

1,4-Bis(2,2-dimethyl-3,4-dioxobutyl)benzene (27): Selenium(IV) oxide (2.22 g, 20.0 mmol) was dissolved in a solution of dioxane (15 mL) and water (1 mL) at 50−60 °C. The bis(ketone) **26** (4.00 g, 14.6 mmol) was added in one portion, and the mixture was heated at reflux. Further solutions of selenium(IV) oxide (833 mg, 7.5 mmol and 655 mg, 5.9 mmol) in dioxane (5 mL and 4 mL) and water (1.5 mL and 1 mL) were added after 30 h and 70 h, respectively. Heating at reflux was continued for an additional 26 h. The hot solution was filtered through a short column of Celite 545 to remove the precipitated selenium. Benzene (100 mL) was added to the yellow filtrate; the solution turned turbid and was filtered again. The addition of benzene and subsequent filtration were repeated once again. Evaporation of the solvents yielded the bis(glyoxal) derivative (**27**) as a brittle yellow solid. Compound **27** was characterized as the quinoxaline derivative (**28**).

1,4-Bis(2-methyl-2-quinoxalin-2-ylpropyl)benzene (28): 1,2-Phenylenediamine (630 mg, 5.84 mmol) was added to a solution of freshly distilled bis(glyoxal) derivative **27** (880 mg, 2.92 mmol) in dioxane (22 mL). After the mixture had been stirred at 100 °C for 3 h, half of the solvent was removed and the mixture was allowed to stand at 5 °C overnight. The precipitated solid was collected by filtration and purified by column chromatography on silica gel (elution with petroleum ether/diethyl ether, 1:1) to give the bis(quinoxaline) derivative **28** as a colorless, glittering solid in 48% yield (626 mg, 1.40 mmol), m.p. 149−151 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 (s, 12 H, CH_3), 3.04 (s, 4 H, CH_2), 6.63 (s, 4 H, Ar-H), 7.72 (m, 4 H, Ar-H), 8.05 (m, 4 H, Ar-H), 8.72 (s, 2 H, H−CN) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.7 (CH_3), 42.1 [$C(CH_3)_2$], 49.4 (CH_2), 129.6 (CH_{ar}), 130.0 (CH_{ar}), 130.3 (CH_{ar}), 130.5 (CH_{ar}), 136.6 (C_{ar}), 141.4 (C_{ar}), 142.3 (C_{ar}), 144.3 (H−CN), 163.0 (CN) ppm. MS (positive EI): *m*/*z* = 446 $[M]^+$, 275 $[M - C_{11}H_{11}N_2]^+$, 171 $[C_{11}H_{11}N_2]^+$, 129 $[C_8H_5N_2]^+$, 104 $[C_8H_8]^+$, 77 $[C_6H_5]^+$. IR (KBr): $\tilde{\nu}$ = 2969, 1556, 1465, 1124, 1075, 961, 768 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 218 (4.41), 236 (4.76), 280 (3.69), 2.98 (3.90), 310 (4.16), 320 (4.22) nm. $C_{30}H_{30}N_4$ (446.59): calcd. C 80.68, H 6.77, N 12.55; found C 80.54, H 6.76, N 12.42.

4,6,16,18-Tetrahydroxy-3,3,8,8,15,15,20,20-octamethyl-29,30-dioxapentacyclo[20.2.2.2.^{10,13}.1^{4,7}.1^{16,19}]triaconta-6,10,12,18,22,24,25,27-octaene-5,17-dione (29): Water (300 mL) was added to a solution of freshly distilled bis(glyoxal) derivative **27** (6.10 g, 20.2 mmol) in ethanol (300 mL). The resulting yellow solution was added dropwise over a period of 7 h to a solution of potassium cyanide (290 mg, 4.45 mmol) in aqueous ethanol (50%, 60 mL). After addition, stirring was continued at ambient temperature for 2 d. The

solution was concentrated and filtered. The residue was then stirred with dichloromethane (120 mL) for 8 h. The yellow residue was collected and recrystallized from methanol to afford the bis(formoin) **29** (67 mg, 1.11 mmol, 1%). Colorless crystals, m.p. 226−231 °C (red liquid). HRMS (positive EI): calcd. for $C_{36}H_{44}O_8$ $[M]^+$ 604.3036; found 604.3026 (−1.0 mmu). MS (positive EI): *m*/*z* = 604 $[M]^+$, 586 $[M - H_2O]^+$, 576 $[M - CO]^+$, 199, 187, 145 $[C_{11}H_{13}]^+$, 131 $[C_{10}H_{11}]^+$, 104 $[C_8H_8]^+$. IR (KBr): $\tilde{\nu}$ = 3421, 2978, 1693, 1602, 1236 cm^{-1}.

