Synthesis, Characterization and Crystal Structure of 2-Dicyanomethylene-1,3-bis(ferrocenylmethyl)-1,3-diazolidine†

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By reaction of *N,N'*-ethylenebis(ferrocenylmethylamine) **1** with tetracyanoethylene in dichloromethane the yellow compound 2-dicyanomethylene-1,3-bis(ferrocenylmethyl)-1,3-diazolidine **2** can be isolated. The single-crystal structure of **2** has been determined. It crystallizes in the non-centrosymmetric trigonal space group $P3_221$, a = 12.255(2), c = 13.831(7) Å, Z = 3. Refinement of the atomic parameters by least-squares techniques gave a final R factor of 0.038 (R' = 0.034) for 1782 observed reflections having $I > 2.5\sigma(I)$. Anomalous values of the bond distances and the vinyl carbon chemical shift in the ^{13}C NMR spectrum of **2** are explained on the basis of a polarization due to a combination of the electron-donating behaviour of the nitrogen atoms with the electron-acceptor character of the cyano groups in the dicyanovinyl diamine fragment. The non-linear optical properties were investigated. A second harmonic generation signal for **2** was detected by powder techniques with a low efficiency. Electrochemical experiments in dimethyl sulfoxide revealed a two-electron diffusion-controlled oxidation process according to two consecutive one-electron steps involving the two ferrocenyl fragments the potentials of which are separated by 43 mV. A comproportionation constant K_c of 5.3 was found by differential pulse voltammetry, indicating that the mixed-valence species $[Fe^{III}Fe^{II}]^+$ is basically not stabilized.

There is a considerable interest in the functionalization of ferrocene and its incorporation in the skeleton of classical chelating groups which are able to co-ordinate to metal ions.[1] Such systems are interesting, not only as potential multielectron redox mediators in redox-catalytic processes,[2] or as species containing redox recognition sites,[3] but also because the presence of redox-active centres makes them good candidates to prepare donor (ferrocene)–acceptor electron-transfer complexes in order to seek materials with novel magnetic and/or conductivity properties.

In our laboratory we have undertaken the synthesis of ferrocene-containing molecules with N- or N,O-donor groups which are able to act as ligands towards transition-metal ions. Recently, we reported the synthesis and characterization of the ferrocene-containing ligand *N,N'*-ethylenebis(ferrocenylmethylamine) **1** and its copper(II) complexes.[4] The present work was undertaken in order to check the possibility of obtaining electron-transfer complexes with **1** and the planar acceptor tetracyanoethylene (tcne). However, tcne is known to be highly reactive and it has been reported that, in addition to charge-transfer products,[5] reacts with primary and secondary aliphatic amines to yield *N*-(tricyanovinyl)- or *N,N'*-(dicyanovinyl)-amines with evolution of hydrogen cyanide.[6] The occurrence in **1** of secondary amines leads to the formation of 2-dicyanomethylene-1,3-bis(ferrocenylmethyl)-1,3-diazolidine **2**, precluding the formation of charge-transfer complexes. We report here the synthesis, characterization, electrochemical behaviour, crystal structure and non-linear optical properties of **2** obtained by reaction of **1** with tcne.

Experimental

Solvents and Reagents.—*N,N'*-Ethylenebis(ferrocenylmethylamine) was prepared by the method described previously.[4] Tetracyanoethylene obtained from commercial sources was used without further purification. Tetra-*n*-butylammonium hexafluorophosphate was recrystallized from ethanol solutions and dried at 80 °C under vacuum for 48 h. Dimethyl sulfoxide used in electrochemical experiments was distilled over CaH_2 and stored under nitrogen. Elemental analyses (C, H, N) were performed by Servicio de Microanálisis Elemental de la Universidad Autónoma de Madrid (Spain).

