Molecular materials for non-linear optics. Second harmonic generation and the crystal and molecular structure of the 4-nitrophenylimine of ferrocenecarboxaldehyde

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(Received July 14, 1992; revised October 20, 1992)

Abstract

Ferrocenyl derivatives of the form $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)CHN\text{-}(p\text{-}C_6H_4X)]$, where $X = NO_2$, F, Br, were tested for second harmonic generation (s.h.g.). Only when $X = NO_2$ was such activity observed. This was not large, however, at 1/3 times that of the urea standard. X-ray analysis confirms that the material is non-centrosymmetric, crystallizing in the space group $P2_12_12_1$. This dictates that despite being acentric the crystal arrangement essentially ensures a cancelling of the dipolar nature of the molecule. The residual s.h.g. must arise from *intermolecular effects*. This is only the second structural report of such a metallocene derivative to display s.h.g. The possible influence of the molecular shape of **1** and of related compounds is also discussed.

Introduction

Recently, chemists have shown considerable interest in designing molecular materials which exhibit large non-linear optical (n.l.o.) properties [1, 2]. In common with n.l.o. processes in general, second harmonic generation (s.h.g.) requires molecules with large differences between the ground and excited state dipole moments [3]. Such requirements are best met by donor-π-acceptor systems (D-π-A). However, this does not in itself ensure activity, as the molecules must also be in a non-centrosymmetric arrangement.

Since Green *et al.* [2, 4] first reported on ferrocenyl-4-(4-phenyl)ethylenes, that exhibited considerable s.h.g., there has been increasing interest in the incorporation of metals into n.l.o. materials through coordination and organometallic compounds [5–16]. The ferrocenyl group as a donor substituent has now been used in a number of materials [7–16]. However, there has only been one previous X-ray structural report of an active compound [2, 4]. We have recently reported on a series of ferrocenyl Schiff bases which were designed with the aim of producing materials for s.h.g. [16]. Here we present the results of a study of the s.h.g. properties of three ferrocenyl imines and report the crystal and molecular structure of the s.h.g. active material, the 4-nitrophenylimine of ferrocenecarboxaldehyde (**1**).

Experimental

The compounds were prepared as described elsewhere [16]. Recrystallization from CH_2Cl_2 afforded crystals of **1** suitable for single-crystal X-ray study.

Crystal structure determination of 1

Crystal data. $C_{17}H_{14}FeN_2O_2$, $M = 334.16$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a = 8.301(1)$, $b = 11.135(1)$, $c = 15.575(1)$ Å, $Z = 4$, $D_c = 1.54$ g cm^{-3}, $V = 1439.7$ Å^3, μ(Mo Kα) = 10.5 cm^{-1}, λ(Mo Kα) = 0.71073 Å.

Unit cell dimensions were obtained by a least-squares procedure from the setting angles of 25 centred reflections with Bragg angle $22 < \theta < 24°$, using an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Data were collected in the range $0 < \theta < 25°$ for reflections *h*09, *k*013, *l*018. The space group was determined by systematic absences, from Harker planes in the Patterson function, and the absence of inversion symmetry was detected statistically from an *E*-map and ultimately confirmed by the s.h.g. measurement. The usual corrections for Lorentz and

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polarization factors were made and an empirical absorption correction was also made after scanning nine reflections each at 36 different azimuthal angles (Ψ-scan). The iron atom position was determined from the Patterson function. The structure was determined by multiple superposition and by difference Fourier techniques and was refined by full matrix least-squares methods using Killean and Lawrence weights [17]. Hydrogen atoms (isotropic) were constrained to ride on their bonded atoms, all other atoms being refined anisotropically. The refinement converged with *R*(unweighted) 0.032, *R*(weighted) 0.042 for 1483 unique reflections. A final difference Fourier map showed maximum positive and negative peaks of 0.27 and −0.53 e/Å^3, respectively. Neutral atom scattering factors were used. Computations were carried out on a MicroVax using SHELXS86 [18] and MolEN [19] programmes. Diagrams were drawn with ORTEP [20] and PLUTO [21]. See also 'Supplementary material'.

Second-harmonic measurements were made on powder samples at a pump wavelength of 1.9 μm using urea as standard.

Results and discussion

Second harmonic generation measurements

The powder second harmonic generation measurements of the compounds, $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)CHN(p\text{-}C_6H_4X)]$ where X = NO_2, F, Br, showed only the nitrophenyl derivative to be active. This was however small at 0.33 times that of urea (measured at a pump wavelength of 1.9 μm). The inactivity of the fluoro and bromo derivatives indicates that they crystallize in centric arrangements.

