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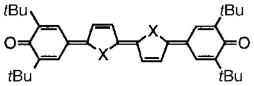
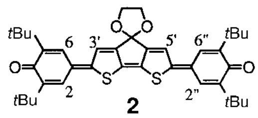
The First Heterotriquinone and Dicyanoheterotriquinone Methide That Undergo a Five-Stage Amphoteric Redox Reaction[**]

Kazuko Takahashi,* Satoshi Fujita, Kimio Akiyama, Misao Miki, and Kazunori Yanagi

In recent years heterocycle-incorporated conjugated molecules possessing interesting electrochemical and optical properties have been widely developed in the field of fundamental molecular and supramolecular chemistry.[1] We have recently synthesized heteroquaterphenoquinones **1a**–**d**, which exhibit an intense absorption band in the near-IR (NIR) region and undergo amphoteric redox reactions.[2] However, these quinones exist in a flexible conformation in solution at around room temperature, and afford unstable anion radicals on electrochemical reduction. Furthermore, they have relatively weak electron-accepting abilities, which are sometimes unfavorable when these quinones are to be employed as functional molecules such as electron-accepting or electron-transporting mediators, and as functional units in supramolecular electric systems that can be modulated by external electrical stimulation.[3] To create a new type of organic redox system that does not have these disadvantages, we have now designed and synthesized the novel heterotriquinone **3** and the novel dicyanoheterotriquinone methide **4**, as the first heterotriquinonoid systems. On the grounds of the enhanced conjugation between the three terminal electron-withdrawing groups, each of these compounds should have a rigid conformation and thus exhibit strong electron-accepting properties, which should facilitate the formation of stable radical anions and radical trianions. Indeed, we have found that **4** exhibits very characteristic electrochemical behavior and strong electron-accepting ability; it undergoes a novel amphoteric five-stage one-electron redox reaction.



1a : X = O, **1b** : X = S
1c : X = Se, **1d** : X = NMe



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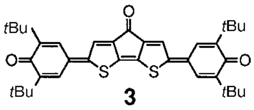

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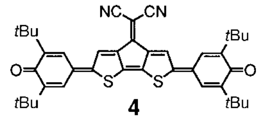

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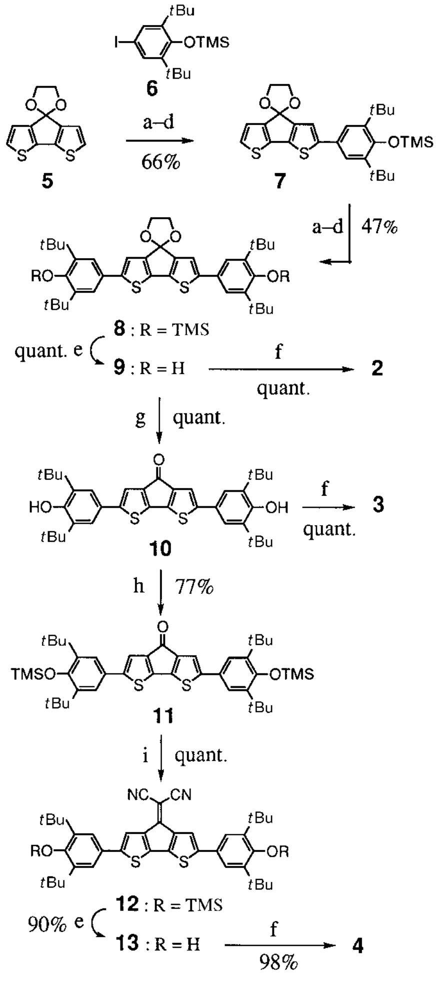
The heterotriquinone **3**, the dicyanoheterotriquinone methide **4**, and the ethylenedioxy derivative **2** (a reference compound for **3** and **4**) were synthesized according to the routes shown in Scheme 1, starting from the reaction of **5**[4]



Scheme 1. Reagents and conditions: a) BuLi (1.0 equiv), diethyl ether, 0°C, 1 h; b) $ZnCl_2$ (1.0 equiv), THF, 0°C, 1.5 h; c) $[PdCl_2(PPh_3)_2]$ (0.5 equiv), THF, DIBAH (0.1 equiv), room temperature, 15 min; d) **6** (1.0 equiv), THF, room temperature, 1 h; e) TBAF (2 equiv), THF, 0°C, 2 min; f) PbO_2 (10 equiv), CH_2Cl_2, room temperature, 30 min; g) conc. HCl/THF (1/10), room temperature, 1 h; h) *N,O*-bistrimethylsilylacetamide (BSA) (ca. 1.2 equiv), CH_3CN, 75°C, 1 h; i) $CH_2(CN)_2$ (1.2 equiv), benzene/piperidine (cat.), reflux, 22 h.

