Preparation and Magnetic Properties of a Range of Metal and Organic Cation Salts of 2,3-Dicyano-1,4-naphthoquinone (DCNQ). *X*-Ray Crystal Structure of (Methyltriphenylphosphonium)$_1$ (DCNQ)$_1$ (H_2O)$_1$ and 2-Dicyanomethylene-indan-1,3-dione (DCID). The Rearrangement of DCID to DCNQ

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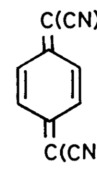
A series of salts (**11**) formed by the 2,3-dicyano-1,4-naphthoquinone (DCNQ) radical anion with the following counterions has been studied: (*a*) lithium, (*b*) methyltriphenylphosphonium, (*c*) sodium, (*d*) tetrabutylammonium, (*e*) tetraphenylarsonium, (*f*) rubidium, (*g*) caesium, (*h*) copper, (*i*) nickel, (*j*) cobalt, (*k*) zinc, (*l*) tetrathiafulvalene (TTF), and (*m*) tetramethyl-TTF. A novel method for the preparation of DCNQ salts (**11a–c**), (**11l**), and (**11m**) is described: this involves isomerisation of 2-dicyanomethyleneindan-1,3-dione (**7**) which is initiated by one-electron transfer to (**7**) from iodide ion, from sodium metal, or from TTF and TMTTF. DCNQ salts (**11b–l**) have been prepared from the lithium-DCNQ salt (**11a**) by cation exchange. The magnetic properties of a selection of these salts have been studied: salts (**11a**), (**11b**), (**11e**), and (**11l**) are diamagnetic while salts (**11d**) and (**11h**) are paramagnetic. The single crystal *X*-ray structures of the acceptor molecule 2-dicyanomethyleneindan-1,3-dione (**7**) and the anion radical salt (**11b**)·H_2O have been determined. The anions of salt (**11b**)·H_2O pack in pairs across a centre of symmetry in the crystal lattice. The TTF and TMTTF salts (**11l**) and (**11m**) are both semiconductors, $\sigma_{rt} = 1.0$ and 4×10^{-3} S cm^{-1}, respectively, whereas salts (**11a**), (**11b**), (**11d**), and (**11h**) are electrical insulators.

Seminal observations at the DuPont laboratories in the early 1960s established that many salts of the electron-acceptor 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) (**1**) were organic semiconductors.[1] Some ten years later, the prototype organic metal, TTF–TCNQ, entered the arena.[2] Since then the focal point for many chemists and physicists interested in the organic solid state has remained with the most highly conducting materials. However, studies on complexes and salts of lower conductivity continue to add greatly to progress in this field. Many review articles[3–9] and conference proceedings[10] concerned with the organic solid state and organic conductors are available. It is apparent that new electron-acceptors that form stable radical anions or dianions still have much to offer in the study of organic materials with novel properties. From this viewpoint, this paper is concerned with the acceptors 2-dicyanomethyleneindan-1,3-dione (DCID) (**7**), and 2,3-dicyano-1,4-naphthoquinone (DCNQ) (**12**).

Acceptors, other than simple derivatives of TCNQ (**1**), that are of current interest include: fused-ring TCNQ derivatives, fused-ring quinones, quinone di-imines, cyano-substituted heteroaromatics, and nitrobenzenes. To place the present work in context we will briefly consider recent results published on these acceptors. 11,11,12,12-Tetracyano-9,10-anthraquinodimethane (TCAQ) (**2**) has been reported independently by Yamaguchi *et al.*,[11] Kini *et al.*,[12] and by Aumuller and Hunig.[13] Electrochemical studies reveal a single-wave, two-electron reduction to the dianion $TCAQ^{2-}$ at a potential comparable to the second reduction of TCNQ; salts or complexes of TCAQ were not characterised in the solid state. Tetracyanobianthraquinone has been shown by *X*-ray analysis to be severely distorted and, again, complexes were not reported.[14] However, 1:1 complexes formed between TTF and thiophene-fused TCNQ acceptors, *e.g.* compound (**3**) and isomers, are conducting (σ_{rt} 0.9–4.8 S cm^{-1}); the acceptor (**3**) exhibits two, reversible, one-electron reductions in the cyclic voltammogram.[15] The bithiophene-derived acceptor (**4**) also displays two one-electron reductions and forms salts with TTF and tetrathiatetracene (TTT)[16] which have conductivities of *ca.* 10^{-4} S cm^{-1}. Benzoquinone derivatives fused with sulphur heterocycles [*e.g.* compound (**5**) and analogues] are also strong acceptors and some of their 1:1 complexes with TTF show moderately high conductivity (σ_{rt} typically 1×10^{-3} S cm^{-1}).[17] Quinone di-imine (**6**) has been shown by Aumuller *et al.*[18] to be a very promising acceptor. The copper salt of derivative (**6**) (1:2 stoicheiometry) is metallic with conductivity values as high as 5×10^5 S cm^{-1} at 3.5 K. Complexes of TTF with acceptors that have aromatic ground states are also receiving attention: cyano-substituted tetrazines and triazines form semi-conducting 1:1 complexes,[19] while we have shown that 1,3-dinitrobenzene forms an insulating 1:1 complex with TTF in which there is no significant charge-transfer and no significant intermolecular interactions in the crystal structure.[20]

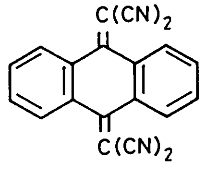
Results and Discussion

Preparation of Salts (**11a–j**).—We were attracted to DCID (**7**) as an acceptor for the formation of charge-transfer salts for the following reasons: (*i*) the molecule should be planar or very nearly planar, facilitating well-ordered crystal structures of salts, (*ii*) delocalised radical anion species derived from DCID



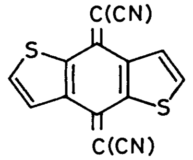
TCNQ

(1)



TCAQ

(2)



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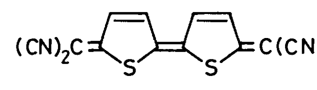

