Electron Acceptor Molecules: New, Expedient Synthesis of Substituted 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ) Derivatives and the X-Ray Crystal Structure of 2,5-Dibromo-TCNQ

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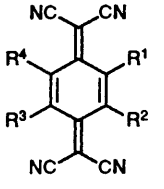
A range of TCNQ derivatives, *viz.* 2,5-dichloro-, 2,5-dibromo-, 2,5-dimethoxy-, 2-methoxycarbonyl- and benzo-TCNQ, and 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TNAP), have been efficiently synthesised using 2-chlorobenzyl thiocyanate as the source of electrophilic cyanide in reactions with the corresponding di(cyanomethyl)benzene or di(cyanomethyl)naphthalene derivatives. The X-ray crystal structure of 2,5-dibromo-TCNQ has been determined: the molecule is essentially planar with the dicyanomethylene groups bent away from the adjacent bromine atoms. There are close intermolecular Br • • • N contacts in the structure.

Since the discovery that certain charge-transfer salts formed by the tetracyano-*p*-quinodimethane (TCNQ) radical anion were organic semiconductors,[1] there has been unabated interest in this acceptor molecule. Derivatives of TCNQ **1** have been central to the development of organic metals[2] and, more recently their potential as components of organic ferromagnets,[3]



1

	R^1	R^2	R^3	R^4
a	H	H	H	H
b	Me	Me	Me	Me
c	Cl	H	Cl	H
d	Br	H	Br	H
e	OMe	H	OMe	H
f	CO_2Me	H	H	H
g	Cl	Cl	Cl	Cl

nonlinear optical materials[4] and molecular rectifiers[5] has been exploited. The majority of TCNQ derivatives undergo two reversible, single-electron reductions and the intermediate radical anion has high thermal stability.[6] The dicyanomethylene groups make TCNQ a far stronger acceptor than benzoquinone[7] and the acceptor properties can be finely tuned by the choice of substituents attached to the TCNQ ring.[6]

The synthesis of many TCNQ derivatives is not straightforward which has greatly restricted the use of these acceptors in the development of new organic materials. Early routes proceeded *via* cyclohexanedione derivatives[8] or *via* 1,4-di-(cyanomethyl)benzene derivatives **3**. Formation of the dicyanomethylene group by the latter procedure was a painstaking, multistep procedure involving the use of highly toxic cyanogen chloride as the electrophilic cyanating reagent.[9] The need for alternate methodology has been widely recognised and recently a few new approaches to the TCNQ system have been developed.

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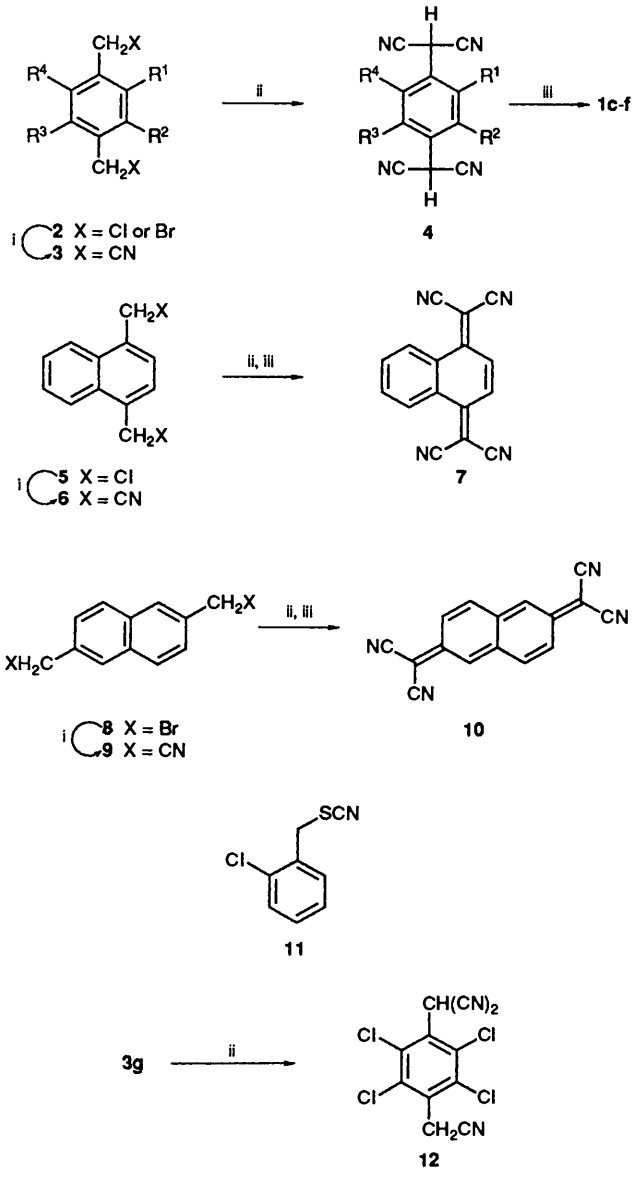
(i) The corresponding quinone can be directly bis(dicyanomethylated) using Lehnert's conditions (malononitrile, $TiCl_4$, pyridine)[10] but this reaction can be capricious;[11] it fails with some quinones,[12] and seems to be generally applicable only to tetrasubstituted derivatives[13] (*e.g.* tetramethyl-TCNQ **1b**[13a] and tetracyanoanthraquinodimethane[13b]).

