Quinaphthin, a Binaphthyl Quinonoid Secondary Metabolite Produced by *Helicoon richonis*

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The aero-aquatic fungus *Helicoon richonis* (Boudier) Linder produces quinaphthin **4**, an $\alpha\beta'$-binaphthyl quinone constituted by union of juglone at position 8 to 3-hydroxyjuglone at position 2. The compound exists as a 6-membered cyclic hemiketal {systematic name 3,6a,9-trihydroxydibenzo[*b*,*kl*]xanthene-4,8,13(6a*H*)-trione}. Methyl iodide in the presence of silver oxide converts quinaphthin into the trimethyl derivative of an isomer of the compound. The structures of both compounds have been determined by X-ray crystallographic analysis.

Helicoon richonis (Boudier) Linder is an aero-aquatic hyphomycete found in decaying wood and leaves in shallow non-saline water. From this fungus we have obtained a red crystalline compound to which we have given the trivial name quinaphthin.[1]

Results and Discussion

Quinaphthin contained only the elements carbon, hydrogen and oxygen. The UV spectrum of a methanol solution of the compound showed intense absorption in the region 210–270 nm but the curve was almost flat except for two emergent peaks at 215 and 231 nm; there was a band of somewhat lower intensity at 420 nm. The IR spectrum (KBr disc) showed hydroxyl absorption (ν_{max}/cm^{-1} 3550–3220 cm^{-1}) and was particularly complex in the carbonyl and carbon–carbon double-bond region (1658, 1654, 1640, 1630, 1612, 1605, 1583 and 1566 cm^{-1}). The ^{1}H NMR spectrum of a solution in deuteriated tetrahydrofuran contained only four groups of signals consisting of three broad singlets at δ 6.86, 11.51 and 12.42, and a complex region δ 6.85–7.75. The singlets disappeared on addition of D_2O to the solution. Comparison of intensities showed the ratio of hydroxyl protons to the remainder to be 3:7.

Determination of the molecular weight initially proved to be difficult. The electron impact mass spectrum (70 eV) gave ions at *m*/*z* 503, 429, 402 and 362. The field desorption mass spectrum showed two prominent ions at *m*/*z* 706 and 688. The fast atom bombardment (xenon) positive ion spectrum showed ions at *m*/*z* 745, 732 and 571. The negative ion spectrum was simpler but had ions at *m*/*z* 761, 745, 729 and 714. The problem was solved by methylation of quinaphthin.

Treatment of quinaphthin with diazomethane in ether or with methyl iodide in potassium carbonate–acetone gave complex mixtures. Fortunately, the reaction with methyl iodide and silver oxide in ethyl acetate proved simpler and gave a trimethylated derivative (M^+, 404); its ^{1}H NMR spectrum in deuteriochloroform had three singlets at δ 3.28, 3.97 and 4.0 (each of intensity 3 H) and the remaining protons (intensity 7 H) at δ 6.65–8.69. The electron impact mass spectrum of quinaphthin at 20 eV (110 °C) gave a highest mass ion *m*/*z* of 362. Taken together with the elemental analysis this gave, uniquely, the molecular formula $C_{20}H_{10}O_7$. It should be noted that an EI mass spectrum at 70 eV gave additional mass ions between *m*/*z* 362 and 503 but these were attributed to ion-molecule interactions.

The molecular formulae of these compounds suggested the likelihood of their being binaphthylquinones but the NMR data could not be reconciled with this. We resorted to the X-ray analysis of the highly crystalline methylated quinaphthin which was found to have structure **1** (Fig. 1). The ketal formulation explained the previous anomaly in the ^{1}H NMR spectrum of one methoxy (δ 3.28) being well separated from the other two (δ 3.97 and 4.00).

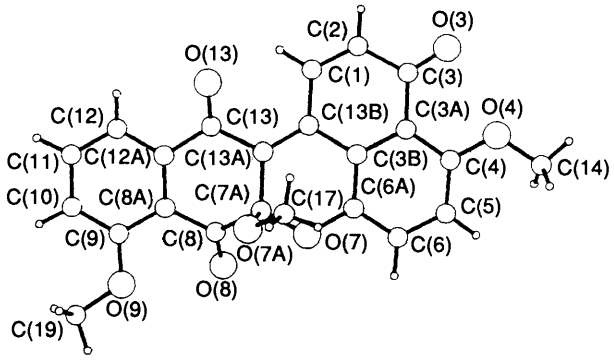
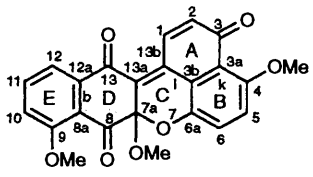
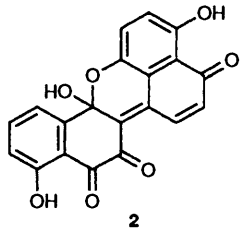