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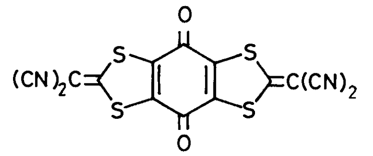
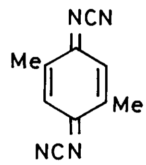
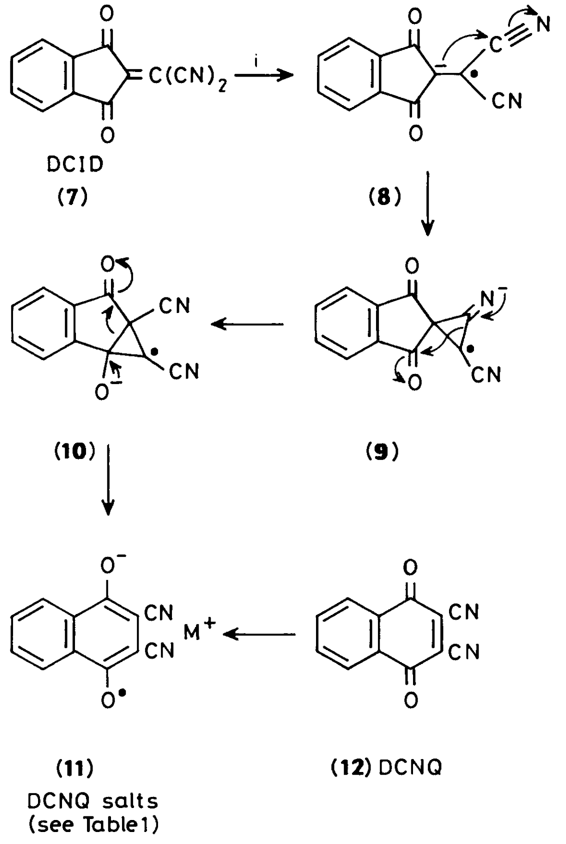


(5)



(6)



Scheme. *Reagents:* i, $M^+ I^-$, MeCN, reflux or Na, THF, 20 °C.

(7) should be formed readily, and (*iii*) DCID has a different skeletal structure from the other dicyanomethylene acceptors studied in charge-transfer complexes. The neutral species, DCID (7), was described in the literature twenty years ago,[21] but surprisingly, this acceptor has received scant attention since then. Compound (7) can be prepared in good yield as yellow, air-stable crystals by reaction of indan-1,3-dione with tetracyanoethene,[21] although we have used a different route, *viz.* reaction of ninhydrin with malononitrile in water, which is equally convenient.

By analogy with TCNQ (**1**)[1] and many other acceptors, we proposed that the lithium salt of DCID (**7**) would be a versatile precursor to a wide range of organic- and metal-cation salts of DCID which would be formed by metathesis reaction. Initial experiments established that reduction of DCID (**7**) by reaction with lithium iodide or with methyltriphenylphosphonium iodide led to the isolation of crystalline salts in good yields; the stoicheiometry of these two salts, determined by elemental analysis, was consistent with a cation:DCID ratio of 1:1. However, our suspicions that the anionic component of these salts was not DCID (**7**) were quickly aroused by the fact that the cyanide absorption in the i.r. spectrum moved to slightly shorter wavelengths on formation of the lithium salt: ν_{max} neutral DCID (**7**) 2 230 cm^{-1}, *cf.* Li^+ salt 2 235 cm^{-1}. This contrasts strikingly with the expected bathochromic shift to longer wavelengths in the lithium salt. (*cf.* TCNQ neutral absorbs at ν_{max} 2 215 cm^{-1} while the anion radical salt, Li^+ $TCNQ^{-\bullet}$, absorbs at ν_{max} 2 180 cm^{-1}.)[22] Single crystal *X*-ray analysis of the methyltriphenylphosphonium salt (see below) confirmed that DCID (**7**) had isomerised to DCNQ (**12**) and, therefore, the salts (**11a**) and (**11b**) we had isolated were *naphthoquinol* (*DCNQ*) *salts*, not DCID salts! (Table 1). The structure of the lithium salt (**11a**) was confirmed by the identical i.r. spectra of samples prepared from DCID (**7**) and from authentic quinone (**12**) (prepared from 2,3-dichloronaphthoquinone),[23] and the structure of the methyltriphenylphosphonium salt (**11b**) was confirmed by single crystal *X*-ray analysis (see below). Furthermore, both lithium and phosphonium salts (**11a**) and (**11b**), prepared from DCID (**7**), when treated with concentrated hydrochloric acid, as described previously for authentic salt (**11a**),[23] gave neutral DCNQ (**12**) in 65% and 40% yields, respectively. Under these reaction conditions, DCID (**7**) could be recovered unchanged in quantitative yield, with no isomerisation to compound (**12**). There is no doubt that our starting material DCID (**7**) was assigned the correct structure, as a single crystal *X*-ray analysis of compound (**7**) has been carried out (see below).[24]

The rearrangement of compound (**7**) to yield salts (**11**) is a fascinating isomerisation which we had not anticipated would occur: the notable features are the ring expansion of the indandione skeleton into the naphthoquinone skeleton with the formal 1,2-migration of a cyanide group.[25] It was important to establish if the mechanism of formation of salts (**11a**) and (**11b**) from DCID (**7**) required nucleophilic attack of iodide ion on (**7**), or whether single electron-transfer from iodide to (**7**) could be the initial step. Conclusive evidence that nucleophilic attack on (**7**) was *not* required was obtained by reacting DCID (**7**) with sodium metal suspended in THF: this yielded the rearranged sodium salt (**11c**) in 22% yield. This salt (**11c**) was identical (i.r. comparison) with the sodium salt obtained (50% yield) from metathesis reaction of lithium salt (**11a**) and sodium iodide in water. A possible mechanism for the isomerisation is outlined in the Scheme; it is promoted by initial single electron-transfer to the dicyanomethylene group of DCID (**7**). This would lead to the symmetrical radical anion (**8**) in which the anion is stabilised by the two flanking ketone groups. Nucleophilic closure onto either of the cyanide groups would then give intermediate spirocyclopropane derivative (**9**). Rearrangement of (**9**), as shown, leads to formal 1,2-migration of a cyanide group and

Table 1. Analytical data for the DCNQ salts.