4,4,5′,5′-Tetrahydroxy-2,2,2′,2′,7,7,7′,7′-octamethyl[8.8]paracyclophane-3,3′,4′,5,6,6′-hexaone (31): Concd. nitric acid (3 mL) was added dropwise to a stirred and ice-cooled suspension of the crude bis(formoin) **29** in dichloromethane and water (3.5 mL). After a few minutes, the mixture turned red and became homogeneous. The layers were separated, and the organic layer was dried with $MgSO_4$. After removal of the solvents, the reddish residue was dissolved in a minimal amount of acetone and 2−4 drops of water were added. Crystals of the yellow bis(hydrate) **31** were formed at −25 °C over a period of months. M.p. 146−148 °C (red liquid, dehydration). HRMS (positive FAB): calcd. for $C_{36}H_{44}O_{10}Na$ $[M + Na]^+$ 659.2832; found 659.2826 (−0.6 mmu).

2,2,2′,2′,7,7,7′,7′-Octamethyl[8.8]paracyclophan-3,3′,4,4′,5,5′,6,6′-octaone (9): The bis(tetraketone) **9** was obtained quantitatively by heating of the bis(hydrate) **31** in vacuo, during which the yellow crystals melted to form a red oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.30 (s, 24 H, CH_3), 2.98 (s, 8 H, CH_2), 6.88 (s, 8 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.6 (CH_3), 44.8 (CH_2), 47.5 [$C(CH_3)_2$], 130.1 (CH_{ar}), 135.4 (C_{ar}), 188.1 (C=O), 203.1 (C=O) ppm. HRMS (positive FAB): calcd. for $C_{36}H_{41}O_8$ $[M + H]^+$ 601.2802; found 601.2812 (+1.0 mmu). MS (positive FAB): *m*/*z* = 659 $[M + 2\,H_2O + Na]^+$, 623 $[M + Na]^+$, 601 $[M + H]^+$, 583 $[M + H - H_2O]^+$, 573 $[M + H - CO]^+$. IR ($CDCl_3$): $\tilde{\nu}$ = 2970, 2926, 1728, 1692, 1514, 1365, 824 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 252 (3.32), 290 (3.10), 366 (2.70), 528 (2.19) nm. $C_{36}H_{40}O_8$ (600.70): calcd. C 71.98, H 6.71; found C 71.65, H 7.08.

General Procedure for the Synthesis of the Formoins 18−23: A solution of KCN in 50% aqueous ethanol was added to an ice-cold and stirred solution of the freshly distilled glyoxal derivative in ethanol. The formed precipitate was collected by filtration. If not otherwise noted, recrystallization from ethanol gave the pure formoin.

Benzoylformoin (18):[18] Reaction mixture: phenylglyoxal hydrate (4.80 g, 31.5 mmol), KCN (247 mg, 3.8 mmol), ethanol (17 mL), water (5 mL). Yellow solid, yield 27% (2.29 g, 8.5 mmol), m.p. 182−185 °C. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 7.36−7.43 (m, 3 H, Ar-H), 7.46−7.51 (m, 2 H, Ar-H), 7.56−7.61 (m, 3 H, Ar-H), 8.12−8.18 (m, 2 H, Ar-H), 8.32 (s, 1 H, OH), 9.58 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 100.2 (O−C−OH), 125.4 (CH_{ar}), 126.5 (CH_{ar}), 128.3 (CH_{ar}), 128.8 (CH_{ar}), 128.9 (CH_{ar}), 129.0 (C), 131.3 (CH_{ar}), 132.0 (C), 137.2 (C), 162.6 (C=C−Ph), 195.2 (C=O) ppm.