Fig. 1 X-Ray molecular crystal structure of trimethylated quinaphthin **1**, showing the atom labelling

Since quinaphthin has a non-phenolic hydroxyl group (δ 6.86) and two phenolic hydroxyls (δ 11.51 and 12.42) it seemed reasonable to assume it to be the hemiketal corresponding to **1**. This conclusion, however, had to be abandoned on UV evidence. The UV spectra of natural products containing complex chromophores[2] usually consist of overlapping absorption bands due to charge transfers.[3] Quinaphthin has absorption at 420 nm (ε dm^3 mol^{-1} cm^{-1} 7660) but methylated quinaphthin has no such band. The problem of finding an acceptable formula for quinaphthin can be approached theoretically from **1** (OH in place of OMe) by fission of the heterocyclic ring followed by all possible prototropic tautomerisations and cyclisations to produce 6-membered cyclic hemiketals. This leads to 18 structures but only four have credibility on energy grounds as they are the only ones to possess two aromatic rings. In addition to **1** (OH in place of OMe) they are **2**, **3** and **4**. Formula **2** is essentially an angular modification of **1** and it is difficult to see how its UV absorption could differ markedly from that compound. Formula **3** is that of a 1,2-naphthaquinone and would be expected to show a pronounced M + 2 peak in its mass spectrum[4] due to reduction by adsorbed water in the mass spectrometer. Quinaphthin had no detectable M + 2 peak. The deduction leads to the 1,4-naphthaquinone formula **4** and this was



1 Methylated quinaphthin



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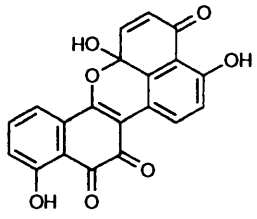

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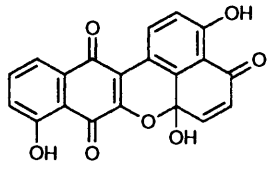


4 Quinaphthin

unequivocally established by X-ray crystallography (Fig. 2). The compound is, therefore, an αβ′-binaphthyl quinone constituted by union of juglone at position 8 and 3-hydroxyjuglone at position 2, which exists in the cyclised (xanthene) form.

The only hemiketal of a natural quinone we found in the literature was that of (+)-skyrin **5** (R = R′ = H). Howard and Raistrick[5] found that hexaacetylskyrin **6** (R = R′ = Ac) on treatment with methanol–sulfuric acid gave a dimethyl derivative, tentatively regarded as **7** (R = Me, R′ = H), which readily reverted to skyrin with acetic acid or aqueous sodium hydroxide. Shibata and colleagues[6] advanced formula **8** (R = Me) for the compound and the structure was put beyond doubt by a total synthesis[7] of **7** (R = Me, R′ = H) which was stable. (+)-Skyrin itself crystallises in yellow and orange–red forms[5] and the two give different colour reactions with sulfuric acid. The structure **9** (R = H) of the yellow form, pseudoskyrin, was deduced[8] by its UV spectrum being virtually identical with that of the dimethyl derivative **8** (R = Me) and quite different from that of the usual orange–red form; the latter form has now been shown[9] by its ^{13}C NMR spectrum to have structure **5** (R = R′ = H). Many natural quinones are structurally capable of forming 5-membered ring hemiketals but evidently do not do so. In skyrin and quinaphthin the rings are 6-membered.