DCNQ salt	Cation	Source of cation	Appearance of salt	Stoicheiometry cation:DCNQ:H_2O	Formula	Found (%)	Calc. (%)	Yield (%)	I.r. (KBr)[b] CN absorption/cm^{-1}
(**11a**)	Li	LiI	dark green	1:1	$C_{12}H_4LiN_2O_2$	C, 66.9; H, 1.9; N, 13.1; Li, 3.3	C, 67.0; H, 1.9; N, 13.0; Li, 3.2	94	2 235
(**11b**)	$MePPh_3$	$MePPh_3I$	black	1:1:(1)[a]	$C_{31}H_{22}N_2O_2P$	C, 76.2; H, 5.0; N, 5.4	C, 76.7; H, 4.6; N, 5.8	93	2 197
(**11c**)	Na	NaI or Na	dark green	1:1:3	$C_{12}H_{10}N_2O_3$	C, 50.0; H, 2.9; N, 9.2	C, 50.5; H, 3.5; N, 9.8	50	2 210
(**11d**)	$Bu^t{}_4N$	$Bu^t{}_4NI$	red	1:1	$C_{28}H_{40}N_3O_2$	C, 75.4; H, 9.3; N, 9.2	C, 74.6; H, 9.0; N, 9.3	90	2 200
(**11e**)	$AsPh_4$	$AsPh_4Cl$	pale green	1:1	$C_{36}H_{24}AsN_2O_2$	C, 72.7; H, 3.9 N, 4.5	C, 73.1; H, 4.1; N, 4.7	35	2 180
(**11f**)	Rb	RbI	dark green	1:1:2	$C_{12}H_{18}N_2O_4Rb$	C, 44.2; H, 2.3; N, 8.4; Rb, 25.0	C, 43.7; H, 2.5; N, 8.5; Rb, 25.9	44	2 205
(**11g**)	Cs	CsI	green	1:1:3	$C_{12}H_{10}CsN_2O_5$	C, 37.5; H, 1.6; N, 7.3	C, 36.8; H, 1.8; N, 7.1	48	2 200
(**11h**)	Cu	$CuCl_2{\cdot}2H_2O$	black	1:2	$C_{24}H_8CuN_4O_4$	C, 60.2; H, 1.5; N, 11.6; Cu, 13.5	C, 60.1, H, 1.7; N, 11.7; Cu, 13.2	78	2 215
(**11i**)	Ni	$Ni(NO_3){\cdot}6H_2O$	green	1:2:11	$C_{24}H_{30}N_4NiO_{15}$	C, 43.4; H, 4.2 N, 8.4; Ni, 8.5	C, 42.8; H, 4.5; N, 8.3; Ni, 8.7	60	2 220
(**11j**)	Co	$CoCl_2{\cdot}6H_2O$	green	1:2:10	$C_{24}H_{28}CoN_4O_{14}$	C, 43.9; H, 4.3; N, 8.4	C, 44.0; H, 4.3; N, 8.5	50	2 218
(**11k**)	Zn	$Zn(NO_3)_2$	green	1:2:11	$C_{24}H_{28}N_4O_{14}Zn$	C, 42.5; H, 3.9; N, 7.8; Zn, 9.6	C, 42.4; H, 4.4; N, 8.2; Zn, 9.6	50	2 215
(**11l**)	TTF	TTF	black	3:2	$C_{42}H_{20}N_4O_4S_{12}$	C, 48.9; H, 1.9; N, 5.4	C, 49.0; H, 1.9; N, 5.5	79	2 190
(**11m**)	TMTTF	TMTTF	black	3:2	$C_{54}H_{55}N_4O_4S_{12}$	C, 53.9; H, 3.5; N, 4.3	C, 54.2; N, 3.7; N, 4.7	75	2 195(?)[c]

[a] Salt (**11b**), without water of crystallisation, was obtained from reactions of DCID (**7**) and $MePPh_3{}^+I^-$ in dry acetonitrile: the analytical data given above are for this sample. Hydrated salt (**11b**) was obtained from salt (**11a**) and $MePPh_3{}^+I^-$ in water (Found: C, 74.3; H, 4.2; N, 5.4. Calc. for $C_{31}H_{24}N_2O_3P$: C, 73.9; H, 4.4; N, 5.6%.) [b] The position of cyanide absorption was the only peak to vary significantly between the different salts (**11a**–**k**). The remainder of the spectrum of the DCNQ radical anion was superimposable (±5 cm^{-1}) in all the salts (**11a**–**k**) *viz.* 1 545, 1 500, 1 270, 1 114, 915, 882, 750, 742, 720, 680, 508, 500, and 490 cm^{-1}. [c] Tentative assignment, as the peak is largely obscured by a broad charge-transfer band.

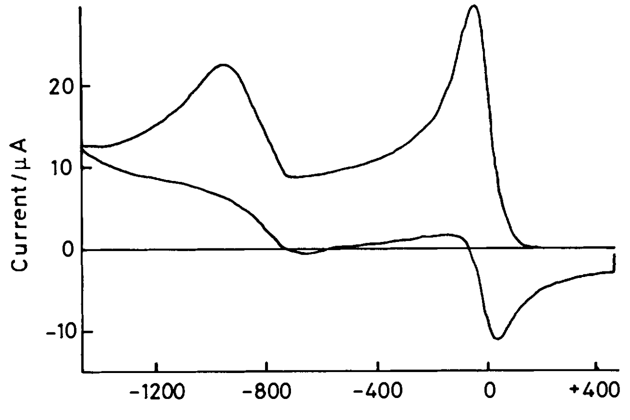


Figure 1. Cyclic voltammogram of DCID (**7**), *versus* Ag/AgCl, Pt electrode, electrolyte $NBu_4{}^+$ $ClO_4{}^-$, scan rate 100 mV s^{-1}.

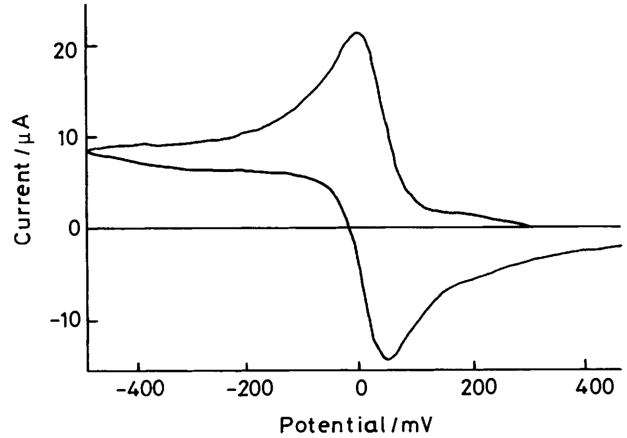


Figure 2. Cyclic voltammogram of first reduction wave of DCID (**7**).

the formation of a second cyclopropane compound (**10**). Compound (**10**) can ring open to form the delocalised naphthoquinol radical anion, and hence the salts (**11**), which we isolated.