***p*-Toluoylformoin (19):** Reaction mixture: *p*-tolylglyoxal[19] (2.76 g, 18.6 mmol), KCN (175 mg, 2.7 mmol), ethanol (20 mL), water (5 mL). Yield 71% (1.96 g, 6.61 mmol). Cyclic hemiacetal: brown-red solid, m.p. 144−148 °C. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 2.28 (s, 3 H, CH_3), 2.39 (s, 3 H, CH_3), 7.18 (d, ^3J = 8.2 Hz, 2 H, Ar-H), 7.35 (d, ^3J = 8.2 Hz, 2 H, Ar-H), 7.39 (d, ^3J = 8.2 Hz, 2 H, Ar-H), 8.04 (d, ^3J = 8.2 Hz, 2 H, Ar-H), 8.21 (s, 1 H, OH), 9.44 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 20.8 (CH_3), 21.3 (CH_3), 100.4 (O−C−OH), 125.4 (CH_{ar}), 126.4 (C), 126.6 (CH_{ar}), 128.9 (CH_{ar}), 129.6 (CH_{ar}), 131.5 (C), 134.5 (C), 138.3 (C), 141.6 (C), 163.0 (C=C), 195.0 (C=O) ppm. MS (positive EI): *m*/*z* = 296 $[M]^+$, 177 $[M - C_8H_7O]^+$, 119 $[C_8H_7O]^+$, 91 $[C_7H_7]^+$. Enediol: ^1H NMR (300 MHz, $CDCl_3$): δ = 2.44 (s, 6 H, CH_3), 7.30 (d, ^3J = 8.2 Hz, 4 H, Ar-H), 8.16 (d, ^3J = 8.2 Hz, 4 H, Ar-H), 12.34 (s, 2 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.2 (CH_3), 129.4 (CH_{ar}), 130.9 (CH_{ar}), 133.7 (C), 144.3 (C), 145.2 (C), 196.2 (C=O) ppm.

Pivaloylformoin (20): Reaction mixture: *tert*-butylglyoxal[20] (1.56 g, 14.1 mmol), KCN (100 mg, 1.5 mmol), ethanol (10 mL), water (1 mL). Purification was performed by dissolution of the crude formoin in ethanol and precipitation of **20** by addition of water. Colorless crystals, yield 45% (724 mg, 3.2 mmol), m.p. 165−168 °C. ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 0.91 (s, 9 H, CH_3), 1.25 (s, 9 H, CH_3), 7.14 (s, 1 H, OH), 7.98 (s, 1 H, OH) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 26.7 [$C(CH_3)_3$], 26.9 [$C(CH_3)_3$], 34.3 [$C(CH_3)_3$], 37.1 [$C(CH_3)_3$], 103.0 (O−C−OH), 131.5 (C=C−OH), 177.5 (=C−O−), 197.3 (C=O) ppm. HRMS (positive EI): calcd. for $C_{12}H_{20}O_4$ $[M]^+$ 228.1362; found 228.1342 (−2.0 mmu). MS (positive EI): *m*/*z* = 228 $[M]^+$, 143 $[M - C_5H_9O]^+$, 57 $[C_4H_9]^+$. $C_{12}H_{20}O_4$ (228.28): calcd. C 63.14, H 8.83; found C 63.26, H 8.72.