X-Ray Crystal Structures of **1** *and* **4**.—The bond lengths and angles for both structures are displayed comparatively in Tables 1 and 2, and the resulting molecular structures are illustrated in Figs. 1 and 2. The bond lengths immediately illustrate the different bonding patterns found within the same ring skeleton in methylated quinaphthin and quinaphthin. For each structure

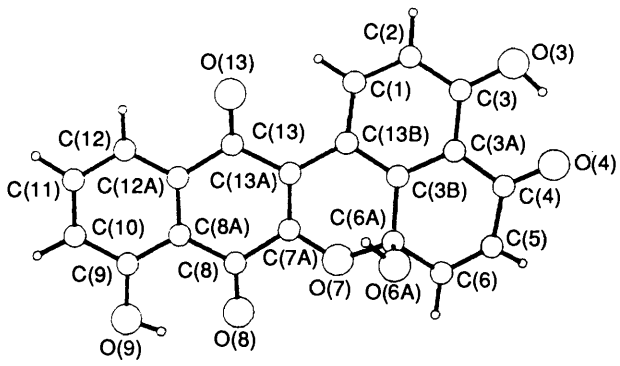
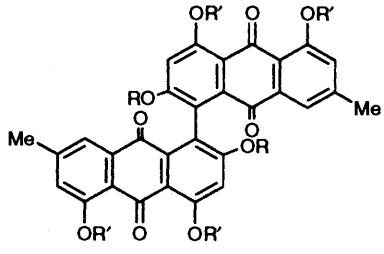
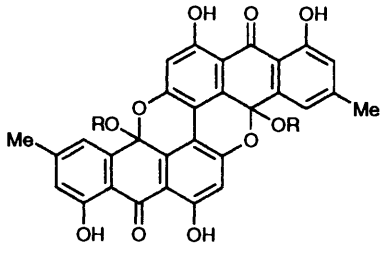


Fig. 2 X-Ray molecular crystal structure of quinaphthin **4**, showing the atom labelling



5 R = R′ = H
6 R = R′ = Ac
7 R = Me, R′ = H



8 R = Me
9 R = H

the shortest C–C bond [C(1)–C(2) 1.333 Å in **1** and C(5)–C(6) 1.324 Å in **4**] is quinonoid in character; while the next shortest [C(13a)–C(13b) 1.363 Å and C(7a)–C(13a) 1.362 Å respectively] is quinonoid but also a member of a ring including a saturated carbon atom. There are then 12 bonds clearly aromatic in character (average 1.395 Å), but in different positions within **1** and **4**. For each structure there follow seven bonds between sp^2 hybridised carbons that are nominally single but conjugated (average 1.473 Å) and again at different sites in **1** and **4**. Finally there are two bonds involving sp^3 hybridised carbons (average 1.516 Å) also at different sites.

The carbonyl C=O bond lengths are also of interest. All are slightly long because of conjugation. The shortest [C(8)–O(8) in **1** 1.206 Å] is only conjugated on one side. Three more, close to 1.218 Å, are longer because they are conjugated on both sides. Finally there are two [C(4)–O(4) and C(8)–O(8) both in **4**], close to 1.235 Å, which are longer still, presumably because they are involved in strong intramolecular hydrogen bonds.

In contrast to the bond lengths which show clear differences between the two structures, the bond angles are notable for their similarity between methylated quinaphthin **1** and quinaphthin **4** despite the changed bonding patterns, away from the enforced distortions at the differing sites of the sp^3 hybridised carbon atom. These are presumably controlled by packing rather than bonding considerations. This is most obviously seen in the exocyclic bond angles at C(13a) and C(13b) in both structures

Table 1 Bond lengths (Å) for methylated quinaphthin **1** and quinaphthin **4** with standard deviations in parentheses

		1	4
C(1)	C(2)	1.333(2)	1.373(5)
C(1)	C(13b)	1.453(2)	1.409(5)
C(2)	C(3)	1.469(2)	1.388(5)
C(3)	C(3a)	1.481(2)	1.408(5)
C(3)	O(3)	1.217(2)	1.348(4)
C(3a)	C(3b)	1.418(2)	1.408(5)
C(3a)	C(4)	1.408(2)	1.468(5)
C(3b)	C(6a)	1.392(2)	1.508(5)
C(3b)	C(13b)	1.456(2)	1.391(5)
C(4)	C(5)	1.394(2)	1.464(6)
C(4)	O(4)	1.360(2)	1.237(4)
C(5)	C(6)	1.381(2)	1.324(5)
C(6)	C(6a)	1.387(2)	1.500(5)
C(6a)	O(7)	1.371(2)	1.453(4)
C(6a)	O(6a)		1.404(4)
O(7)	C(7a)	1.414(2)	1.352(4)
C(7a)	C(8)	1.546(2)	1.478(5)
C(7a)	C(13a)	1.509(2)	1.362(5)
C(7a)	O(7a)	1.408(2)	
C(8)	C(8a)	1.480(2)	1.461(5)
C(8)	O(8)	1.206(2)	1.233(4)
C(8a)	C(9)	1.407(2)	1.399(5)
C(8a)	C(12a)	1.408(2)	1.403(5)
C(9)	C(10)	1.393(2)	1.393(5)
C(9)	O(9)	1.353(2)	1.361(4)
C(10)	C(11)	1.389(3)	1.371(6)
C(11)	C(12)	1.378(2)	1.402(5)
C(12)	C(12a)	1.392(2)	1.379(5)
C(12a)	C(13)	1.488(2)	1.484(5)
C(13)	C(13a)	1.486(2)	1.491(4)
C(13)	O(13)	1.217(2)	1.220(4)
C(13a)	C(13b)	1.363(2)	1.460(4)
O(4)	C(14)	1.424(2)	
O(7a)	C(17)	1.429(2)	
O(9)	C(19)	1.424(2)	