Crystal and molecular structure of 1

A single crystal X-ray structure determination confirmed the acentric nature of **1**. Atomic coordinates are given in Table 1. Table 2 contains selected bond lengths and angles for **1**. The structure reveals almost eclipsed cyclopentadienyl rings which are tilted slightly (3.6°) with respect to each other. The molecule exhibits an E configuration (that is the donor and acceptor groups are *trans*). The Cp rings are essentially planar, as is the nitrophenyl group. However, despite the available resonance pathway and an E configuration, the $(\eta\text{-}C_5H_4)$ and the $(C_6H_4NO_2)$ groups are inclined at an angle of ~66° (see Fig. 1). It is likely that steric interaction between the CH=N hydrogen and one of the *ortho* hydrogens of the benzene ring causes this lack of planarity. Rotation about the N2–C7 bond, so that the two aromatic rings are essentially coplanar, produces a H...H distance of ~1.6 Å, as compared with ~2.5 Å in the actual conformation.

TABLE 1. Positional parameters and their e.s.d.s

Atom	*x*	*y*	*z*
Fe1	0.47343(7)	0.21650(4)	0.63912(3)
O1	0.5218(6)	0.8409(4)	0.2255(2)
O2	0.4634(6)	0.9862(3)	0.3108(3)
N1	0.4837(5)	0.8802(4)	0.2963(3)
N2	0.3947(5)	0.5574(3)	0.5705(2)
C1	0.5071(5)	0.3960(3)	0.6558(2)
C2	0.6439(5)	0.3302(4)	0.6850(2)
C3	0.5943(6)	0.2531(4)	0.7507(2)
C4	0.4246(6)	0.2682(4)	0.7625(3)
C5	0.3710(5)	0.3566(4)	0.7039(3)
C6	0.5111(5)	0.4856(3)	0.5869(2)
C7	0.4165(5)	0.6358(3)	0.4997(3)
C8	0.3910(6)	0.7578(4)	0.5118(3)
C9	0.4151(6)	0.8382(4)	0.4463(3)
C10	0.4622(5)	0.7949(4)	0.3668(2)
C11	0.4822(5)	0.6731(4)	0.3511(2)
C12	0.4594(6)	0.5941(4)	0.4182(3)
C15	0.5275(7)	0.0419(4)	0.6094(3)
C16	0.3597(7)	0.0547(4)	0.6270(3)
C17	0.2969(6)	0.1382(4)	0.5672(3)
C18	0.4233(7)	0.1768(4)	0.5135(3)
C19	0.5673(6)	0.1167(4)	0.5392(3)

TABLE 2. Selected bond lengths (Å) and angles (°)

Fe–C(C_5H_5) (av.)	2.049(5)
Fe–C(C_5H_4) (av.)	2.040(4)
Fe–ring(C_5H_5)	1.656(5)
Fe–ring(C_5H_4) (av.)	1.645(5)
C–C(C_5) (av.)	1.418(6)
C1–C6	1.466(6)
N–O (av.)	1.220(6)
C6–N2	1.279(6)
C10–N1	1.463(5)
N2–C7	1.418(5)
C1–Ĉ6–N2	123.7(4)
C6–N̂2–C7	116.3(4)

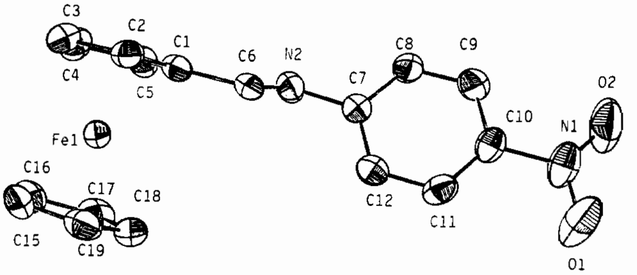

Fig. 1. View of $(\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_4)CHN(C_6H_4NO_2)$ showing the inclination of the $(C_6H_4NO_2)$ group and the $(\eta\text{-}C_5H_4)$ moiety.

Calabrese *et al.* [11] have recently stated the advantages for s.h.g. of E-type substitution over Z-type (in the latter the donor and acceptor groups are *cis*), in that (i) the latter type can often cause a lack of coplanarity between donor and acceptor groups which leads to their coupling diminishing and (ii) the reduction of the through space distance between them results in the change in dipole per unit charge separation being less. As **1** exhibits an E-type configuration it was expected to fit these criteria; however, the steric interaction between H atoms upsets the coplanarity.

A similar lack of planarity was observed for *Z*-ferrocenyl-4-(4-nitrophenyl)ethylene [2, 4] and was attributed to steric interactions between the Cp_α and benzene *ortho* hydrogens. Although the angle of twist (47°) is less compared to ~66° in **1**, allowing for slightly better coupling via resonance, this is not the likely cause of the large difference in s.h.g. performance between the two materials (0.33 versus 62). *Z*-Ferrocenyl-4-(4-nitrophenyl)ethylene crystallizes [2] in the space group *F2dd* which allows the vector sum of molecular dipoles to be non-zero.