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with **6**.[5] Compounds **2**–**4**[6] are quite stable both in the solid state and in solution in common organic solvents and possess a rigid conformation even in solution, as evident from the inequivalence of the 2/2″ protons and carbon atoms from the 6/6″ positions of the six-membered ring in ^{1}H and ^{13}C NMR spectra. The X-ray crystallographic analysis disclosed that **4** adopts an essentially coplanar conformation (Figure 1).[7] The torsion angle between the dicyanomethylene group and the central 4*H*-cyclopentadithiophene moiety and that between the terminal six-membered rings and this moiety are 2.02° and 2.31°, respectively. Selected spectroscopic data of **2**–**4** are listed in Table 1. The IR frequencies of the carbonyl groups on the six-membered rings of **3** and **4** are higher by 6 and 8 cm^{-1} than that of **2**. The ^{13}C NMR resonances of C-4/4″, C-1/1″, and C-3′/5′ of **3** and **4** appear at lower field than the respective carbon atoms of **2**. These facts indicate that the carbonyl and the dicyanomethylene groups at the C-4′ position exert a significant electron-withdrawing effect on the terminal six-membered rings and that the effect is stronger in the dicyanomethylene than in the carbonyl group. These quinones exhibit a very intense π-π* absorption maximum at 650–700 nm, which is accompanied by a weak n-π* absorption band at 790–890 nm due to the carbonyl groups in the six-membered rings (Table 1). Both the π-π* and n-π* absorption maxima of **4** showed marked bathochromic shifts of 30 and 88 nm, respectively, from those of **2**, while the bathochromic shifts are much smaller for **3**. According to MNDO PM-3 calculations,[8] the LUMO of **4** (−2.764 eV) lies 0.13 eV lower in energy than that of **3** (−2.631 eV) and 0.31 eV lower than that of **2** (−2.454 eV). In contrast, the HOMO of **4** is only 0.07 eV lower in energy than that of **3**. Therefore, the large bathochromic shifts of the π-π* and n-π* bands of **4** can be mainly ascribed to the lowering of the LUMO of **4**. This is also supported by the strong electron-accepting ability of **4** (see below).

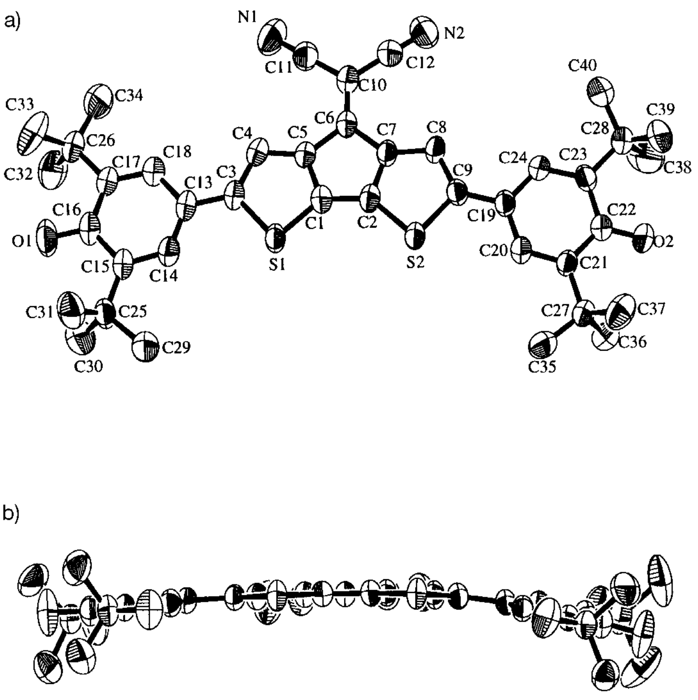


Figure 1. Molecular structure of **4** (ORTEP): a) top view, b) side view.