which are all greater than 123° irrespective of bonding. One of the exocyclic bond angles at both C(3) and C(13) in both structures is also consistently larger than 120°. In contrast, the exocyclic bond angles at C(12a) are significantly less than 120°, and this is also true of the endocyclic angles at C(8).

Both molecules are planar with the one sp^3 hybridised carbon atom [C(7a) in **1** 0.58 Å and C(6a) in **4** 0.49 Å] the furthest cyclic atom from the mean plane, with their respective oxygen substituents [O(7a) 1.90 Å and O(6a) 1.88 Å] completely out of and approximately perpendicular to the plane. Quinaphthin **4** is significantly more planar than the methylated quinaphthin **1** structure. Closer examination of the individual rings within both molecules showed that all fully conjugated rings are almost perfectly planar, however, in quinaphthin **4** the contiguous conjugated rings D and E are coplanar, whereas the corresponding rings A and B in **1** are inclined at 3° to each other. For both molecules the planar extremities are not themselves coplanar, but significantly inclined to each other (angle between A and E 17.9° and between B and E 16.4° in **1** and between AB and E 15.0° in **4**). All remaining rings incorporate an sp^3 hybridised carbon [C(7a) in **1** and C(6a) in **4**]. In **1** ring C adopts a half-chair conformation with O(7) and C(7a) out-of-plane, and ring D is an envelope with C(7a) as the flap. In **4** rings B and C adopt a shallow boat conformation with C(6a) and C(4) and C(13a), respectively, at the bow and stern of the boat.

In the crystal of quinaphthin **4** the molecule forms two intramolecular hydrogen bonds [O(3) H···O(4)] 2.604 Å, and [O(9) H···O(8)] 2.603 Å, and one intermolecular hydrogen bond [O(6) H···O(9) ($1 - x$, $0.5 + y$, $0.5 - z$)] 2.822 Å. The hydrogen atoms located in the difference map fitted correctly into these bonds.

Table 2 Bond angles in degrees for methylated quinaphthin **1** and quinaphthin **4** with standard deviations in parentheses