This is not the case for **1**. The low s.h.g. performance might have been anticipated from the symmetry of the $P2_12_12_1$ space group. The molecules are aligned with their dipoles at an angle of ~45° to the 2_i^z axis (see Fig. 2). However, the presence of the other 2_1 axes necessitates that the sum of the four molecular dipoles in the unit cell is zero. The crystal arrangement, despite being non-centrosymmetric, effectively leads to a cancelling of the molecular dipoles. The residual s.h.g. must arise from intermolecular effects.

Electrostatic interactions between adjacent molecules are often cited as being responsible for the centrosymmetric head-to-tail pairing of many, otherwise promising, materials. Whitesell *et al.* [22] have recently made an analysis of the Cambridge Structural Database to test the validity of this conception. Their results demonstrate that the magnitude of the molecular dipole does not correlate with the relative molecular orientations in the space group $P2_1$, nor vary significantly between centrosymmetric $P\bar{1}$ and non-centrosymmetric $P1$. They concluded that the high preference for centrosymmetric solid state organization in molecular crystals could not be attributed to dipole–dipole interactions. However the authors do acknowledge that although their study considers neither interactions between polar groups, nor molecular shape, these factors do play a significant role.

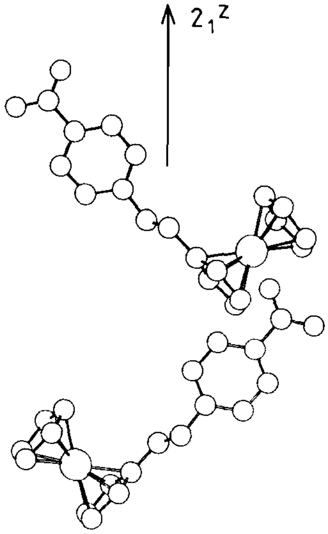

Fig. 2. Head-to-tail alignment of the molecular dipoles along the 2_1^z axis.

The importance of molecular shape has been drawn to our attention through the recent work of Mingos and Rohl [23, 24] and is well demonstrated in the structure of *trans*-(η-C_5H_5)Fe(η-C_5H_4)CHNNCH-*p*-$C_6H_4NO_2$. The extension of the conjugate link between the donor and acceptor groups, produces a structure that satisfies the suggested criteria of Calabrese *et al.* [11] for n.l.o. properties. The molecule has an almost idealized coplanar arrangement between the ferrocenyl donor and the nitrophenyl moiety. However, this molecular shape facilitates intermolecular π–π interactions, producing stacked centrosymmetric dimers which can pack efficiently in the solid state (Fig. 3). The material is thus inactive with regard to s.h.g. despite the apparently encouraging molecular structure. The nonplanar shapes of **1**, and the material reported by Green *et al.* [2] would not be expected to pack efficiently as centrosymmetric dimer pairs. This may account for the absence of this structural feature in these compounds and increase the possibility of acentric crystallization.

Excluding ionic and hydrogen-bonded solids, the largest driving force for the adoption of any molecular arrangement is the efficient filling of space. Weaker forces cannot then dictate the resulting structure. However, when such interactions occur and lead to the production of efficiently packed dimeric or multimolecular assemblies, then these structural features would be expected to be retained by the crystallization process. Such interactions might be: (a) the antiparallel alignment of dipoles, (b) the maximization/minimization of

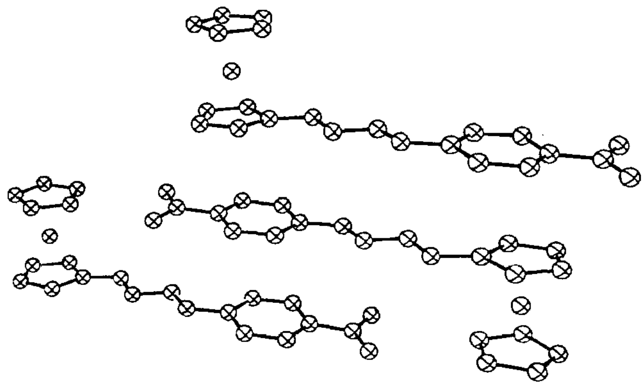

Fig. 3. Packing of centrosymmetric dimer pairs of (η-C_5H_5)Fe(η-C_5H_4)CHNNCH(*p*-$C_6H_4NO_2$) in DAAD-type stacks.

attractive/repulsive intermolecular interactions, i.e. π–π interactions, or some combination of (a) and (b). As (a), and many cases (b), are achieved by centrosymmetric arrangements, irregularly shaped molecules would be advantageous for the production of solid-state materials with s.h.g. properties.

For **1**, while coplanarity is not observed between donor and acceptor, the greatest restriction to the s.h.g. performance must be identified as the space group.

Supplementary material

Atomic coordinates, bond lengths, inter-bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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