(ii) 1,4-Diiodobenzenes react with malononitrile anion in the presence of a palladium catalyst to yield phenylenedimalononitrile derivatives[14] which are readily oxidised to the TCNQ system as described previously.[9]

(iii) Terephthaloyl chlorides react in a two-step procedure with cyanotrimethylsilane–pyridine, followed by phosphorus oxychloride–pyridine to yield the TCNQ system.[14d,15]

In this paper we describe alternative and efficient methodology for the synthesis of a range of TCNQ derivatives including the previously unreported derivative **1f**.[16]

Synthetic Studies: Results and Discussion.—We required TCNQ derivatives bearing both electron-withdrawing and electron-donating substituents as acceptors for charge-transfer complexes and as components of novel zwitterionic molecules for nonlinear optical studies.[4] The only known synthetic route that would tolerate a wide variety of substituents on the TCNQ frame proceeded *via* compounds **3** which were treated with cyanogen chloride, as mentioned above.[9] A few years ago, Staab *et al.* reported that 2-chlorobenzyl thiocyanate **11** was a convenient alternative to cyanogen chloride for the preparation of tetramethyl-TCNQ.[14b] This was the only TCNQ derivative these workers synthesised: we have now investigated the scope of reagent **11** in this context. Reagent **11** is straightforward to prepare from commercially available 2-chlorobenzyl chloride in large amounts (*e.g.* 50 g batches) and is a shelf-stable, non-toxic liquid.[17] There is current interest in new sources of electrophilic cyanide,[18] and we note that thiocyanates have rarely been used in this context.[14b,19] Compounds **3c–f**, **6** and **9** were all readily obtained from their dihalogeno precursors **2c–f**, **5** and **8**, respectively. Compounds **3c–f**, **6** and **9** were deprotonated using 4 equiv. of lithium diisopropylamide (LDA); subsequent reaction with 4 equiv. of thiocyanate reagent **11** introduced two further cyano groups into the molecules to afford dihydro-TCNQ derivatives **4**. These compounds **4** could be isolated, if required, but generally there was no advantage in doing so, as they proved very difficult to purify and their oxidation with



Scheme 1 i, NaCN; ii, reagent **11**, LDA, then HCl; iii, Br_2

bromine to afford the TCNQ derivatives **1c–f**, **7** and **10** was readily achieved on crude material. By this procedure, TCNQ derivatives **1c–f** and **7** were obtained in optimised yields of 35–45%, after purification, from di(cyanomethyl) precursors **3** and **6**. The yield of TNAP **10** was considerably lower (*ca.* 20% from compound **9**), partly because we were not able to obtain **9** in a pure form.

Compound **1f** is notable as it is a new TCNQ derivative* containing a *functionalised* carbon substituent of which there are very few examples.[21] Numerous attempts to prepare the unknown tetrachloro-TCNQ **1g** using reagent **11** were unsuccessful. Only three cyano groups could be introduced into the system, giving compound **12** in low yield; none of the desired tetracyano compounds **4g** or **1g** were obtained.