We have studied the electron-acceptor properties of DCID (**7**) by cyclic voltammetry. The first one-electron reduction, *viz* neutral ⟶ radical anion, occurs at +8 mV; this is followed by a second one-electron reduction to form the dianion at −979 mV (*versus* Ag/AgCl, Pt electrode) (Figure 1). Under these electrochemical conditions the first reduction wave appears to be cleanly reversible (Figure 2) with no detectable change in the voltammogram after 15 min of continuous recycling between +500 mV and −600 mV. The second reduction, *viz* radical anion ⟶ dianion is *irreversible*, and this is clearly shown in Figure 1. It is important to note that we do not detect the presence of any anionic species derived from DCNQ (**12**) in the cyclic voltammogram of DCID (**7**). For comparison, the electrochemical reduction of DCNQ (**12**) is shown in Figure 3. DCNQ is a stronger electron acceptor than the isomer DCID. The first reduction, DCNQ ⟶ DCNQ$^{-\bullet}$, is fully reversible, occurring at +218 mV, so the presence of any DCNQ$^{-\bullet}$ formed from DCID should be clearly observable in Figure 1. The second, one-electron reduction of DCNQ$^{-\bullet}$ to the dianion DCNQ^{2-} is irreversible, occurring at −550 mV. [*cf.* TCNQ (**1**):

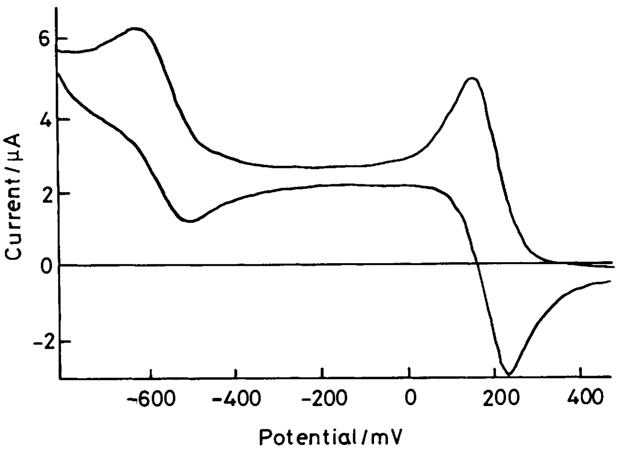


Figure 3. Cyclic voltammogram of DCNQ (**12**) (same conditions as Figure 1).

E_1 = +130 and E_2 = −400 mV.] This apparent electrochemical reversibility between the neutral and radical anion states of DCID (**7**) (Figure 2) is puzzling in the light of the chemical reactivity of the DCID radical anion discussed above. To reconcile these data, it is tempting to suggest that the conversion of DCID (**7**) into DCNQ salts (**11**) (Scheme) involves an intermediate DCID dianion, which could possibly be formed with a strong reducing agent, *e.g.* sodium metal. However, this is not supported by the fact that rearrangement also occurs on reduction of DCID by the comparatively weak electron-donor tetrathiafulvalene, giving salt (**11l**) (see below): the reduction potentials for TTF are E_1 +0.34 V and E_2 +0.78 V *versus* Ag/AgCl.

With lithium salt (**11a**) readily available, we have used this material in metathesis reactions with a range of cation salts to furnish, mostly in good yields, a series of dicyanonaphthoquinol salts (**11a–k**) that have organic and metal counterions (Table 1). DCNQ salts of 1:1 stoicheiometry (**11a–g**) are formed with lithium, methyltriphenylphosphonium, sodium, tetrabutylammonium, tetraphenylarsonium, rubidium, and caesium cations, respectively, and three of these are hydrated [*viz.* (**11b**), (**11f**), and **11g**)]. In contrast, copper, nickel, cobalt, and zinc form 1:2 salts (**11h–k**), three of which are hydrated. The cation: DCNQ stoicheiometry was, in all cases, unambiguous from the microanalytical data and, where applicable, a stoicheiometric amount of water was added to give a best-fit to the analytical data.* The i.r. spectra of all these salts (**11a–k**) show a very strong cyanide absorption in the range 2 180–2 235 cm^{-1} compared with the very weak cyanide absorption peak for neutral DCID (**7**) at 2 230 cm^{-1}, and the absence of cyanide absorption peak for neutral DCNQ (**12**). On the other hand, the carbonyl absorption, which is very strong in both neutral DCID and neutral DCNQ (observed at 1 705 and 1 680 cm^{-1}, respectively) is absent in the 1:1 quinol salts (**11a–g**) although it is present in the 1:2 salts (**11–k**), albeit in reduced intensity relative to (**12**). From this we infer that neutral DCNQ is present in the 1:2 salts, along with the DCNQ$^{-\bullet}$ radical anion. The hydrated salts all show the expected OH stretch in the i.r. spectrum.

Tetrathiafulvalene (TTF) has become the classical electron-donor for the formation of electroactive donor-acceptor complexes.[2–10] Reaction of equimolar amounts of TTF and DCID (**7**) in acetonitrile yielded a black microcrystalline complex (**11l**) (79%) for which elemental analysis supported a TTF: acceptor stoicheiometry of 3:2. The same 3:2 complex (**11l**) was obtained from TTF and DCNQ (**12**) (identical i.r. spectra). This result shows that TTF is a sufficiently strong reducing agent to effect the isomerisation of DCID into DCNQ. Complex (**11l**) is moderately conducting: the room temperature conductivity for compressed wafers, using standard four-probe techniques is σ_{rt} = *ca.* 1.0 S cm^{-1}. Tetramethyl-TTF (TMTTF), which is a stronger electron-donor than TTF, also forms a 3:2 complex (**11m**) when mixed with DCID. The room temperature conductivity of complex (**11m**) is 4×10^{-3} S cm^{-1}. These conductivity values clearly imply crystal structures for the TTF and TMTTF complexes with segregated stacks of donor and DCNQ molecules; however, we have been unable to obtain single crystals of (**11l**) or (**11m**) suitable for *X*-ray analysis. Variable temperature conductivity measurements on (**11l**) were performed over the temperature range 300–160 K and the exponential temperature dependence characteristic of a semiconductor is observed with activation energy E_a = 0.25 eV. This activation energy value is high when compared with the values for many organic salts with similar conductivities. However, it must be emphasised that the activation energy value is less reliable when obtained from data on compressed wafers than on single crystals, since the former samples are subject to the effects of electrical resistance associated with imperfect interparticle contact.[26]

While conducting salts of DCNQ (**12**) have not been reported previously it should be noted that substituted *p*-benzoquinones are well-known acceptors in this field. Torrance and co-workers first reported that chloranil and bromanil form both conducting and insulating salts with tetramethyl-TTF.[27] Also, a few examples of conducting salts of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) are known, *e.g.* with donors dibenzo-TTF[28] and thiopyrylium cations.[29] Conductivity measurements were performed on compressed pellets of DCNQ salts (**11a**), (**11b**), (**11d**), and (**11h**) and they are all insulators.