Interestingly, the electrochemical behavior of **4** is remarkably different from that of **3**. The reduction of **4** occurs in three consecutive reversible one-electron transfer steps, as shown by cyclic voltammetry (Figure 2), affording the stable radical anion ($\mathbf{4}^{\cdot -}$), dianion ($\mathbf{4}^{2-}$), and radical trianion ($\mathbf{4}^{\cdot 3-}$). In contrast, **3** is reduced apparently in a one-step, two-electron transfer process affording the dianion ($\mathbf{3}^{2-}$) at a half-wave reduction potential of −0.44 V vs. standard calomel electrode (SCE), and in a subsequent one-step, one-electron transfer process that affords the radical trianion ($\mathbf{3}^{\cdot 3-}$) at a half-wave reduction potential of −1.37 V vs. SCE (Table 2). By considering that **2** is also reduced apparently in a one-step, two-electron transfer process affording the dianion ($\mathbf{2}^{2-}$) at −0.50 V vs. SCE, the one-electron transfer at −1.37 V in **3** should correspond to the reduction of the carbonyl group in the central five-membered ring. The coalescence of the first

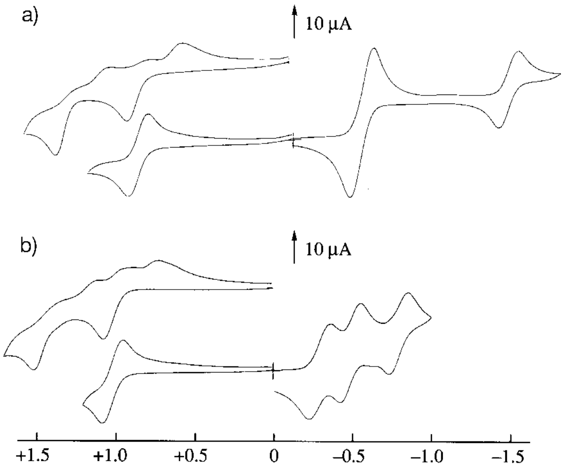


Figure 2. Cyclic voltammograms of a) **3** and b) **4**; compound (1.0 mM), electrolyte: Bu_4NClO_4 (ca. 0.1 M) in CH_2Cl_2 at room temperature, (scan rate: 50 mV s^{-1}), reference electrode: SCE.

Table 1. Spectroscopic data of **2**–**4**.

Compound	^{13}C NMR (CDCl$_3$): δ[a]					IR (KBr): $\tilde{\nu}$ [cm^{-1}]		Vis/NIR (CH$_2$Cl$_2$): λ [nm] (lg ε)	
	C-4/4″	C-1/1″	C-3′/5′	C-4′	C-7′a/7′b	CO(6)[b]	CO(5)[c] or CN	π-π*	n-π*[d]
2	185.42	126.24	117.70	104.68	142.23	1583	–	606 (4.85), 660 (5.29), 718 sh (4.70)	790 sh (3.80)
3	185.54	128.62	120.61	179.53	144.29	1589	1714	615 (4.84), 665 (5.27)	804 br (3.61)
4	185.62	129.27	123.48	149.95	139.71	1591	2225	637 (4.96), 692 (5.15	878 br (3.12)

[a] 150 MHz, SiMe$_4$. [b] The CO frequency of the six-membered ring. [c] The CO frequency of the five-membered ring. [d] This band showed a blue shift on changing the solvent from nonpolar to polar.

Table 2. Oxidation and reduction potentials[a] of **2**–**4** in CH_2Cl_2.