We have established that reagent **11** is versatile in that a wide range of substituents (electron-donating and electron-withdrawing) can be tolerated on the benzene ring of compounds **3**. Moreover, in contrast to CNCl, reagent **11** does not react with the phenylmalononitrile anion to form the tricyanomethyl group, so there is no need to insert (and later remove) ester groups and proceed *via* dimethyl tetracyanophenylenediacetate derivatives **4** (H = CO_2Me), as was previously necessary,[9] to obtain the TCNQ system.

* The preparation of an impure sample of compound **1f** (3% yield from compound **3f** and cyanogen chloride) has been reported.[20]

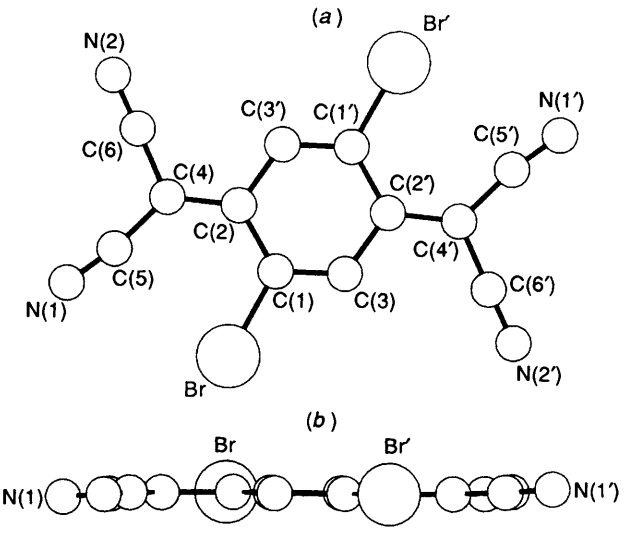


Fig. 1 Single crystal X-ray structure of 2,5-dibromo-TCNQ **1d**: (*a*) showing atom numbering scheme and (*b*) showing the planarity of the molecule

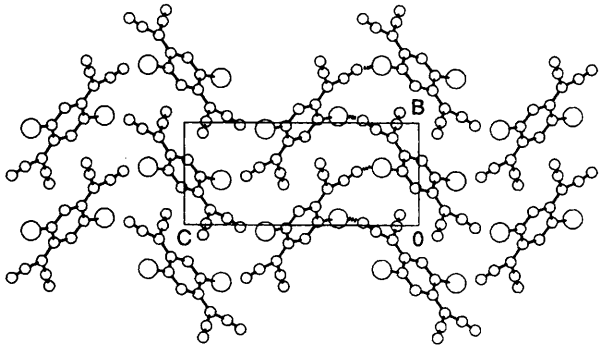


Fig. 2 Crystal structure of 2,5-dibromo-TCNQ **1d**, viewed along the *a* axis: the shortest Br · · · N contacts are shown by dotted lines

X-Ray Crystal Structure of 2,5-*Dibromo-TCNQ* **1d**.—Hitherto, compound **1d** has been a relatively inaccessible TCNQ derivative[9a] and, consequently, only a few charge-transfer complexes and ion radical salts of this acceptor have been characterised.[22] The X-ray structures of a few salts containing the radical anion $TCNQBr_2^{-\bullet}$ are known,[22] but the structure of the neutral molecule **1d** has not been reported. This acceptor is of particular interest as one can envisage the polarisable bromine atoms participating in interstack interactions, similar to the chalcogen–chalcogen interactions that are crucially important in stabilising the metallic state in salts of organo-sulfur and - selenium donor systems.[23] With this in mind several bromine-substituted tetrathiafulvalene (TTF) derivatives have recently been synthesised.[24] It was, therefore, timely to obtain the crystal structure of compound **1d**.