Synthesis of 2-*Dicyanomethylene*-1,3-*bis*(*ferrocenylmethyl*)-1,3-*diazolidine* **2**.—To a solution of *N,N'*-ethylenebis(ferrocenylmethylamine) **1** (100 mg, 0.25 mmol) in refluxing dichloromethane, tetracyanoethylene (50 mg, 0.25 mmol) dissolved in CH_2Cl_2 was added dropwise during 1 h. To the resulting yellow solution, methanol was added and heated to 50 °C (to remove CH_2Cl_2). The yellow crystalline solid, identified as **2**, was filtered off and dried under vacuum. **CAUTION**: hydrogen cyanide is evolved. Yield: 78% (Found: C, 63.85; H, 4.95; N, 10.70. Calc. for $C_{28}H_{26}Fe_2N_4$: C, 63.45; H, 4.90; N, 10.55%). IR (KBr): 3107w, 2925w, 2855w, 2198s, 2172s, 1638m, 1501s, 1438m, 1396w, 1378w, 1335m, 1287s, 1231m, 1203w, 1193w, 1125m, 1102m, 1042w, 1029w, 999w, 923w, 902w, 821s, 753w, 694w, 507s and 480s cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 3.32 (s, 4 H,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

CH_2), 4.17 (s, 10 H, C_5H_5), 4.19 (t, 4 H, C_5H_4), 4.28 (t, 4 H, C_5H_4) and 4.53 (t, 4 H, CH_2); $^{13}C-\{^1H\}$, δ 29.69 (C=C), 46.32 (CH_2), 48.08 (CH_2), 68.94 (C_5H_5 and C_5H_4), 69.59 (C_5H_4), 79.93 (C_5H_4), 118.05 (CN) and 195.15 (C=C).

Physical Measurements.—Infrared spectra were taken on a Perkin Elmer 1750 spectrophotometer as KBr pellets, NMR spectra on a Bruker AC-200 FT spectrometer operating at 300 K. Chemical shifts for ^1H and $^{13}C-\{^1H\}$ NMR spectra are referenced to $SiMe_4$ and $CDCl_3$ respectively. The UV spectra were taken on a Shimadzu 160A spectrophotometer in dichloromethane solutions. Cyclic voltammograms were obtained with a Tacusel IMT-1 programmable function generator, connected to a Tacusel PJT 120-1 potentiostat. The working electrode was platinum, with a saturated calomel reference electrode separated from the test solution by a salt bridge containing the solvent and supporting electrolyte. The auxiliary electrode was a platinum wire. The electrochemical cell used for controlled-potential electrolysis was of conventional H-type design with anodic and cathodic compartments separated by a porous frit. The electrolysis was stopped when the current intensity was 1% of the initial, and the total charge was obtained by integration of the intensity *vs.* time curve. Differential pulse voltammetry was done with a Metrohm 626 instrument, with a pulse amplitude of 10 mV, a sweep rate of 2 mV s^{-1} and a 'drop time' of 0.5 s. Tetra-*n*-butylammonium hexafluorophosphate and dimethyl sulfoxide were used as supporting electrolyte and solvent respectively. The system was calibrated against ferrocene. Evidence of non-linear optical properties was sought by second harmonic generation measurements. These were carried out by the Kurtz and Perry powder technique[7] at Laboratoire de Physico-Chimie des Rayonnements in Orsay. A few milligrams of polycrystalline powder of compound **2** were placed between glass plates. Irradiation of the sample by the primary beam (1.064 μm) of a Nd-YAG picosecond pulse (10 Hz) laser induced the appearance of the second harmonic green light (532 nm). The through-sample second harmonic signal was measured by a set-up including an interference filter and a photomultiplier connected to an ultrafast Tektronix 7834 oscilloscope.

Structure Determinations.—*Crystal data.* $C_{28}H_{26}Fe_2N_4$ **2**, $M = 529.6$, trigonal, space group $P3_221$, $a = 12.255(2)$, $c = 13.831(7)$ Å, $U = 1790(1)$ Å^3, $Z = 3$, $D_c = 1.54$ g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, crystal size 0.2 × 0.2 × 0.4 mm, $\mu = 14.4$ cm^{-1}, $F(000) = 822$.