			1	4
C(2)	C(1)	C(13b)	121.2(1)	121.7(3)
C(1)	C(2)	C(3)	123.5(1)	120.4(3)
C(2)	C(3)	C(3a)	117.0(1)	119.9(3)
C(2)	C(3)	O(3)	118.6(1)	118.8(3)
C(3a)	C(3)	O(3)	124.3(2)	121.4(3)
C(3)	C(3a)	C(3b)	118.4(1)	118.5(3)
C(3)	C(3a)	C(4)	122.7(1)	121.2(3)
C(3b)	C(3a)	C(4)	118.8(1)	120.0(3)
C(3a)	C(3b)	C(6a)	119.6(1)	118.9(3)
C(3a)	C(3b)	C(13b)	122.0(1)	121.9(3)
C(6a)	C(3b)	C(13b)	118.3(1)	119.0(3)
C(3a)	C(4)	C(5)	120.0(1)	117.5(3)
C(3a)	C(4)	O(4)	117.3(1)	121.4(4)
C(5)	C(4)	O(4)	122.7(1)	121.0(4)
C(4)	C(5)	C(6)	120.8(1)	122.8(3)
C(5)	C(6)	C(6a)	119.8(1)	121.1(4)
C(3b)	C(6a)	C(6)	121.0(1)	114.1(3)
C(3b)	C(6a)	O(7)	122.6(1)	109.6(3)
C(3b)	C(6a)	O(6a)		112.1(3)
C(6)	C(6a)	O(7)	116.3(1)	105.9(3)
C(6)	C(6a)	O(6a)		105.8(3)
O(7)	C(6a)	O(6a)		109.0(3)
C(6a)	O(7)	C(7a)	121.1(1)	116.6(2)
O(7)	C(7a)	C(8)	106.4(1)	112.3(3)
O(7)	C(7a)	C(13a)	113.8(1)	123.5(3)
O(7)	C(7a)	O(7a)	110.6(1)	
C(8)	C(7a)	C(13a)	111.1(1)	124.1(3)
C(8)	C(7a)	O(7a)	102.0(1)	
C(13a)	C(7a)	O(7a)	112.2(1)	
C(7a)	C(8)	C(8a)	115.0(1)	117.7(3)
C(7a)	C(8)	O(8)	120.7(1)	120.1(3)
C(8a)	C(8)	O(8)	124.3(1)	122.2(3)
C(8)	C(8a)	C(9)	122.1(1)	120.6(3)
C(8)	C(8a)	C(12a)	118.7(1)	120.0(3)
C(9)	C(8a)	C(12a)	119.2(1)	119.4(3)
C(8a)	C(9)	C(10)	119.4(1)	120.2(3)
C(8a)	C(9)	O(9)	117.3(1)	122.3(3)
C(10)	C(9)	O(9)	123.3(1)	117.5(3)
C(9)	C(10)	C(11)	120.4(2)	119.4(3)
C(10)	C(11)	C(12)	120.8(2)	121.5(3)
C(11)	C(12)	C(12a)	119.6(2)	119.0(3)
C(8a)	C(12a)	C(12)	120.4(1)	120.5(3)
C(8a)	C(12a)	C(13)	122.0(1)	121.1(3)
C(12)	C(12a)	C(13)	117.6(1)	118.4(3)
C(12a)	C(13)	C(13a)	118.3(1)	118.7(3)
C(12a)	C(13)	O(13)	119.7(1)	120.2(3)
C(13a)	C(13)	O(13)	122.0(1)	121.1(3)
C(7a)	C(13a)	C(13)	114.1(1)	118.3(3)
C(7a)	C(13a)	C(13b)	122.1(1)	118.5(3)
C(13)	C(13a)	C(13b)	123.7(1)	123.0(3)
C(1)	C(13b)	C(3b)	117.6(1)	117.4(3)
C(1)	C(13b)	C(13a)	123.4(1)	125.0(3)
C(3b)	C(13b)	C(13a)	118.9(1)	117.3(3)
C(4)	O(4)	C(14)	118.3(1)	
C(7a)	O(7a)	C(17)	116.3(1)	
C(9)	O(9)	C(19)	117.6(1)	

Fractional atomic coordinates, thermal parameters and mean-plane calculations for both methylated quinaphthin **1** and quinaphthin **4** have been deposited with the Cambridge Crystallographic Data Centre.*

Experimental

Methylated Quinaphthin, 4,7a-9-*Trimethoxydibenzo*[b,kl]-*xanthene*-3,8,13 (7aH)-*trione* **1**.—Quinaphthin (50 mg) was dissolved in ethyl acetate (40 cm^3) with gentle warming. Silver oxide (4 g) and methyl iodide (6 cm^3) were added to the mixture

* For details see *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

which was then refluxed for 40 min. After being cooled and filtered the filtrate was evaporated to dryness on a rotary film evaporator. The residue was dissolved in dichloromethane (5 cm^3) and portions (2 mm^3) were subjected to TLC analysis using (a) silica gel plates (Merck 5735) with developing solvent tetrahydrofuran–ethyl acetate–acetic acid (20:80:1, v/v/v) and (b) reverse phase plates (Whatman KC18F) with acetone–water (5:3, v/v) as developing solvent. No quinaphthin remained. Three products were detected: (1) cherry red R_F 0.41, system (a) and R_F 0.48 system (b); (2) bright yellow R_F 0.48 (a) and R_F 0.57 (b); (3) ochre yellow R_F 0.34 (a) and R_F 0.65 (b). The main products were (1) and (2); subsequent work showed that (2) was a mixture which was not further investigated. HPLC on silica (Spherisorb S1OW) using a gradient of 2.5–5.0% (v/v) of ethyl acetate in dichloromethane for 40 min followed by 25% (v/v) ethyl acetate gave methylated quinaphthin **1** which crystallised in beautiful rhombic rods. When heated the compound decomposed without prior melting; *m/z* (70 eV E.I.) 404 (M^+), 389, 374 (base peak) and 359; λ_{max}(MeOH)/nm 322sh (ε/dm^3 mol^{-1} cm^{-1} 16 400) and 342 (18 600); δ_H(Bruker WH-360 spectrometer, 360 MHz, $CDCl_3$; Me_4Si) 3.28 (s, 7a-OMe), 3.97 (s, 4-OMe), 4.00 (s, 9-OMe), 6.65 (d, ^3J 10.3, 2-H), 7.22 (d, ^3J 9.2, 5-H), 7.32 (dd, ^3J 8.4, ^4J 0.7, 10-H), 7.49 (d, ^3J 9.2, 6-H), 7.71 (dd, ^3J 8.3, 7.8, 11-H), 7.84 (dd, ^3J 7.8, ^4J 1.0, 12-H) and 8.69 (d, ^3J 10.3, 1-H).