The X-ray crystal structure of $TCNQBr_2$ **1d** is presented in Figures 1 and 2. Intramolecular bond angles and distances are shown in Table 2 and fractional atomic co-ordinates in Table 1. The molecule is essentially planar with C_{2h} symmetry. The C(2)–C(4) bond bends in the plane of the ring away from the adjacent bromine atoms, presumably for steric reasons, such that the bond angle C(4)–C(2)–C(3') is 118.6(4)° while C(4)–C(2)–C(1) is opened to 125.4(4)°. Consistent with this, one

Table 1 Fractional atomic coordinates ($\times 10^4$) for compound **1d**

	x	*y*	*z*
Br	1205.9(6)	638.6(6)	3436.6(3)
N(1)	3165(7)	5228(7)	2629(3)
N(2)	8658(7)	6025(6)	4212(3)
C(1)	3395(6)	317(5)	4319(3)
C(2)	5174(5)	1792(5)	4416(2)
C(3)	3272(6)	−1353(6)	4866(3)
C(4)	5440(6)	3561(6)	3902(2)
C(5)	4082(7)	4362(6)	3187(3)
C(6)	7257(7)	4906(6)	4073(3)
H	2111(63)	−2291(60)	4750(24)

Table 2 Molecular dimensions of compound **1d**

Bond lengths (Å)			
C(1)–Br	1.874(6)	C(5)–N(1)	1.138(7)
C(6)–N(2)	1.144(6)	C(2)–C(1)	1.460(6)
C(3)–C(1)	1.344(6)	C(3′)–C(2)	1.446(6)
C(4)–C(2)	1.378(6)	C(5)–C(4)	1.432(6)
C(6)–C(4)	1.439(6)	H–C(3)	0.953(40)

Key to symmetry operations relating designated atoms to reference atoms at (*x*, *y*, *z*): (′) 1.0 − *x*, −*y*, 1.0 − *z*

Bond angles (°)			
C(2)–C(1)–Br	122.3(4)	C(3)–C(1)–Br	117.1(4)
C(3)–C(1)–C(2)	120.7(4)	C(3′)–C(2)–C(1)	116.0(4)
C(4)–C(2)–C(1)	125.4(4)	C(4)–C(2)–C(3′)	118.6(4)
C(2′)–C(3)–C(1)	123.3(4)	C(5)–C(4)–C(2)	128.8(4)
C(6)–C(4)–C(2)	120.0(4)	C(6)–C(4)–C(5)	111.2(4)
C(4)–C(5)–N(1)	171.0(4)	C(4)–C(6)–N(2)	177.9(5)
H–C(3)–C(1)	116.7(22)	H–C(3)–C(2′)	120.0(22)

Key to symmetry operations relating designated atoms to reference atoms at (*x*, *y*, *z*): (′) 1.0 − *x*, −*y*, 1.0 − *z*

C≡N group of the dicyanomethylene unit is also bent away from the bromine atom, with bond angles C(6)–C(4)–C(2) = 120.0(4)° and C(5)–C(4)–C(2) = 128.8(4)°. The cyanide group adjacent to the bromine atom deviates significantly from linearity: the angle C(4)–C(5)–N(1) is 171.0(4)° while the cyanide group removed from the bromine is almost linear, *i.e.* C(4)–C(6)–N(2) = 177.9(5)°. In the unsubstituted TCNQ molecule **1a** all the cyanide groups are essentially linear.[25] The molecules of compound **1d** pack in a herringbone fashion in the unit cell. There are close intermolecular bromine–nitrogen contacts, *viz.* N(1)···Br = 3.119 Å (at $-x$, 0.5 + *y*, 0.5 − *z*) (sum of the Van der Waals radii for the two atoms = 3.73 Å).

In conclusion, we have established that 2-chlorobenzyl thiocyanate **11** is a valuable electrophilic cyanating reagent for the synthesis of the dicyanomethylene group, thereby providing an expedient, non-toxic route to many TCNQ derivatives which were hitherto very laborious to obtain. These electron acceptors should now enjoy increased usage in organic solid-state chemistry.

Experimental

General.—Details of instrumentation and equipment are unchanged from those reported recently.[26]

Synthesis of Di(cyanomethyl)arenes **3c–e,g, 6** *and* **9**.—These compounds were all known. Derivatives **3c**,[9a] **3d**[9a] and **3g**[27] were prepared from the corresponding dihalogenocompounds **2d**, **2c** and **2g** as described previously. Dichloro derivatives **2c** (X = Cl) and **3c** were prepared in an analogous fashion, whereas previous workers had used alternative, less desirable methodology.[9a] In our hands, compound **2c** (X = Cl) was readily obtained [54% yield, m.p. 98–100 °C (lit.,[9a] 98–100 °C)] from 2,5-dichloro-*p*-xylene and *N*-chlorosuccinimide. Compound **2c** (X = Cl) was then converted into compound **3c** [m.p. 184–187 °C (lit.,[9a] 184–186 °C)] in 72% yield using sodium cyanide (4 equiv.) in aqueous dioxane, *i.e.* standard conditions for analogous reactions.[9a] We did not find it necessary to use a sodium cyanide–hydrogen cyanide mixture for this step, in contrast to the report from other workers.[9a] Compound **6** was prepared as described.[28]