Data collection and refinement. A well shaped pale yellow crystal of compound **2** grown by evaporation of dichloromethane solutions was used for the structure determination. X-Ray intensities were recorded on a Enraf-Nonius CAD4 diffractometer using monochromatized Mo-Kα radiation. From the angular setting of 25 reflections several possible unit cells, from hexagonal to triclinic, were obtained. The only condition limiting possible reflection was found to be $l = 3n$, indicating that the correct unit cell is hexagonal or trigonal, and the space group $P3_221$ was confirmed from the structure determination. A total of 3429 reflections were measured, *hkl* range (−12, 0, 0) to (6, 14, 16) using the ω–2θ scan technique, with a maximum scan time of 50 s per reflection. Three standard reflections were monitored every 60 min. Some Friedel pairs were averaged, $R_{int} = \Sigma(|I| - \langle I\rangle)/\Sigma I = 0.020$, resulting in 2016 unique reflections, 1782 of which were observed [$I > 2.5\sigma(I)$]. Lorentz and polarization corrections were applied but not absorption. The position of the iron atom was determined from a Patterson interpretation, using the program SHELX 86.[8] The remaining non-hydrogen atoms were located using SHELX 76,[9] from successive difference electron-density maps. The structure refinement was carried out by weighted full-matrix least squares, first with isotropic and then with anisotropic thermal parameters. A difference synthesis allowed the location of all the hydrogen atoms which were refined isotropically riding on their parent atoms. The final agreement factors were $R = 0.036$ and $R' = 0.034$, $w = 1.454/[\sigma^2(F_o) + 0.00021(F_o)^2]$. Atomic scattering factors were taken from ref. 10. The geometry calculations were performed with PARST[11] and the molecular illustrations were drawn with ORTEP.[12] All calculations were done on a IBM-3090 computer at the Centro de Cálculo de la Universitat de València.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Crystal Structure of Compound **2**.—The structure of compound **2** can be seen as formed by units of *N,N'*-ethylenebis(ferrocenylmethylamine) **1** where the two hydrogen atoms from the secondary amine groups have been substituted by one dicyanovinyl [$>C=C(CN)_2$] moiety. An ORTEP view of the molecule is depicted in Fig. 1. Final atomic coordinates for non-hydrogen atoms and selected bond distances and angles are listed in Tables 1 and 2, respectively. The compound crystallizes in the non-centrosymmetric space group $P3_221$ with $Z = 3$ and the C(3), C(4) atoms from the vinyl group lying on a two-fold axis. Perpendicular to the two-fold axis the three-fold screw axis gives a helicoidal distribution of the molecules along the *c* axis. Fig. 2 shows a projection of the structure in the *ab* plane. The cyclopentadienyl groups are planar within the limits of experimental error. The dihedral angle between the planes C(10)–C(14) and C(15)–C(19) is only 2.0(2)° and the Fe atom is at 1.632(1) and 1.654(1) Å from these planes. The Fe–C(cyclopentadienyl) distances range from 1.999(10) to 2.045(5) Å [average 2.022(7) Å] and intracyclopentadienyl C–C bond lengths lie in the range 1.29(2)–1.427(6) Å [average 1.382(12) Å]. The ferrocenyl group is in an eclipsed conformation with a twist angle of 3.7(5)°. These angles are calculated as averages of the dihedral angle, defined as (cyclopentadienyl C)–(centroid)–(centroid)–(cyclopentadienyl C). These results agree with those obtained from the crystal structure of $[CuL_2(NO_3)_2]\cdot 2MeOH$[4] (L = **1**) where **1** is acting as ligand as well as with other known structures of ferrocene derivatives.[13] However a different relative orientation for the ferrocenyl groups was found in **1** and **2** because of the free rotation through the corresponding C(1)–C(10) bond in order to minimize steric effects present in $[CuL_2(NO_3)_2]\cdot 2MeOH$ (L = **1**) but not in **2**. The C(3)N(1)-C(2)C(2^I)N(1^I) ring is not planar and adopts the usual chair conformation with a torsional angle N(1)–C(2)–C(2^I)–N(1^I) of 11.7(5)°.

The $>C=C(CN)_2$ group is attached to the two nitrogen atoms giving a dicyanovinyl diamine group. Around the N(1) atom the N(1)–C(1) and N(2)–C(2) bond lengths are greater by ≈0.1 Å than the N(1)–C(3) bond distance. The short N(1)–C(3) distance is not the only unexpected feature in the $>C=C(CN)_2$ fragment. Thus, the C(3)–C(4) bond length [1.440(9) Å] is longer than C(4)–C(5) [1.413(5) Å] and greater than expected for a double bond. The C=C bond length in neutral tcne is 1.344(4) Å.[14] The combination of nitrogen atoms with the strong electron-acceptor character of the cyano group in **2** could lead to a polarization as is shown in Scheme 1.