2,5-Bis(furan-2-yl)-2,4-dihydroxyfuran-3(2*H*)-one (21): Reaction mixture: furan-2-ylglyoxal[16] (6.30 g, 50.7 mmol), KCN (245 mg, 3.76 mol), ethanol (40 mL), water (1 mL). Orange solid, yield 66% (4.16 g, 16.8 mmol), decomposition > 180 °C. ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 6.47 (m, 1 H, Ar-H), 6.54 (m, 1 H, Ar-H), 6.80−6.81 (m, 1 H, Ar-H), 7.28 (m, 1 H, Ar-H), 7.65 (m, 1 H, Ar−H), 8.04 (m, 1 H, Ar-H), 8.58 (s, 1 H, OH), 9.57 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 97.5 (O−C−OH), 109.1 (CH_{ar}), 110.5 (CH_{ar}), 113.1 (CH_{ar}), 116.5 (CH_{ar}), 130.0 (C), 143.3 (C), 143.7 (CH_{ar}), 146.7 (CH_{ar}), 149.7 (C), 156.2 (C), 191.0 (C=O) ppm. HRMS (positive EI): calcd. for $C_{12}H_8O_6$ $[M]^+$ 248.0321; found 248.0292 (−2.9 mmu). MS (positive EI): *m*/*z* = 248 $[M]^+$, 220 $[M - CO]^+$, 153 $[C_7H_5O_4]^+$, 95 $[C_5H_3O_2]^+$. IR (KBr): $\tilde{\nu}$ = 3437, 3123, 1452, 1306, 1086, 780 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 242 (3.92), 318 (3.88), 418 (4.14) nm. $C_{12}H_8O_6$ (248.19): calcd. C 58.07, H 3.25; found C 58.01, H 3.39.

2,4-Dihydroxy-2,5-bis(thiophen-2-yl)furan-3(2*H*)-one (22): Reaction mixture: thiophen-2-ylglyoxal[17] (16.0 g, 114 mmol), KCN (800 mg, 12 mmol), ethanol (65 mL), water (5 mL). Orange solid, yield 46% (7.42 g, 26.5 mmol), m.p. 193−196 °C. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 7.02−7.03 (m, 1 H, Ar-H), 7.11 (m, 1 H, Ar-H), 7.33 (m, 1 H, Ar-H), 7.54−7.55 (m, 1 H, Ar-H), 7.85−7.86 (m, 1 H, Ar-H), 8.00−8.02 (m, 1 H, Ar-H), 8.62 (s, 1 H, OH), 9.74 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 100.1 (O−C−OH), 125.4 (CH_{ar}), 127.0 (CH_{ar}), 127.0 (CH_{ar}), 128.7 (CH_{ar}), 129.3 (C), 129.7 (CH_{ar}), 130.2 (C), 132.4 (CH_{ar}), 140.4 (C), 160.0 (C), 191.5 (C=O) ppm. HRMS (positive EI): calcd. for $C_{12}H_8O_4S_2$ $[M]^+$ 279.9864; found 279.9866 (0.2 mmu). MS (positive EI): *m*/*z* = 280 $[M]^+$, 169 $[C_7H_5O_3S]^+$, 111 $[C_5H_3OS]^+$. IR (KBr): $\tilde{\nu}$ = 3427, 3104, 1408, 1270, 1061, 731 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 240 (3.61), 260 (3.53), 328 (3.69), 422 (4.00) nm. $C_{12}H_8O_4S_2$ (280.31): calcd. C 51.42, H 2.88, S 22.87; found C 51.47, H 3.03, S 22.92.

2,4-Dihydroxy-2,5-bis(selenophen-2-yl)furan-3(2*H*)-one (23): Reaction mixture: selenophen-2-ylglyoxal (1.92 g, 10.3 mmol), KCN (80 mg, 1.2 mol), ethanol (10 mL), water (1 mL). Brown-red solid, yield 39% (755 mg, 2.02 mmol), m.p. 192−194 °C. ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 7.24 (m, 1 H, Ar-H), 7.28 (m, 1 H, Ar-H), 7.54 (m, 1 H, Ar-H), 8.00 (m, 1 H, Ar-H), 8.17 (m, 1 H, Ar-H), 8.56 (s, 1 H, OH), 8.66−8.67 (m, 1 H, Ar-H), 9.88 (s, 1 H, OH) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 101.2 (O−C−OH), 127.1 (CH_{ar}), 129.2 (CH_{ar}), 129.3 (C), 130.5 (CH_{ar}),

Table 4. Crystal data and structure refinement for **17**, **29**, **30** and **31** (from acetone and acetonitrile)