2,6-Di(cyanomethyl)naphthalene **9**, prepared from the precursor **8** by the literature method,[9e] could not be obtained pure: a small amount of 2-bromomethyl-6-cyanomethylnaphthalene (*ca.* 10–15% as judged by ^{1}H NMR and elemental analysis) was always present as a contaminant, and could not be removed by recrystallisation or chromatography.

Methyl 2,5-Di(bromomethyl)benzoate **2f** (X = Br).—Methyl 2,5-dimethylbenzoate[29] (5.53 g, 0.034 mol), *N*-bromosuccinimide (13.5 g, 0.075 mol) and azoisobutyronitrile (0.3 g) were mixed in methylene dichloride (60 cm^3) and refluxed for 2 h. Standard aqueous work-up afforded compound **2f** (X = Br) 7.2 g, 66%) as a white solid, m.p. 81–83 °C (from methanol) (Found: C, 37.3; H, 3.1; Br, 49.9; $C_{10}H_{10}Br_2O_2$ requires C, 37.3; H, 31.1; Br, 49.6%); *m/z* 324 (M^+); δ_H($CDCl_3$) 7.95 (1 H, s), 7.40 (2 H, s), 4.95 (2 H, s), 4.39 (2 H, s) and 3.95 (3 H, s); ν_{max}(KBr)/cm^{-1} 1725, 1445, 1290, 1092, 997 and 920.

Methyl 2,5-di(cyanomethyl)benzoate **3f**.—Compound **2f** (X = Br) (4.6 g, 0.014 mol), and sodium cyanide (4.5 g, 0.09 mol) were suspended in a mixture of dioxane (30 cm^3) and water (30 cm^3) and stirred vigorously for 24 h at 20 °C. Solvent was partially removed under reduced pressure and the solid product filtered off, washed with water, dried and recrystallised from methanol to yield compound **3f** (2.6 g, 84%) a white solid, m.p. 98–99 °C (Found: C, 67.5; H, 4.7; N, 13.0. $C_{12}H_{10}N_2O_2$ requires C, 67.3; H, 4.7; N, 13.1%); *m/z* 214 (M^+); δ_H 7.95 (1 H, s), 7.55 (2 H, s), 4.08 (2 H, s), 3.90 (3 H, s) and 3.74 (2 H, s); ν_{max}(KBr)/cm^{-1} 2290 (C≡N), 1724 (C=O), 1460, 1444, 1300, 1098, 1000 and 961.

Conversion of Di(cyanomethyl) Compounds **3c–f**, **6** *and* **9** *into TCNQ Derivatives* **1c–f**, **7** *and* **10**, *respectively: General Procedure.*—The di(cyanomethyl)-compound (1.0 g) and lithium di-isopropylamide (LDA; 4 equiv.) were suspended in dry benzene (50 cm^3) at 0–5 °C under nitrogen. 2-Chlorobenzyl thiocyanate **11** (4 equiv.) dissolved in benzene (*ca.* 10 cm^3), was then added dropwise over 20 min. The solution was stirred at 0–5 °C for 4 h, extracted with water (*ca.* 100 cm^3) and the aqueous extract was acidified with conc. hydrochloric acid. (*o*-Chlorobenzyl disulphide remained in the organic layer and could be isolated, if required.) To the stirred aqueous layer (which now contains the dihydro-TCNQ derivative **4**) was added bromine (*ca.* 4 equiv. or until a red colour persisted). The mixture was stirred at 20 °C until all the TCNQ derivative had been precipitated (typically 24–48 h). The product was filtered, dried and purified by column chromatography or recrystallisation as stated below. There was thus obtained: compound **1c**, yellow crystals (from acetonitrile) {38%, m.p. 305–307 °C [lit.,[9a] 305 °C (decomp.)]}; compound **1d**, orange crystals (from acetonitrile) {40%, m.p. 315 °C (decomp.) [lit.,[9a] 316–318 °C (decomp.)]}; compound **1e**, red powder (from 1,1,2-trichloroethane) {38%, m.p. 300–305 °C [lit.,[9a] 300–305 °C (decomp.)]}; compound **7**, golden crystals (from methylene chloride–light petroleum, after column chromatography on silica, eluent methylene dichloride–cyclohexane [9:1 (v/v)] {45%, m.p. 216–218 °C [lit.,[30] 244–245 °C (decomp.)]}; compound **10**, purple powder (from acetonitrile) [*ca.* 20%, m.p. >350 °C, lit.,[9e] >365 °C].