Compound	E_1^{ox}	E_{p2}^{ox}	E_1^{red}	E_2^{red}	E_3^{red}	ΔE_{1-2}^{red}	ΔE_{2-3}^{red}	$E_1^{sum[b]}$
2	+0.88	+1.49	−0.50 (2e)		–	0	–	1.38
3	+0.98	+1.52	−0.44 (2e)		−1.37	0	0.93	1.42
4	+1.01	+1.51	−0.30	−0.50	−0.80	0.20	0.30	1.31

[a] In V vs. SCE, obtained from the cyclic voltammogramm (0.1 M TBAP, scan rate: 50 mV s^{-1}). [b] $E_1^{sum} = E_1^{ox} + (-E_1^{red})$.

and second one-electron reduction potentials in **3** reveals a short life time of **3**$^{\bullet-}$ and a very small Coulomb repulsion[9] in **3**$^{2-}$, thus the bulk of the negative charges in **3**$^{2-}$ should localize on the well-separated oxygen atoms at the six-membered rings, as in **2**$^{2-}$. On the other hand, the Coulomb repulsion in **4**$^{2-}$ is significantly larger than that of **3**$^{2-}$, since the ΔE_{1-2}^{red} ($= E_2^{red} - E_1^{red}$) value of **4** is 0.2 V. This evidence indicates that the negatively charged centers in **4**$^{2-}$ should be located much closer than in **3**$^{2-}$. Moreover, the Coulomb repulsions in **4**$^{2-}$ and **4**$^{\bullet 3-}$ are not significantly different from each other: the difference between the values of ΔE_{1-2}^{red} and ΔE_{2-3}^{red} is not very large (Table 2). These facts indicate that the first one-electron transfer reaction in **4** occurs on the central dicyanomethylene group at −0.30 V (vs. SCE), followed by the stepwise second and third one-electron transfers at each of the oxygen atoms at the six-membered rings. This is remarkable if one considers that the dicyanomethylene group is bound to a cyclopentadienylidene-type unsaturated five-membered ring, which might induce an antiaromatic $4n\pi$ electronic structure and the radical anion might be highly stabilized by the contribution of the aromatic galvinoxyl unit, if the first one-electron reduction occurs at one of the oxygen atoms at the six-membered rings.

The radical anion **4**$^{\bullet-}$ (deep red species) and the radical trianions **4**$^{\bullet 3-}$ (deep orange species) and **3**$^{\bullet 3-}$ (yellow species) are highly stable species that exhibit well-resolved EPR spectra (Figure 3). These were obtained by electrolyses of **3** and **4** in dichloromethane with Bu_4NClO_4 as an electrolyte at room temperature, although **3**$^{\bullet-}$ could not be detected by the EPR spectroscopy. The hyperfine structure (hfs) constants, a^H (2H) = 0.065 mT and a^N (2N) = 0.106 mT, provided from the EPR spectrum of **4**$^{\bullet-}$, can be assigned to the protons H-3′ and 5′ and two equivalent nitrogen atoms of the CN groups, respectively. This hfs pattern is consistent with the prominent feature of the LUMO of **4**, which bears large π-AO coefficients at the dicyanomethylene group and its adjacent C-2′, C-3′, C-3′a, C-4′, C-4′a, C-5′, and C-6′ carbon atoms, as shown in Figure 3d. Thus the existence of significant spin density on the dicyanomethylene group and the adjacent carbon atoms in **4**$^{\bullet-}$ has been proved. The unpaired electron of **4**$^{\bullet 3-}$ mainly delocalizes on the cyclopentadithiophene carbon atoms: the EPR spectrum of **4**$^{\bullet 3-}$ (Figure 3b) gave a hfs constant a^H (2H) = 0.122 mT which can be assigned to H-3′ and H-5′, and there are relatively large π-AO coefficients at the cyclopentadithiophene carbon atoms in the NLUMO of **4** (Figure 3e). The unpaired electron of **3**$^{\bullet 3-}$ mainly delocalizes on the carbonyl group at the five-membered ring and the adjacent C-2′, C-3′, C-3′a, C-4′, C-4′a, C-5′, and C-6′ carbon atoms: the hfs constant, a^H (2H) = 0.15 mT, assigned to H-3′ and H-5′, could be deduced from the EPR spectrum of **3**$^{\bullet 3-}$ (Figure 3c) and there are large π-AO coefficients on these atoms in the NLUMO of **3** (Figure 3f). From these EPR spectroscopic analyses it is revealed that the spin density of the galvinoxyl units appears to be very small in **4**$^{\bullet 3-}$ and **3**$^{\bullet 3-}$, although the π coefficients of the phenoxyl units are not negligibly small.[10] These characteristic properties of **3** and **4** can be rationalized by the remarkable difference in the electron-accepting abilities between the dicyanomethylene and carbonyl groups at the C-4′ position. It is also surprising that the reduction potential at the C-4′ position shifted to a more positive value by 1.07 V when a carbonyl group was replaced by a dicyanomethylene group!