Assuming these two canonical structures the shorter N(1)–C(3) and C(4)–C(5) bond distances than that expected for a single bond are justifiable as is the large C(3)–C(4) bond length. The presence of some single-bond character for C(4)–C(3) appears to be in line with the fact that the dicyanovinyl diamine group is not totally planar with a dihedral angle between the $C(N)_2$ and $C(CN)_2$ groups of 17.9(1)°. Neutral tcne has been reported to be planar and deviations of planarity have only been found when it acts as monoanion or especially when it acts as dianion.[15] This polarization effect also affects the vinyl carbon chemical shifts in the ^{13}C NMR spectrum of **2** (see below). The $>C=C(CN)_2$ group has also been reported bonded to an aryl group[16] and the observed distances are more similar to the ones reported for neutral tcne than those obtained for **2**. This fact

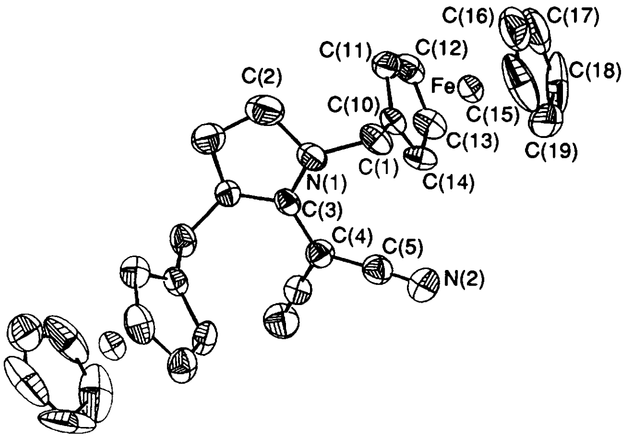


Fig. 1 An ORTEP drawing of compound **2** with the atom numbering scheme used. Hydrogen atoms were omitted for claity

Table 1 Final atomic coordinates* for compound **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe	0.8899(1)	0.5302(1)	0.0834(1)
N(1)	0.9863(3)	0.9035(3)	0.1994(3)
N(2)	1.4031(4)	1.1504(4)	0.0636(3)
C(1)	0.9519(4)	0.7702(4)	0.2022(3)
C(2)	0.8841(5)	0.9292(5)	0.1827(4)
C(3)	1.0965(5)	1.0	1/6
C(4)	1.2142(5)	1.0	1/6
C(5)	1.3171(5)	1.0849(4)	0.1087(3)
C(10)	0.9479(4)	0.7139(4)	0.1040(3)
C(11)	0.8425(4)	0.6586(4)	0.0397(3)
C(12)	0.8764(5)	0.6119(4)	−0.0417(3)
C(13)	1.0006(5)	0.6378(4)	−0.0284(3)
C(14)	1.0460(4)	0.7004(4)	0.0604(3)
C(15)	0.8345(12)	0.4417(6)	0.2122(5)
C(16)	0.7381(7)	0.3836(7)	0.1488(9)
C(17)	0.7757(12)	0.3421(5)	0.0775(6)
C(18)	0.8968(13)	0.3693(9)	0.0908(8)
C(19)	0.9347(7)	0.4358(7)	0.1785(7)

* Estimated standard deviations in the last significant digits, as observed from the least-squares refinement, are given in parentheses.

Table 2 Selected bond distances (Å) and angles (°) for compound **2***

N(1)–C(1)	1.466(6)	N(1)–C(2)	1.451(8)
N(1)–C(3)	1.350(5)	N(2)–C(5)	1.137(6)
C(1)–C(10)	1.512(6)	C(3)–C(4)	1.440(9)
C(4)–C(5)	1.413(5)	C(2)–C(2^{I})	1.564(8)
Fe–C(10)	2.009(5)	Fe–C(11)	2.019(6)
Fe–C(12)	2.045(5)	Fe–C(13)	2.043(4)
Fe–C(14)	2.025(4)	Fe–C(15)	2.017(7)
Fe–C(16)	2.037(8)	Fe–C(17)	2.008(5)
Fe–C(18)	2.013(14)	Fe–C(19)	1.999(10)
C(2)–N(1)–C(3)	110.4(3)	C(1)–N(1)–C(3)	125.9(3)
C(1)–N(1)–C(2)	116.5(4)	N(1)–C(1)–C(10)	114.1(4)
N(1)–C(2)–C(2^{I})	103.3(5)	N(1)–C(3)–N(1^{I})	118.8(2)
N(1)–C(3)–C(4)	124.1(2)	C(3)–C(4)–C(5)	121.5(2)
N(2)–C(5)–C(4)	176.6(6)	C(5)–C(4)–C(5^{I})	116.9(4)