Methyl 2,5-Bis(dicyanomethylene)-2,5-dihydrobenzoate **1f**. This compound was obtained as a yellow solid (35%), m.p. 224–226 °C (decomp.) (from acetonitrile) (Found: C, 64.2; H, 2.5; N, 21.3, $C_{14}H_6N_4O_2$ requires C, 64.1; H, 2.3; N, 21.4%); *m/z* 262 (M^+); $\delta_H(CDCl_3)$ 8.4–7.6 (3 H, m) and 4.2 (3 H, s); ν_{max}(KBr)/cm^{-1} 2220 (C≡N), 1725 (C=O), 1435, 1295, 1195 and 1084.

1-Cyanomethyl-4-di(cyanomethyl)tetrachlorobenzene **12**.—This compound was obtained from compound **3g** using the above procedure and isolated as a yellow solid (14%), m.p. 236–238 °C (Found: C, 41.2; H, 0.8; Cl, 43.9; N, 13.1. $C_{11}H_3Cl_4N_3$ requires C, 41.4; H, 0.9; Cl, 44.5; N, 13.2%); *m/z* 317 (M^+); $\delta_H(CDCl_3)$ 6.08 (1 H, s) and 4.18 (2 H, s); ν_{max}(KBr)/cm^{-1} 2240 and 2220 (both C≡N).

Crystal Data for 2,5-Dibromo-TCNQ **1d**.—$C_{12}H_2Br_2N_4$, M = 361.98, monoclinic, space group $p2_1/c$, a = 6.184(1), b = 6.445(1), c = 14.653(2) Å, β = 90.56(1)°, U = 583.9(1) Å, Z = 2, D_c = 2.059 g cm^{-3}, $F(000)$ = 344, λ = 0.710 69 Å, μ(Mo-Kα) = 68.6 cm^{-1}, crystal size = 0.37 × 0.22 × 0.05 mm.

Data collection. Unit cell parameters and intensity data were obtained by following previously detailed procedures[31] using a CAD4 diffractometer, with graphite monochromated Mo-Kα radiation. A total of 1030 unique reflections were collected ($3 < 2\theta < 50°$). The segment of reciprocal space scanned was: (h) 0–7, (k) 0–7, (l) −17–17. The reflection intensities were corrected for absorption, using the azimuthal-scan method;[32] maximum transmission factor 1.00, minimum value 0.66.

Structure solution and refinement. The structure was solved by the application of routine heavy-atom methods (SHELX-86[33]), and refined by full-matrix least-squares (SHELX-76[34]). After location, and isotropic refinement, of all non-hydrogen atoms, a further absorption correction was applied, using the program DIFABS;[35] maximum correction 1.37, minimum 0.57. Refinement continued with all non-hydrogen atoms treated anisotropically. The single hydrogen atom of the asymmetric unit was allowed unrestricted isotropic refinement.

The final residuals R and R_w were 0.031 and 0.033, respectively, for the 86 variables and 880 data for which $F_o > 3\sigma(F_o)$. The function minimised was $\Sigma_w (F_o - F_c)^2$ with the weight, w, being defined as $1/[\sigma^2(F_o) + 0.0005F_o^2]$. All computations were made on a DEC VAX-11/750 computer.

Atomic coordinates for compound **1d** are given in Table 1 and molecular dimensions in Table 2. Thermal parameters are available from the Cambridge Crystallographic Data Centre.*

Acknowledgements

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* For details see Instructions for Authors (1992), *J. Chem. Soc., Perkin Trans. 1*, Issue 1.

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