	17	**29**	
Empirical formula	$C_{24}H_{28}O_4$	$C_{40}H_{60}O_{12}$	
Formula mass	380.46	732.88	
Wavelength [Å]	0.71073	0.71073	
Crystal system	triclinic	monoclinic	
Space group	$P\bar{1}$	$P2_1/c$	
Temperature [K]	223(2)	200(2)	
Z	2	2	
a [Å]	6.300(2)	15.2111(7)	
b [Å]	12.370(5)	7.5574(4)	
c [Å]	14.641(7)	18.8004(10)	
α [°]	111.59(3)	90	
β [°]	95.89(3)	111.2310(10)	
γ [°]	103.34(3)	90	
V [Å^3]	1009.9(7)	2014.54(18)	
$D_{calcd.}$ [g/cm^3]	1.251	1.208	
Absorption coefficient μ [mm^{-1}]	0.084	0.088	
Max./min. transmission	0.9875/0.9632	1.00/0.75	
Crystal shape	prism	plate	
Crystal size [mm]	0.45 × 0.20 × 0.15	0.45 × 0.32 × 0.03	
θ range for data collected [°]	2.84−27.97	1.44−25.56	
Index ranges	$0 \le h \le 8$ $-16 \le k \le 15$ $-19 \le l \le 19$	$-18 \le h \le 18$ $-9 \le k \le 9$ $-22 \le l \le 22$	
Reflections collected	5289	14347	
Independent reflections [R(int)]	4852 (0.0121)	3501 (0.0498)	
Observed reflections	3496	2173	
Data/restraints/parameters	4852/0/365	3501/2/351	
Goodness-of-fit on F^2	1.033	1.02	
$R(F)$	0.038	0.056	
$R_W(F^2)$	0.097	0.136	
$\Delta\rho_{max.}/\Delta\rho_{min.}$ [e·Å^{-3}]	0.294/−0.303	0.31/−0.34	
	30	**31** (acetone)	**31** (acetonitrile)
Empirical formula	$C_{27}H_{34}O_6$	$C_{36}H_{44}O_{10}\cdot 2\ C_3H_6O$	$C_{36}H_{44}O_{10}$
Formula mass	454.54	752.87	636.71
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/n$	$P2_1/n$
Temperature [K]	100(2)	113	100
Z	2	4	2
a [Å]	6.0022(4)	14.2242(2)	15.139(2)
b [Å]	16.881(1)	18.4533(3)	6.4997(8)
c [Å]	12.2030(9)	15.5470(2)	16.698(2)
α [°]	90	90	90
β [°]	103.123(1)	99.338(1)	94.693(2)
γ [°]	90	90	90
V [Å^3]	1204.2(1)	4026.8(1)	1637.5(3)
$D_{calcd.}$ [g/cm^3]	1.254	1.24	1.291
Absorption coefficient μ [mm^{-1}]	0.087	0.09	0.094
Max./min. transmission	0.98/0.97	0.99/0.96	0.98/0.97
Crystal shape	polyhedron	plate	polyhedron
Crystal size [mm]	0.35 × 0.33 × 0.20	0.45 × 0.3 × 0.15	0.36 × 0.25 × 0.21
θ range for data coll. [°]	1.71 to 28.31	1.7 to 28.3	2.45 to 28.34
Index ranges	$-8 \le h \le 7$ $-22 \le k \le 22$ $-16 \le l \le 16$	$-18 \le h \le 18$ $-24 \le k \le 24$ $-20 \le l \le 20$	$-20 \le h \le 20$ $-8 \le k \le 8$ $-22 \le l \le 22$
Reflections collected	16473	38408	16002
Independent reflections [R(int)]	5962 (0.0388)	37796 (0.062)	4026 (0.0223)
Observed reflections	5695	6433	3565
Data/restraints/parameters	5962/1/434	37796 (0.062)	4026/0/296
Goodness-of-fit on F^2	1.05	0.99	1.02
$R(F)$	0.032	0.045	0.042
$R_W(F^2)$	0.079	0.098	0.111
$\Delta\rho_{max.}/\Delta\rho_{min.}$ [e·Å^{-3}]	0.28/−0.17	0.30/−0.20	0.42/−0.20