* Equivalent position relative to x, y, z: I $1 + x - y, 2 - y, \frac{1}{3} - z$.

suggests that the presence in **2** of nitrogen atoms may induce structure **II** (Scheme 1) to have a greater contribution. The CN bond length could also be expected to be affected by the polarization effect present in **2**, however the obtained bond distance of 1.137(6) Å is very close to that found in neutral tcne. However this behaviour has also been observed in other related structures.[15]

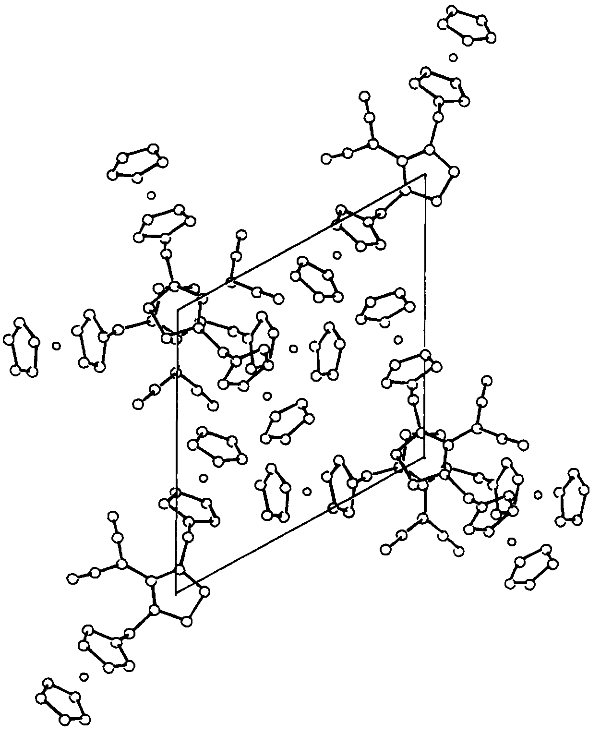
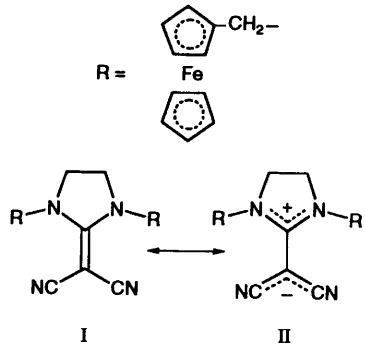


Fig. 2 Crystal structure of compound **2** projected in the *ab* plane



Scheme 1

Synthesis and Spectroscopic Characterization.—Reaction of *N*,*N*′-ethylenebis(ferrocenylmethylamine) **1** with tetracyanoethylene in dichloromethane gives yellow solutions from which compound **2** was isolated in good yield. It is known that reaction of tcne with ferrocene derivatives allows the isolation of different final products such as charge-transfer salts with decamethylferrocene[17] or a 1 : 1 charge-transfer complex of the neutral close-shell components using ferrocene as starting material.[18] The latter is unstable and a transformation of tcne to pentacyanopropenide[18] and tricyanoethenolate[19] occurs. In our case no such compounds were isolated and **2** was the only complex characterized. The formation of **2** can be understood by assuming nucleophilic attack of the secondary amines from **1** on the carbon–carbon double bond in tcne, activated by the presence of cyano substituents, and the sequential replacement of the two of the four cyano groups, removed as hydrogen cyanide.