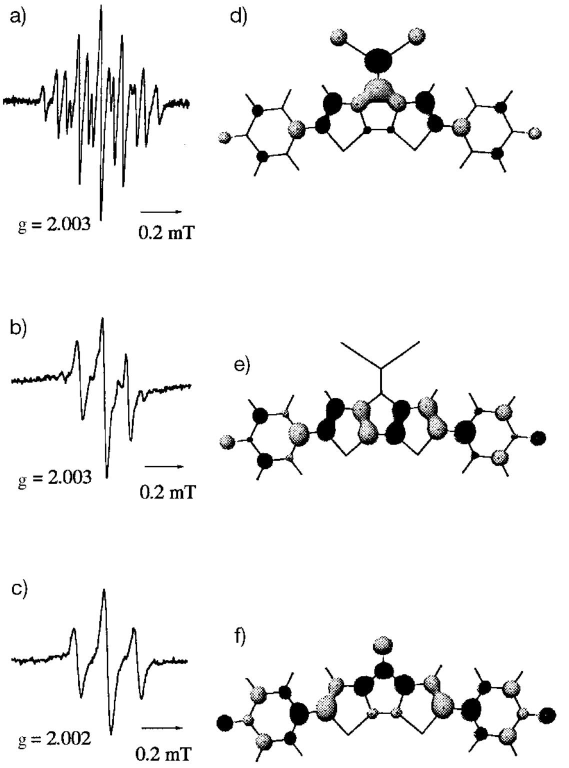
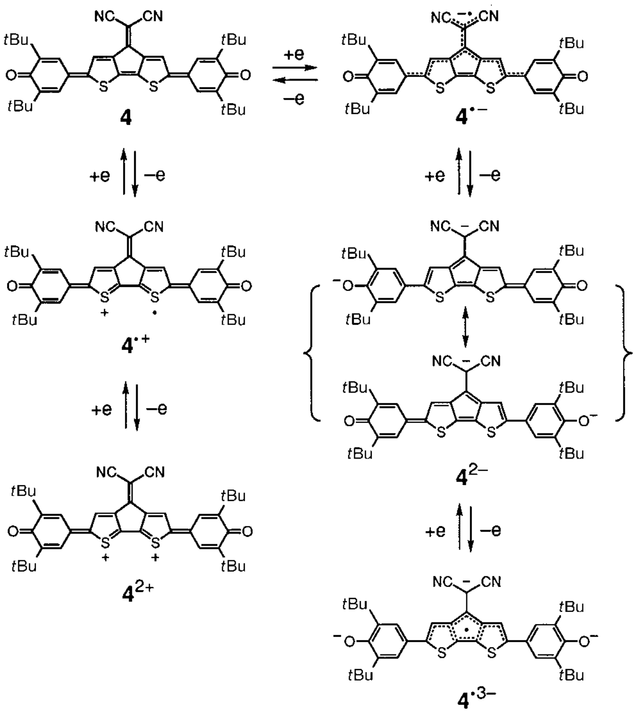


Figure 3. EPR spectra of a) **4**$^{\bullet-}$, b) **4**$^{\bullet 3-}$, and c) **3**$^{\bullet 3-}$ in CH_2Cl_2 at room temperature, and π-AO coefficients in the d) LUMO of **4**, e) NLUMO of **4**, and f) NLUMO of **3**, which were obtained from MNDO PM3 calculations. The *tert*-butyl groups of **4**, **3**, and **2** were replaced by hydrogen atoms for the calculations.

The E_1^{red} values become more positive in the series **2** < **3** < **4** (Table 2) in accord with the increase in the electron-accepting ability of the C-4′ group. This order also coincides well with the extent of stabilization of the LUMOs of these compounds. The quinones **2**–**4** are amphoteric compounds: they undergo two successive one-electron oxidations in the anodic direction affording the corresponding radical cations and dications of these quinones analogous to those of **1b**.[2] The E_1^{ox} values of **2**–**4** increase with increasing electron-accepting ability of the C-4′ group, but the extent of the increase on going from **3** to **4** is fairly small. Since the E_1^{sum} ($= E_1^{ox} + (-E_1^{red})$)[11] value, a convenient measure for evaluating the amphotericity of a specified molecule, is smallest in **4**, the amphotericity is highest in **4**.