Quinaphthin, 3,6a,9-*Trihydroxydibenzo*[b,kl]*xanthene*-4,8,13 (6aH)-*trione* **4**.—The isolation and biological properties of this compound are given in ref. 1 (Found: C, 65.6, 66.1; H, 2.9, 3.0. $C_{20}H_{10}O_7$ requires C, 66.30; H, 2.78%). When heated the compound decomposed without melting; λ_{max} (MeOH)/nm 215 (ε/dm^3 mol^{-1} cm^{-1} 28 400), 231 (28 300) and 420 (7660); δ_H(JEOL PS/PFT-100 spectrometer, 100 MHz, [$^2H_8$]-THF; Me_4Si) 6.85 (d, ^3J 10.3, 5-H), 7.15 (d, ^3J 10.3, 6-H), 7.27 [d, ^3J ~ 8, ^4J 1 (approximate due to overlap), 10-H], 7.28 (d, ^3J 8.1, 2-H), 7.60 (dd, ^3J 7.6, ^4J 1.7, 12-H), 7.71 (d, ^3J 8.1, 1-H), 7.75 (t, ^3J 7.6, 7.6, 11-H), 6.86 (br s, 6a-OH), 11.51 (br s, 3-OH) and 12.42 (br s, 9-OH).

Crystallographic Analyses of Methylated Quinaphthin **1** *and Quinaphthin* **4**.—*Crystal data.* Methylated quinaphthin, $C_{23}H_{16}O_7$, M = 404.38, Triclinic, a = 8.878(1), b = 10.177(1), c = 11.830(1) Å, α = 91.86(1), β = 102.07(1), γ = 121.02(1)°, U = 883.02 $Å^3$, Z = 2, D_c = 1.52 g cm^{-3}, $F(000)$ = 420, Space group $P\bar{1}$, Cu-Kα radiation, λ = 1.54178 Å, μ(Cu-K_α) = 9.6 cm^{-1}.

Quinaphthin, $C_{20}H_{10}O_7$, M = 362.30, Monoclinic, a = 9.808(1), b = 8.542(1), c = 17.815(1) Å, β = 95.30(1)°, U = 1486.32 $Å^3$, Z = 4, D_c = 1.62 g cm^{-3}, $F(000)$ = 744, Space group $P2_1/c$, Cu-Kα radiation, λ = 1.54178 Å, μ(Cu-Kα) = 10.7 cm^{-1}.

Data collection and processing. For each structure a crystal was selected and mounted on an Enraf-Nonius CAD4 diffractometer and 25 reflections were used to determine accurate lattice parameters. Intensity data were collected for $1° < \theta < 76°$, (**1**), and $1° < \theta < 66°$, (**4**), using a $\omega/2\theta$ scan, and totals of 3677 (**1**) and 2591 (**4**) independent reflections were measured of which 3241 and 1628 respectively had $I > 3\sigma(I)$ and were considered observed and used in the subsequent refinement. Periodic measurement of standard reflections throughout data collection demonstrated their stability. The data were corrected for Lorentz and polarisation factors but no absorption corrections were made because of the low values of the linear absorption coefficient. Crystallographic calculations were performed using the CRYSTALS system of programs.[10]

Structure analysis and refinement. The structures were both solved by direct methods using the MULTAN program.[11] Least-squares refinement including anisotropic thermal parameters for non-hydrogen atoms and hydrogen atoms refined isotropically (**1**) but located in a difference Fourier synthesis and included in structure factor calculations without further refinement (**4**), terminated at R 0.0491 (R_w 0.0722) (**1**) and R 0.0464 (R_w 0.0631) (**4**). The final rounds of refinement used weighting schemes based on Chebyshev polynomials.

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