The IR spectrum of compound **2** displays the characteristic ferrocene absorptions[20] with well defined bands at 480 [ν_{asym}(metal–ring) mode], 821 (out-of-plane CH deformation), 1102 (asymmetric ring breathing) and 2800–3100 cm^{-1} [ν(C–H) stretching]. The corresponding ν(N–H) stretching vibration in the region 3300–3100 cm^{-1} in the spectrum of **1** is lacking for **2**. The spectrum also shows two strong ν(CN) stretching peaks at

2198 and 2172 cm^{-1}. The UV/VIS spectrum (CH_2Cl_2 solution) shows a weak band centred at 420 nm and two intense and sharp absorptions at 230 and 260 nm.

The ^1H NMR spectrum of compound **2** shows two resonances at δ 3.32 and 4.53 for the two different CH_2 groups, in the N(1)C(2)C(2^I)N(1^I)C(3) ring. Three signals at δ 4.17, 4.19 and 4.28 (10:4:4 ratio) are ascribed to the protons of the cyclopentadienyl rings. One is a singlet which corresponds to the unsubstituted cyclopentadienyl group, the protons being equivalent because of free rotation of the ring. The other two resonances are pseudo-triplets, in accord with a coupling between the α-and β-protons (the α-protons are those closest to the *ipso*-carbon). In contrast for **1**, the three signals from the substituted cyclopentadienyl ring were found to be singlets.[4] The ^{13}C-{^1H} NMR chemical shifts of the vinyl carbon atoms of **2** are in accord with the structures depicted in Scheme 1. It is well known that ^{13}C chemical shifts for sp^2-hybridized carbon atoms in ethylene derivatives depend on the electron acceptor/donor properties of the fragment attached to these atoms. Thus the chemical shifts for the methylidene carbons in cyanoethylene are δ 108.2 and 137.5, the former being assigned to the carbons bonded to the cyano group.[21] The chemical shifts for the formally vinyl sp^2-hybridized carbons in **2** are δ 195.15 and 29.69. The shift of these signals with respect to the value found for tcne (δ 107.8) can be attributed to a pronounced polarization of the double bond (see Scheme 1). The downfield signal is assigned to the carbon bonded to the two nitrogen atoms, whereas the upfield signal is assigned to the carbon linked to the CN groups. In addition the ^{13}C-{^1H} NMR spectrum of **2** showed the resonance for the CN carbon at δ 118.05, a similar value to those found for related compounds.[21]

The remaining ^{13}C-{^1H} NMR signals for compound **2** are similar to those previously reported for **1**: δ 68.94 and 69.59 for the α- and β-carbons of the substituted cyclopentadienyl groups and δ 79.93 for the *ipso*-carbon. The unique signal for the carbons from the unsubstituted cyclopentadienyl groups also appears at δ 68.94. The signals for the two methylene groups show different chemical shifts (δ 46.32 and 48.08) in contrast to **1** for which only one signal was present.[4]

Non-linear Optical Properties.—Structural features of compound **2** such as its acentric character in the solid state and the occurrence of some polarization in the $(N)_2C{=}C(CN)_2$ framework, together with its pale yellow colour, led us to investigate its non-linear optical properties. A second harmonic generation phenomenon was observed. Although the Kurtz and Perry powder technique performed on **2** does not allow us to obtain absolute values of the second-order susceptibility, the appearance of the second harmonic generation is itself quite interesting. The signal for the uncalibrated polycrystalline powder was compared to that of urea powder measured under the same conditions. The former signal was found to be about 2/3 of the latter.

Some non-linear optical studies performed on organometallic compounds have been reported,[22,23] the strategy for some of the compounds being to link an electron-donating metallocene and an electron-withdrawing organic group by a conjugated system.[23] In compound **2** the ferrocene and cyano groups are not conjugated and the nonlinear optical properties observed appear to be attributed to conjugation of the nitrogen atoms and the cyano groups. A similar low second harmonic generation has been found in a related compound containing oxygen atoms and cyano groups attached at the vicinal carbons of a ethenic bond.[24]

The low second harmonic generation efficiency for compound **2** could be attributed partially to an unfavourable molecular packing. The crystal point symmetry 32, to which belongs the space group $P3_221$, is one of the eighteen non-centrosymmetric crystal point groups which are expected to display macroscopic non-linear optical properties.[25] However it is obvious from Fig. 2 that **2** cannot exhibit significant second-order harmonic generation. Assuming that the charge-transfer axis coincides with the ethenic C(3)=C(4) bond, there is no good alignment of **2** in the crystal giving mainly a non-polar packing arrangement and therefore a poor constructive addition of the hyperpolarizability to the second-order susceptibility.