130.9 (CH_{ar}), 132.8 (CH_{ar}), 133.6 (C), 139.4 (CH_{ar}), 147.0 (C), 161.5 (C), 191.3 (C=O) ppm. HRMS (positive EI): calcd. for $C_{12}H_8O_4{}^{80}Se_2$ $[M]^+$ 375.8753; found 375.8756 (0.3 mmu). MS (positive EI): *m/z* = 378, $[C_{12}H_8O_4{}^{82}Se^{80}Se]^+$, 376 $[C_{12}H_8O_4{}^{80}Se_2]^+$, 374 $[C_{12}H_8O_4{}^{82}Se^{78}Se]^+$, 372 $[C_{12}H_8O_4{}^{80}Se^{76}Se]^+$, 219 $[C_7H_5O_3{}^{82}Se]^+$, 217 $[C_7H_5O_3{}^{80}Se]^+$, 215 $[C_7H_5O_3{}^{78}Se]^+$, 213 $[C_7H_5O_3{}^{76}Se]^+$, 161 $[C_5H_3O{}^{82}Se]^+$, 159 $[C_5H_3O{}^{80}Se]^+$, 157 $[C_5H_3O{}^{78}Se]^+$, 155 $[C_5H_3O{}^{76}Se]^+$. IR (KBr): $\tilde{\nu}$ = 3094, 1414, 1258, 1046, 720 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 256 (3.86), 346 (3.93), 428 (4.24) nm. $C_{12}H_8O_4Se_2$ (374.11): calcd. C 38.53, H 2.16; found C 38.50, H 2.32.

Selenophen-2-ylglyoxal: This compound was synthesized according to the procedure for the glyoxal derivative **15**. Reaction mixture: 2-Acetylselenophene[15] (2.37 g, 13.7 mmol), selenium(IV) oxide (2.12 g, 21.0 mmol), dioxane (12 mL), water (1.5 mL). Reaction time 12 h.

Furan-2-ylglyoxal, thiophen-2-ylglyoxal and selenophen-2-ylglyoxal were characterized as quinoxaline derivatives, according to this general procedure: 1,2-phenylenediamine was added to a solution of freshly distilled glyoxal derivative in dioxane. After the mixture had been stirred at 100 °C for 5 h, the solvent was removed and the residue was purified by column chromatography on silica gel.

2-(Furan-2-yl)quinoxaline: Reaction mixture: furan-2-ylglyoxal[16] (1.07 g, 8.6 mmol), 1,2-phenylenediamine (0.93 g, 8.6 mmol), dioxane (20 mL). Elution with petroleum ether/diethyl ether (1:1). Pale-pink solid, yield 86% (1.45 g, 7.4 mmol), m.p. 96−98 °C. ^1H NMR (500 MHz, CD_2Cl_2): δ = 6.64−6.65 (m, 1 H, Ar-H), 7.31−7.32 (m, 1 H, Ar-H), 7.68−7.77 (m, 2 H, Ar-H), 7.69 −7.70 (m, 1 H, Ar-H), 8.02−8.05 (m, 2 H, Ar-H), 9.23 (s, 1 H, N=CH) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 111.9 (CH_{ar}), 112.8 (CH_{ar}), 129.4 (CH_{ar}), 129.5 (2 CH_{ar}), 130.7 (CH_{ar}), 141.7 (C_{ar}), 142.3 (C_{ar}), 142.4 (CH_{ar}), 144.2 (C_{ar}), 145.3 (CH_{ar}), 152.2 (C_{ar}) ppm. HRMS (positive EI): calcd. for $C_{12}H_8N_2O$ $[M]^+$ 196.0636; found 196.0643 (0.7 mmu). MS (positive EI): *m/z* = 196 $[M]^+$, 169 $[M - HCN]^+$. IR (KBr): $\tilde{\nu}$ = 3436, 3136, 1552, 1497, 1082, 758 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 254 (4.14), 262 (4.19), 276 (4.24), 284 (4.31), 342 (4.04), 356 (4.16), 368 (4.14) nm. $C_{12}H_8N_2O$ (196.20): calcd. C 73.46, H 4.11, N 14.28; found C 73.48, H 4.28, N 14.30.