Magnetic Properties of DCNQ Salts.—Magnetic properties of a selection of these salts have been studied using a Faraday balance and these data are presented in Table 2. Methyltriphenylphosphonium-DCNQ salt (**11b**) is diamagnetic and this is consistent with strongly interacting spins within the $(DCNQ^-)_2$ dimer unit, as indicated by the relatively short intermolecular spacing observed in the *X*-ray structure. The magnetic susceptibilities of (**11a**), (**11b**), (**11e**), and (**11l**) are temperature independent and the values are consistent with those calculated from Pascal's constants. In contrast, the susceptibilities of the tetrabutylammonium and copper salts, (**11d**) and (**11h**), respectively, have paramagnetic contributions which obey the Curie law (Figure 4). Their susceptibilities vary as $\chi = C/T$ where C = 0.35 and 0.043 emu mol^{-1} K, which corresponds to effective Bohr magneton numbers ($\mu_{eff} = 2.83\ C^{\frac{1}{2}}$) of 1.68 and 0.58 μ_B, respectively. For the tetrabutylammonium salt (**11d**) this value is in close agreement with μ_{eff} = 1.73 μ_B calculated for a well developed spin-one-half system, whereas for the copper salt (**11h**) the data correspond to only *ca.* 0.16 spins per molecule. This weak paramagnetism suggests that the DCNQ$^-$ spins of (**11h**) couple antiferromagnetically, in which case the Curie law behaviour probably arises from the presence of some paramagnetic Cu^{2+} in the host lattice, as the species $Cu^{2+}(DCNQ)_2{}^{2-}$.

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* We have considered the possibility that these salts are not hydrated, but, instead, that one of the cyano groups of DCNQ had been replaced by a hydroxy group derived from solvent water during the metal exchange reaction (a process which could be promoted by complexation to the cation). There are early precedents for CN substitution by OH during reaction of DCNQ with sodium hydroxide[23] and, recently, during complexation of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) with amidopyridines in solvents containing water.[34] However, microanalytical data for our hydrated DCNQ salts (especially the metal and nitrogen analyses) are clearly inconsistent with cyanide displacement having occurred to any significant extent.

Table 2. Magnetic susceptibility data for DCNQ salts.

Salt	χ_{300K}(total)/ emu mol^{-1}	χ(diamag)^a/ emu mol^{-1}	χ_{300K}(paramag)/ emu mol^{-1}	C/ emu mol^{-1} K	μ_{eff}
(11a)	$-1.0(3) \times 10^{-4}$	-1.0×10^{-4}			
(11b)	$-2.9(3) \times 10^{-4}$	-2.9×10^{-4}			
(11d)	$+8.5(3) \times 10^{-4}$	-3.0×10^{-4}	$+11.5(3) \times 10^{-4}$	0.35	1.68
(11e)	$-3.2(3) \times 10^{-4}$	-3.2×10^{-4}			
(11h)	$-0.6(3) \times 10^{-4}$	-2.0×10^{-4}	$+1.4(3) \times 10^{-4}$	0.043	0.58
(11l)	$-4.7(3) \times 10^{-4}$	-4.6×10^{-4}			

^{a} Calculated from Pascal's Constants.

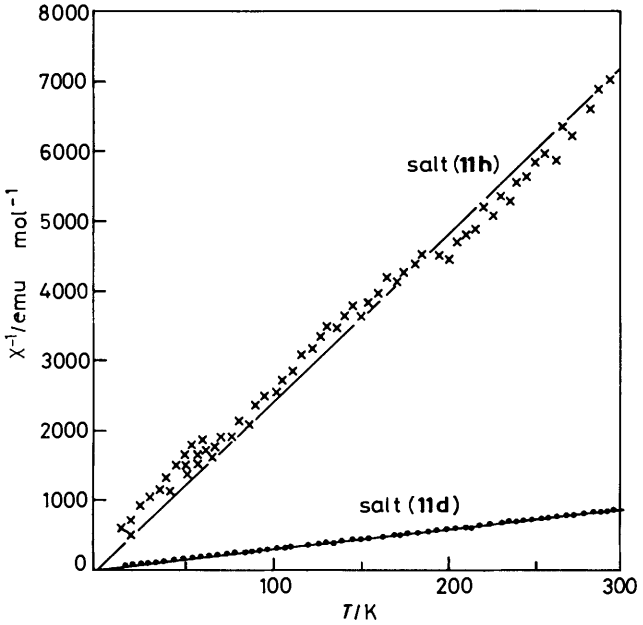

Figure 4. Temperature dependence of the reciprocal susceptibility corrected for core diamagnetism for salts (**11d**) and (**11h**).

X-*Ray Structure of Salt* (**11b**)·H_2O.—Crystals of salt (**11b**) were weakly diffracting, but, nonetheless, the data obtained confirm beyond doubt that the anionic component is DCNQ not DCID, which was the prime objective of the *X*-ray study. The *X*-ray crystal structure of salt (**11b**) was determined at the University of Reading and is shown in Figure 5. The cation has the expected dimensions with the P–Me bond somewhat shorter than the P–Ph bond lengths. The dimensions of the anion are difficult to interpret. Part of the problem lies in the inadequacies of the data due to the weakly diffracting crystal. We note that the crystals did not appear to be twinned and there was no evidence of disorder in the molecule. Thermal parameters for N(22), N(12), and C(13) are noticably larger than for the other atoms of the anion. There is no clear indication that the negative charge on DCNQ is localised, and it seems likely that the charge is delocalised over several positions as would be expected for the naphthoquinol system. There is only one intermolecular contact of note [*viz.* O(10)–O(100) = 2.760(3) Å] which is indicative of a hydrogen bond. Remaining contacts between the cation, anion, and water molecule are consistent with van der Waals radii. Figure 5 shows that the anions pack together in pairs across a centre of symmetry. The closest interatomic distance between the rings is C(5)–C(11) = 3.25 Å.

X-*Ray Structure of DCID* (**7**).—The *X*-ray crystal structure of DCID (**7**) was determined at Queen Mary College and a packing diagram is shown in Figure 6. The data obtained confirm that DCID has been assigned the correct structure.[21] A mean-plane calculation reveals that the two cyanide groups deviate slightly from the very good plane formed by all the ring carbon atoms. The atom numbering scheme is given in Figure 7.

Conclusions

We have been unable to isolate radical anion salts of the acceptor molecule DCID (**7**) due to the fascinating rearrangement of the radical anion derived from (**7**) to yield isomeric DCNQ salts (**11**). The *X*-ray crystal structures of neutral DCID (**7**) and one of the 'rearranged salts' *viz.* the hydrated methyltriphenylphosphonium-DCNQ salt (**11b**) have been determined. A range of DCNQ radical anion salts, with organic and inorganic counterions, has been isolated, and variable temperature magnetic susceptibility data for a selection of these salts discussed. The complexes of DCNQ with tetrathiafulvalene (TTF) and tetramethyl-TTF are both semiconductors.