Electrochemical Study.—The electrochemical behaviour of compound **2** has been studied by cyclic voltammetry, rotating-disk electrochemistry, controlled-potential coulometry and differential pulse voltammetry in dimethyl sulfoxide. Linear sweep voltammetry shows only one oxidation peak (A) at 0.067 V *versus* ferrocene. If the sweep is reversed after peak A the corresponding reduction peak A′ is detected. Plots of i_d *versus* $\omega^{\frac{1}{2}}$ (from rotating-disk experiment; i_d = diffusion intensity and ω = angular velocity of rotating-disk electrode) or i_p *versus* $v^{\frac{1}{2}}$ (from cyclic voltammetry; i_p = anodic peak intensity and v = scan rate) indicate that the electrochemical oxidation is diffusion controlled. Controlled-potential coulometry shows that **2** undergoes a two-electron oxidation process, according to two consecutive one-electron steps [equation (1)].

$$Fe^{II}Fe^{II} \rightleftharpoons [Fe^{III}Fe^{II}]^+ \rightleftharpoons [Fe^{III}Fe^{III}]^{2+} \qquad (1)$$

The couple A–A′ appears to be reversible with the anodic and cathodic current ratio close to unity and a separation (ΔE_p) of about 65 mV (ferrocene gives ΔE_p of 57 mV under the same conditions). Differential pulse voltammetry also shows a unique peak at 0.067 mV *versus* ferrocene, with a 98 mV half-peak width (ferrocene shows a 90 mV half-peak width). These data, ΔE_p and half-peak width, are slightly greater than expected for two one-electron reversible non-interacting sites. A separation of 57 mV in cyclic voltammetry and 90 mV half-peak width in differential pulse voltammetry are expected for an *n*-electron process in a redox system containing *n* non-interfering redox sites.[26] From the method reported in ref. 27 and 98 mV half-peak width corresponds to a $\Delta E_{\frac{1}{2}}$ of 43 mV and therefore the half-reaction potentials are $E_{\frac{1}{2}}{}^1 = 0.051$ V and $E_{\frac{1}{2}}{}^2 = 0.094$ V *versus* ferrocene. This gives a comproportionation equilibrium (2) with

$$Fe^{II}Fe^{II} + [Fe^{III}Fe^{III}]^{2+} \rightleftharpoons 2[Fe^{III}Fe^{II}]^+ \qquad (2)$$

a constant $K_c = 5.3$. A similar value (5.8) was found using cyclic voltammetry.[27]

The obtained K_c value for compound **2** is not far from the characteristic statistical equilibrium constant ($K_c = 4$).[27] This indicates that the mixed-valence species, $[Fe^{III}Fe^{II}]^+$, is basically not stabilized. This is expected assuming the absence in **2** of any electron delocalization between the two redox centres through the organic group attached to the ferrocenyl groups, the equilibrium constant found being greater than the statistical equilibrium constant perhaps due to repulsive electrostatic effects.

Cyclic voltammetry at cathodic potentials revealed a totally irreversible peak at −0.94 V *versus* saturated calomel electrode. We assign this peak to the reduction of the dicyanovinyl group. The tcne molecule undergoes facile reversible reduction processes yielding stable anion radicals, however, as expected, if two cyano groups are substituted the reduction becomes more difficult and reversibility is not found. Thus, for example, tricyanoethenolate exhibits a cathodic peak at −1.56 V relative to an Ag–AgCl electrode in saturated NaCl and acetonitrile as solvent.[19]

Acknowledgements

This work was supported by Dirección General de Investigación Científica y Técnica (proyecto PB91-0807-C02). Thanks are due to the Servicio de Espectroscopia y el Centro de Cálculo de la Universitat de València for instrumental and computing facilities, respectively. We are indebted to Keitaro Nakatani and Jacques Delaire, Equipe ENS Cachan, Laboratoire de Phyico-

Chimie des Rayonnements, Université Paris-Sud, CNRS, Orsay, for the non-linear optical measurements.

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Received 6th November 1992; *Paper* 2/05927D