2-(Thiophen-2-yl)quinoxaline: Reaction mixture: thiophen-2-ylglyoxal[17] (1.56 g, 11.1 mmol), 1,2-phenylenediamine (1.20 g, 11.1 mmol), dioxane (23 mL). Elution with petroleum ether/diethyl ether (3:1). Pale yellow solid, yield 79% (1.83 g, 8.7 mmol), m.p. 110−112 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.16−7.18 (m, 1 H, Ar-H), 7.51−7.52 (m, 1 H, Ar-H), 7.64−7.68 (m, 1 H, Ar-H), 7.70−7.73 (m, 1 H, Ar-H), 7.82−7.83 (m, 1 H, Ar-H), 8.03−8.05 (m, 2 H, Ar-H), 9.20 (s, 1 H, N=CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 127.1 (CH_{ar}), 128.6 (CH_{ar}), 129.2 (2 CH_{ar}), 129.3 (CH_{ar}), 129.9 (CH_{ar}), 130.5 (CH_{ar}), 141.4 (C_{ar}), 142.1 (CH_{ar}), 142.2 (C_{ar}), 142.3 (C_{ar}), 147.5 (C_{ar}) ppm. HRMS (positive EI): calcd. for $C_{12}H_8N_2S$ $[M]^+$ 212.0408; found 212.0396 (−1.2 mmu). MS (positive EI): *m/z* = 212 $[M]^+$, 185 $[M - HCN]^+$, 109 $[C_5H_3NS]^+$, 76 $[C_6H_4]^+$. IR (KBr): $\tilde{\nu}$ = 3436, 1548, 1428, 1320, 1238, 762, 722, 707 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 276 (4.30), 286 (4.27), 342 (4.10), 356 (4.20), 370 (4.17) nm. $C_{12}H_8N_2S$ (212.26): calcd. C 67.90, H 3.80, N 13.20, S 15.10; found C 67.84, H 3.86, N 13.10, S 14.91.

2-(Selenophen-2-yl)quinoxaline: Reaction mixture: selenophen-2-ylglyoxal (670 g, 3.5 mmol), 1,2-phenylenediamine (381 mg, 3.5 mmol), dioxane (6 mL). Elution with petroleum ether/diethyl ether (1:1). Pale-yellow solid, yield 74% (667 mg, 2.57 mmol), m.p. 112 °C. ^1H NMR (300 MHz, CD_2Cl_2): δ = 7.44−7.48 (m, 1 H, Ar-H), 7.69−7. 70 (m, 1 H, Ar-H), 7.71−7.75 (m, 1 H, Ar-H), 7.99−8.06 (m, 3 H, Ar-H), 8.21−8.23 (m, 1 H, Ar-H), 9.26 (s, 1 H, N=CH) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 129.1 (CH_{ar}), 129.3 (CH_{ar}), 129.4 (2 CH_{ar}), 130.7 (CH_{ar}), 131.5 (CH_{ar}), 135.5 (CH_{ar}), 141.7 (CH_{ar}), 141.8 (C_{ar}), 142.5 (C_{ar}), 148.9 (C_{ar}), 149.4 (C_{ar}) ppm. HRMS (positive EI): calcd. for $C_{12}H_8N_2{}^{82}Se$ $[M]^+$ 261.9854; found 261.9854 (0.0 mmu). MS (positive EI): *m/z* = 262 $[C_{12}H_8N_2{}^{82}Se]^+$, 260 $[C_{12}H_8N_2{}^{80}Se]^+$, 258 $[C_{12}H_8N_2{}^{78}Se]^+$, 256 $[C_{12}H_8N_2{}^{76}Se]^+$, 233 $[C_{11}H_7N^{80}Se]^+$. IR (KBr): $\tilde{\nu}$ = 3440, 1549, 1433, 1314, 933, 792, 769, 694 cm^{-1}. UV/Vis (CH_2Cl_2): $\lambda_{max.}$ (log ε) = 242 (4.00), 284 (4.30), 326 (3.94), 344 (4.08), 358 (4.14), 372 (4.12) nm. $C_{12}H_8N_2Se$ (259.16): calcd. C 55.61, H 3.11, N 10.81; found C 55.77, H 3.26, N 10.77.

X-ray Crystallography: Data were collected with Bruker Smart CCD and Bruker APEX diffractometers (Mo-K_α radiation, graphite monochromator). Details are listed in Table 4. CCDC-231944 (**17**), -231945 (**29**), -231946 (**30**), -231947 [**31** (acetone)], and -231948 [**31** (acetonitrile)] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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