Experimental

General.—Reagents were used as supplied (from Aldrich) without further purification. Acetonitrile was freshly distilled from calcium hydride before use. Ether refers to diethyl ether throughout.

Preparation of 2-*Dicyanomethyleneindan*-1,3-*dione* (*DCID*) (**7**).—To a solution of malononitrile (32.0 g, 0.48 mol) dissolved in hot water (500 cm^3) was added a solution of ninhydrin (32.0 g, 0.18 mol) dissolved in hot water (800 cm^3), with mechanical stirring. A yellow precipitate formed quickly and the mixture was boiled for 5 min. The product was cooled, filtered, dried in the air, and then recrystallised from acetonitrile (*ca.* 1.2 dm^3) to yield compound (**7**), 26.0 g (70%) as shining yellow plates. (Found C, 69.6; H, 1.9; N, 13.4. $C_{12}H_4N_2O_2$ requires: C, 69.2; H, 1.9; N, 13.5%); $\nu_{max.}$(Nujol) 2 230 (C≡N, v. weak), 1 749, 1 705, (C=O, v. strong) 1 678, 1 610, 1 580, 1 357, 1 326, 1 280, 1 250, 1 235, 1 222, 1068, 810, 748, 665, and 628 cm^{-1}. This material was identical with that reported in the literature from the reaction of indan-1,3-dione and tetracyanoethene.[21]

Preparation of Lithium Salt (**11a**).—To a boiling solution of DCID (**7**) (1.0 g, 4.8 mmol) dissolved in dry acetonitrile was added lithium iodide (0.96 g, 7.2 mmol) in one batch. The solution, which instantly darkened, was heated at reflux for 1 h then cooled to room temperature and filtered to yield salt (**11a**) as a dark green powder (0.97 g, 94%). Analytical and spectroscopic data are given in Table 1. This material was identical to a sample prepared (45%) from lithium iodide and authentic 2,3-dicyanonaphthoquinone, which was prepared, in turn, from 2,3-dichloronaphthoquinone.[23]

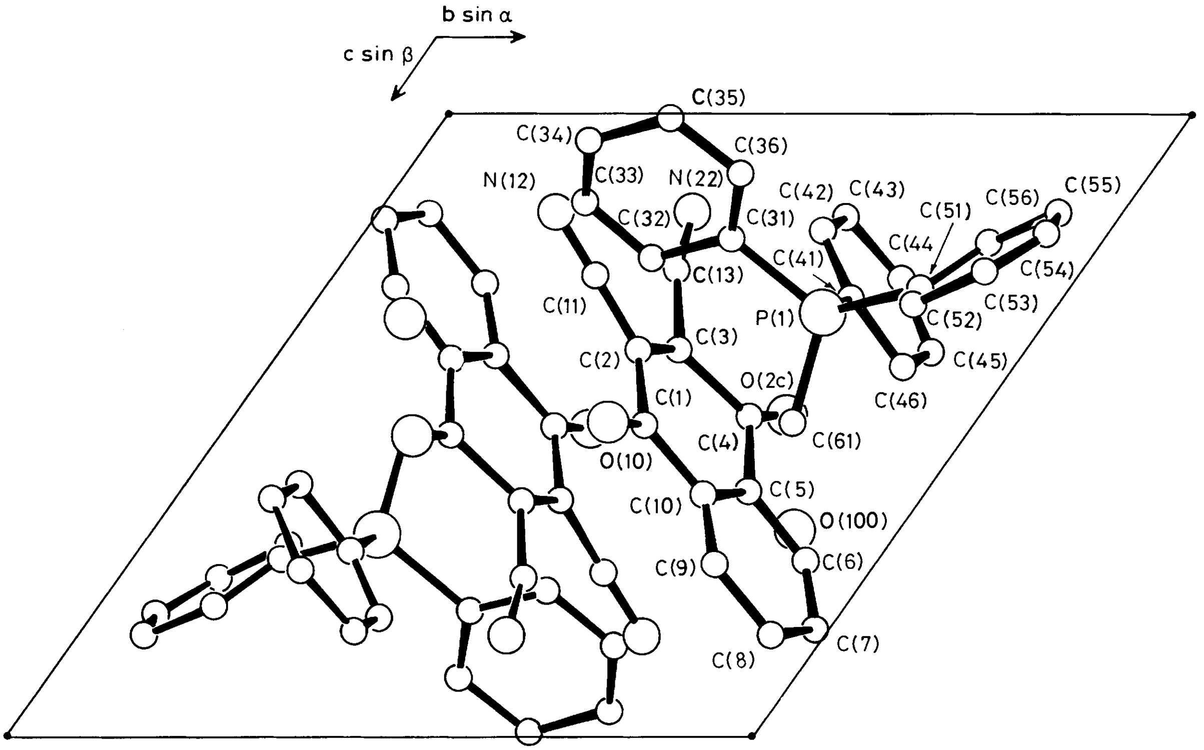

Figure 5. Single crystal *X*-ray structure of salt (**11b**)·H_2O with the unit cell in the *a* projection and the atom numbering scheme.

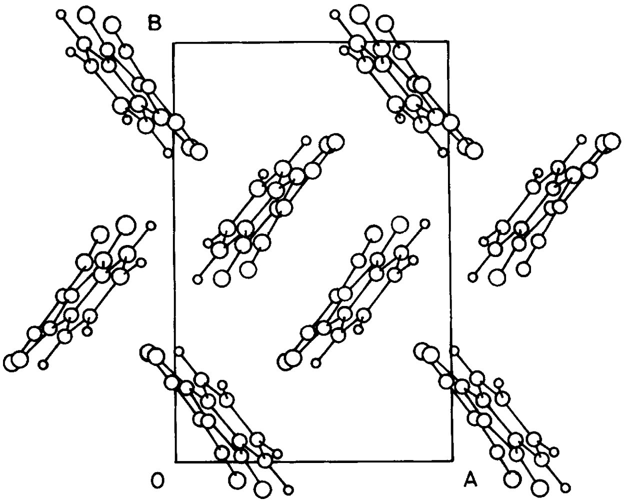

Figure 6. Single crystal *X*-ray structure of DCID (**7**) with the unit cell in the *c* projection.