Thus, we have clarified that the redox reaction sequence of compound **4** proceeds according to the routes shown in Scheme 2. Indeed, **4** is the first example of a redox-amphoteric compound with a closed-shell, which undergoes a reversible five-stage one-electron reaction and has a strong electron-accepting ability. Compounds that undergo more than four-stage one-electron redox reactions are very rare, although one example of a redox-amphoteric compound with a closed-shell is known that undergoes a six-stage redox sequence,[12] but with very low reduction and very high oxidation potentials. Likewise some examples of open-shell radicals that undergo six-stage redox reactions[13] have been reported. Furthermore we have established that the hybridized functionalization of dicyanomethylene and carbonyl groups in triquinonoid systems appears to be fruitful for creating novel and unique redox systems.



Scheme 2. Five-stage one-electron redox reaction sequence for **4**.

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Keywords: heterocycles · quinones · radical ions · redox chemistry

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[6] Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds. Selected physical data for **2**: metallic green powder; m.p. (decomp) >300 °C; ^{1}H NMR (600 MHz, CDCl$_3$): $\delta = 1.35$ (36 H, s, *t*Bu), 4.42 (4 H, s, OCH$_2$CH$_2$O), 7.14 (2 H, s, H-3′, 5′), 7.18 (2 H, d, $J = 2.5$ Hz, H-2, 2″), 7.32 (2 H, d, $J = 2.5$ Hz, H-6, 6″); ^{13}C NMR, IR, and VIS/NIR: see Table 1; MS: m/z (%): 642 (100) [M^+]; **3**: golden needles, m.p. (decomp) 291–292 °C; ^{1}H NMR (600 MHz, CDCl$_3$): $\delta = 1.34$ (18 H, s, *t*Bu), 1.35 (18 H, s, *t*Bu), 7.16 (2 H, d, $J = 2.6$ Hz, H-2, 2″), 7.31 (2 H, d, $J = 2.6$ Hz, H-6, 6″), 7.50 (2 H, s, H-3′, 5′); ^{13}C NMR, IR, and VIS/NIR: see Table 1; MS: m/z (%): 598 (100) [M^+]; **4**: golden crystals, m.p. (decomp) 264–265 °C; ^{1}H NMR (600 MHz, CDCl$_3$): $\delta = 1.35$ (36 H, s, *t*Bu), 7.12 (2 H, d, $J = 2.5$ Hz, H-2, 2″), 7.33 (2 H, d, $J = 2.5$ Hz, H-6, 6″), 7.92 (2 H, S, H-3′, 5′); ^{13}C NMR, IR, and VIS/NIR: see Table 1; MS: m/z (%): 646 (100) [M^+].

[7] The unit cell contains two molecules of **4** which stack along the *a* axis in a face-to-face manner; the dicyanomethylene groups are directed in opposite directions. The asymmetric unit contains 1.5 benzene solvent molecules. Crystal data for **4**: $C_{40}H_{42}N_2O_2S_2 \cdot 1.5\,C_6H_6$, $M_r = 764.07$, triclinic space group $P\bar{1}$ (no. 2); $a = 11.211(2)$, $b = 20.738(3)$, $c = 10.006(2)$ Å, $\alpha = 97.76(1)$, $\beta = 106.54(1)$, $\gamma = 91.04(1)°$; $V = 2211.2(6)$ Å^3; $\rho_{calcd} = 1.147$ g cm^{-3}; $Z = 2$; $F(000) = 814$; Cu$_{K\alpha}$ radiation ($\lambda = 1.54178$ Å); $T = 296$ K. Of a total of 7029 collected reflections, 6558 were unique, and 3227 with $I > 3\sigma(I)$ were observed. The structure was solved by Patterson methods by using DIRDIF92. Final R factor = 0.054 and Rw factor = 0.073. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101013. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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