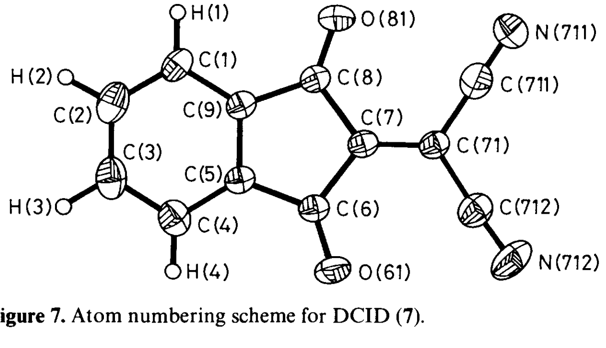

Figure 7. Atom numbering scheme for DCID (**7**).

Preparation of Metal and Organic Cation Salts (**11b–k**).—These salts were prepared by metathesis reaction of lithium salt (**11a**) and the appropriate metal or organic cation salt in water as shown in Table 1. The product precipitated very rapidly and was collected by filtration and then dried *in vacuo*. Salt (**11b**) was also prepared by direct reaction of compound (**7**) with methyltriphenylphosphonium iodide in 45% yield.

Salt (**11b**) is very soluble in dichloromethane, chloroform, ethanol, and acetonitrile, and the salt decomposes when dissolved in these solvents for >0.5 h. After this time, evaporation of the solvent gave a gummy residue of impure salt (**11b**) (i.r. evidence). The salt (**11b**) is insoluble in water, diethyl ether, and light petroleum–ether. Crystals of salt (**11b**)·H_2O suitable for *X*-ray analysis were grown as follows. Salt (**11b**)·H_2O (500 mg) was dissolved in a boiling mixture of ethanol (10 cm^3) and light petroleum–ether (b.p. 100–120 °C, 80 cm^3) and the mixture was allowed to cool slowly to room temperature to give salt (**11b**)·H_2O as shining black crystals which were dried in air. These crystals were analytically pure.

Preparation of Sodium Salt (**11c**).—Compound (**7**) (300 mg, 1.5 mmol) was dissolved in dry tetrahydrofuran (5 cm^3) and finely cut sodium metal (33 mg, 1 mol equiv.) was added. The mixture was stirred at room temperature for 48 h. The precipitate was filtered, washed with ether and dried to afford salt (**11c**) as a green solid (75 mg, 22%). Compound (**11c**) prepared by this route was identical with a sample prepared from lithium salt (**11a**) and sodium iodide in water (50%).

Preparation of Tetrathiafulvalene (*TTF*) *Complex* (**11l**).—A hot solution of TTF (40 mg) dissolved in acetonitrile (5 cm^3) was added to a hot solution of DCID (**7**) (40 mg) in acetonitrile and the mixture cooled slowly to 0 °C. The black, crystalline complex was filtered and dried *in vacuo* (63 mg, 79%). The identical complex (**11l**) was prepared from TTF and authentic quinone (**12**) in 25% yield; $\nu_{max.}$ (KBr) 2 190, 1 542, 1 490, 1 435, 1 370, 1 272, 1 095, 885, 732, 700, 675, 660, and 460 cm^{-1}.

Table 3. Atomic co-ordinates ($\times 10^4$) for the salt (**11b**)·H_2O with estimated standard deviations in parentheses.

Atom	x	y	z
C(1)	6 789(10)	5 386(12)	4 970(13)
C(2)	6 165(10)	4 670(13)	3 800(13)
C(3)	5 146(12)	5 348(15)	3 718(15)
C(4)	4 585(9)	6 951(11)	4 808(11)
C(5)	5 162(10)	7 641(13)	6 070(13)
C(6)	4 735(10)	9 129(12)	7 218(12)
C(7)	5 243(11)	9 868(15)	8 303(14)
C(8)	6 205(10)	9 206(13)	8 421(13)
C(9)	6 742(10)	7 688(12)	7 329(12)
C(10)	6 222(9)	6 923(12)	6 186(12)
O(10)	7 637(6)	4 760(8)	4 988(8)
O(20)	3 736(8)	7 560(10)	4 813(10)
C(11)	6 732(10)	3 265(14)	2 590(14)
C(13)	4 689(15)	4 640(18)	2 456(20)
N(22)	4 313(12)	4 168(15)	1 445(16)
N(12)	7 199(12)	2 126(15)	1 553(15)

Table 4. Molecular dimensions in the anion for the salt (**11b**)·H_2O.

Bond distance/Å	
C(1)–C(2)	1.469(16)
C(1)–C(10)	1.506(15)
C(1)–O(10)	1.178(13)
C(2)–C(3)	1.404(18)
C(2)–C(11)	1.423(16)
C(3)–C(4)	1.526(16)
C(3)–C(13)	1.426(22)
C(4)–C(5)	1.508(15)
C(4)–O(20)	1.157(13)
C(5)–C(6)	1.425(15)
C(5)–C(10)	1.484(16)
C(6)–C(7)	1.317(16)
C(7)–C(8)	1.361(17)
C(8)–C(9)	1.456(16)
C(9)–C(10)	1.375(15)
C(11)–N(12)	1.178(15)
C(13)–N(22)	1.151(18)
Bond angles/°	
C(2)–C(1)–C(10)	115.6(10)
C(2)–C(1)–O(10)	121.7(10)
C(10)–C(1)–O(10)	122.5(10)
C(1)–C(2)–C(3)	124.6(11)
C(1)–C(2)–C(11)	116.5(10)
C(3)–C(2)–C(11)	118.3(11)
C(2)–C(3)–C(4)	123.7(12)
C(2)–C(3)–C(13)	120.7(13)
C(4)–C(3)–C(13)	114.5(12)
C(3)–C(4)–C(5)	111.3(9)
C(3)–C(4)–O(20)	126.8(11)
C(5)–C(4)–O(20)	121.2(10)
C(4)–C(5)–C(6)	119.3(10)
C(4)–C(5)–C(10)	125.1(10)
C(6)–C(5)–C(10)	115.5(10)
C(5)–C(6)–C(7)	123.9(11)
C(6)–C(7)–C(8)	120.7(12)
C(7)–C(8)–C(9)	121.6(11)
C(8)–C(9)–C(10)	117.7(10)
C(1)–C(10)–C(5)	119.1(9)
C(1)–C(10)–C(9)	120.0(10)
C(5)–C(10)–C(9)	120.6(10)
C(2)–C(11)–N(12)	176.9(14)
C(3)–C(13)–N(22)	174.6(18)

Table 5. Bond lengths/Å and bond angles/° for DCID (**7**).

Bond lengths			
C(2)–C(1)	1.381(4)	C(9)–C(1)	1.389(3)
H(1)–C(1)	0.951(21)	C(3)–C(2)	1.392(4)
H(2)–C(2)	0.992(20)	C(4)–C(3)	1.378(4)
H(3)–C(3)	0.961(22)	C(5)–C(4)	1.390(3)
H(4)–C(4)	0.939(22)	C(6)–C(5)	1.473(3)
C(9)–C(5)	1.398(3)	O(61)–C(6)	1.214(3)
C(7)–C(6)	1.503(4)	C(71)–C(7)	1.341(3)
C(8)–C(7)	1.500(4)	C(71)–C(71)	1.441(3)
C(712)–C(71)	1.438(3)	N(711)–C(711)	1.139(3)
N(712)–C(712)	1.133(3)	O(81)–C(8)	1.208(3)
C(9)–C(8)	1.478(3)		
Bond angles			
C(9)–C(1)–C(2)	117.5(3)	C(2)–C(1)–H(1)	120.6(13)
C(9)–C(1)–H(1)	122.0(13)	C(3)–C(2)–C(1)	121.4(3)
H(2)–C(2)–C(1)	117.4(13)	C(3)–C(2)–H(2)	121.2(13)
C(4)–C(3)–C(2)	121.5(3)	H(3)–C(3)–C(2)	119.1(14)
C(4)–C(3)–H(3)	119.4(14)	C(5)–C(4)–C(3)	117.5(3)
H(4)–C(4)–C(3)	121.5(13)	C(5)–C(4)–H(4)	121.0(13)
C(6)–C(5)–C(4)	128.8(3)	C(9)–C(5)–C(4)	121.0(3)
C(9)–C(5)–C(6)	110.2(2)	O(61)–C(6)–C(5)	128.6(2)
C(7)–C(6)–C(5)	106.1(2)	C(7)–C(6)–O(61)	125.3(2)
C(71)–C(7)–C(6)	126.3(2)	C(8)–C(7)–C(6)	107.5(2)
C(8)–C(7)–C(71)	126.3(2)	C(711)–C(71)–C(7)	122.8(3)
C(712)–C(71)–C(7)	121.9(3)	C(712)–C(71)–C(711)	115.3(2)
N(711)–C(711)–C(71)	177.1(2)	N(712)–C(712)–C(71)	178.1(2)
O(81)–C(8)–C(7)	125.9(2)	C(9)–C(8)–C(7)	105.8(2)
C(9)–C(8)–O(81)	128.3(3)	C(5)–C(9)–C(1)	121.1(3)
C(8)–C(9)–C(1)	128.6(3)	C(8)–C(9)–C(5)	110.4(2)

Crystal Data for Salt (**11b**)·H_2O.—$C_{31}N_2H_{22}O_2P$, M = 485.1, Z = 2, triclinic, a = 11.92(1), b = 11.49(1), c = 11.81(1), α = 125.1(1), β = 85.1(1), γ = 83.1(1), U = 1 290.1 Å^3, D_c = 1.28 g cm^{-3}, D_m = 1.28 g cm^{-3}, $F(000)$ = 506, Mo-K_α radiation, λ = 0.7107 Å, μ = 1.45 cm^{-1}, space group $P\bar{1}$.

A crystal of approximate size 0.35 × 0.3 × 0.3 mm was set up to rotate about the a axis on a Stoe Stadi 2 diffractometer and data were collected *via* variable-width ω scan. Background counts were for 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of $(1.5 + \sin\mu/\tan\theta)$: 3 216 independent reflections were measured of which 1 302 with $I > 2\sigma(I)$ were used in subsequent refinement. The structure was determined by statistical methods. The phosphorus atom was refined anisotropically and remaining atoms isotropically. Hydrogen atoms were included in calculated positions although the methyl hydrogen atoms were refined as a rigid group. The water hydrogen atoms were located in a difference Fourier and refined independently apart from a distance constraint (O–H 0.95 Å).

The structure was given a weighting scheme in the form $w = 1/[\sigma^2(F) + 0.003\ F^2]$. The final R values were 0.094 (R_w = 0.097). Calculations were carried out using SHELX 76[30] and some of our own programs on the Amdahl V7 at the University of Reading. Positional parameters are given in Table 3 and molecular dimensions in the anion in Table 4. Dimensions in the cation have been deposited with supplementary publication data together with hydrogen atom co-ordinates and lists of thermal parameters.*

Crystal Data for DCID (**7**).—$C_{12}H_4O_2N_2$, M_r 208.176, crystal system monoclinic, a = 7.735(1) Å, b = 11.551(3) Å, c = 10.708(2) Å, $\alpha = \gamma$ = 90°, β = 101.39(1)°, V = 937.89 Å^3, space group $P21/c$, D_c = 1.47 g cm^{-3}, Z = 4, $F(000)$ = 424, Cu-K_α radiation, λ = 1.5419, μ = 8.234 cm^{-1}, θ min/max = 3, 69, T = 279 K, total data measured = 2 041, total data unique = 1 740, total data observed = 1 537, significant test $F_o > 3\sigma(F_o)$,

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* *Supplementary data:* See 'Instructions for Authors' (1989), *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

Table 6. Fractional atomic co-ordinates (× 10^4) for DCID (**7**).

Atom	*x*	*y*	*z*
C(1)	1 715(2)	5 051(2)	3 030(2)
C(2)	1 973(3)	5 550(2)	1 909(2)
C(3)	3 092(3)	6 495(2)	1 912(2)
C(4)	4 007(3)	6 964(2)	3 033(2)
C(5)	3 755(2)	6 467(1)	4 166(1)
C(6)	4 544(2)	6 798(1)	5 484(2)
O(61)	5 648(2)	7 535(1)	5 851(1)
C(7)	3 754(2)	6 001(1)	6 329(1)
C(71)	4 035(2)	6 036(1)	7 605(1)
C(711)	3 261(2)	5 217(2)	8 348(2)
N(711)	2 694(3)	4 588(2)	8 980(2)
C(712)	5 106(3)	6 919(2)	8 326(2)
N(712)	5 918(3)	7 614(2)	8 916(2)
C(8)	2 574(2)	5 170(1)	5 483(1)
O(81)	1 772(2)	4 376(1)	5 835(1)
C(9)	2 625(2)	5 522(1)	4 164(2)

No. of parameters 161, absorption correction psi-scan, weighting scheme $1/[\sigma^2(F_o) + 0.00001\ F_o^2]$, final $R = (F)/(F_o) = 0.0406$, final $R_g = 0.0479$.

Data were collected on a CAD 4 diffractometer following previously detailed procedures.[31] The structure was solved by direct methods (SHELX 86)[32] and developed and refined using standard Fourier and least-squares procedures (SHELX 80).[33] Non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. Bond lengths and angles are given in Table 5. Fractional atomic co-ordinates, excluding hydrogen atoms, are given in Table 6.

Acknowledgements

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