Crystal structures of amino substituted dicyanoquinodimethanes with potential nonlinear optical applications

Mosurkal Ravi,[a] Marek Szablewski,[a] Nancy-Ann Hackman,[a] Graham H. Cross,*[a] David Bloor,[a] Andrés E. Goeta[b] and Judith. A. K. Howard[b]

[a] Department of Physics and [b] Department of Chemistry, University of Durham, Durham, UK DH1 3LE. E-mail: G.H.Cross@durham.ac.uk

The crystal structures of chiral aminomethylpyrrolidine-substituted 7,7,8,8-tetracyanoquinodimethane (TCNQ) and dipyrrolidine-substituted 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (TCNQF$_4$) have been determined by single crystal X-ray crystallography. The TCNQ derivative crystallised in a noncentrosymmetric space group ($P2_12_12_1$) and showed powder second harmonic generation (SHG) comparable to that of urea. An interesting case of H-bonding observed in its crystal structure is discussed. The TCNQF$_4$ derivative is the first in the class of amino-substituted tetrafluoro-TCNQ derivatives. It has been observed to crystallise in a centrosymmetric space group ($P2_1/c$). Semi-empirical quantum chemical calculations using crystal structure geometries indicate moderate and negative (30–50×10^{-30} esu) hyperpolarisabilities. Crystal structural features and computational results are compared with known analogous systems.

Introduction

Synthesis of organic molecules with large hyperpolarisabilities is under extensive investigation for their possible nonlinear optical (NLO) applications, such as second harmonic generation and electro-optic modulation, for future information technology and telecommunications. Present research is mainly focused on the development of organic chromophores with a large figure of merit, $\mu\beta$ (where μ is the ground state dipole moment and β is the hyperpolarisability), to either dope in a host polymer matrix or covalently incorporate in the polymer backbone for NLO applications.[1]

In 1988, Gompper and Wagner[2] predicted that amino-substituted tetracyanoquinodimethane (TCNQ) derivatives would be of potential interest for NLO applications due to their strong polar character. Earlier, Lalama et al.[3] studied the prototypical molecule (1 in Fig. 1) and reported it to have a large β value of $(-240 \pm 60) \times 10^{-30}$ esu at an excitation wavelength of 1.17 eV, which is comparable to stilbene derivatives having substantially large conjugation lengths.[4] Recently diamino-substituted quinodimethanes have emerged as a new class of chromophores[5] for fabricating materials with large NLO figures of merit in view of their positive features, such as: (i) ease of synthesis and flexibility of introducing a variety of donor groups, (ii) high reaction yields, (iii) thermal stability up to 250–350 °C, (iv) high ground state dipole moments and (v) optical transparency through most of the visible range; $\lambda_{\text{cut-off}}$ (wavelength at which the absorption of the molecule diminishes) is typically around 500 nm. Typical molecular absorption coefficients at maximum absorption (ε_{max}) for this class of compounds[6] fall between 20 000–25 000 M^{-1} cm^{-1}. This suggests that these highly dipolar molecules are potentially useful for local area network applications whose operating wavelengths may be in the visible region. These molecules tend to crystallise in centrosymmetric space groups due to their large ground state dipole moments of around 15–20 D and due to their planarity. Introducing chirality to induce necessary noncentrosymmetry is a popular strategy for the design of NLO crystals based on this class of materials.[7]

The influence of the placement of stereogenic centres and H-bonding on the dipole alignment, which affect the solid state SHG, has been previously studied for this class of materials.[8] In these molecules, a molecular twist between the diaminomethylene plane and the quinoid ring is a common feature and appears to arise from strong steric interactions between groups attached to the amino N-atoms and ortho H-atoms on the benzenoid ring. Experimental and theoretical investigations on these molecules have revealed a strong correlation between β and the molecular twist.[5a] In this paper, we present a theoretical estimate of μ and β for these systems and describe the synthesis and crystal structures of compounds 2 and 4 (Fig. 1) along with a discussion of relevant structural aspects which correlate with their physical properties. The corresponding analogues and previously reported[9]
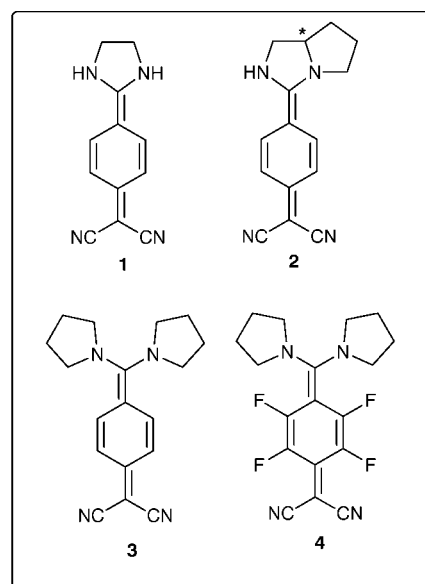

Fig. 1 Molecules considered in this study.

Table 1 Crystallographic data for compounds **2** and **4**

Compound	**2**	**4**
Molecular formula	$C_{15}H_{14}N_4$	$C_{18}H_{16}F_4N_4$
Morphology	Needles	Prisms
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
$a/\text{Å}$	7.803(1)	10.114(1)
$b/\text{Å}$	9.474(1)	14.412(2)
$c/\text{Å}$	17.819(4)	12.142(2)
$\alpha/°$	90.0	90.0
$\beta/°$	90.0	113.634(1)
$\gamma/°$	90.0	90.0
$V/\text{Å}^3$	1317.3(4)	1621.4(4)
Z	4	4
Density/g cm^{-3}	1.262	1.493
μ/mm^{-1}	0.079	0.124
Measured reflections	10616	10751
Independent reflections	3016	3715
$R[I > 2\sigma(I)]$	0.0464	0.0534
$wR2$ (all data)	0.1026	0.1208

compounds **1** and **3** (Fig. 1) are considered for comparison with **2** and **4**, respectively.

Experimental

Synthesis

Compounds **2** and **4** were prepared following the procedure reported by Hertler et al.[10]

Compound 2. To a warm solution of 0.1 g (0.49 mmol) of TCNQ in 20 ml of acetonitrile, 0.107 g (1.07 mmol) of S-(+)-2-aminomethylpyrrolidine was added. A dark green solution appeared immediately and a precipitate began to form. After heating to reflux for 1 h, the solution was allowed to stand at 25 °C for about 4 h. Then the solution was filtered and the resulting product washed with ether to obtain a greenish compound (80% yield). Recrystallisation from acetonitrile gave greenish yellow needles, which did not melt up to 350 °C. The IR spectrum of the compound (KBr wafer) shows absorptions at 2141, 2184 (conjugated nitrile) and 3241 cm^{-1} (N–H absorption). The UV-Vis absorption spectrum in acetonitrile solution shows a band at 411 nm. Elemental analysis, found (calculated): C, 71.63 (71.98); H, 5.67 (5.64); N, 22.50 (22.38)%.

Compound 4. To a warm solution of 0.1 g (0.36 mmol) of TCNQF$_4$ in 20 ml of THF, excess pyrrolidine, 0.14 ml (1.69 mmol), was added. A dark green colour developed immediately and a light coloured compound began to precipitate. The solution was heated to reflux for 4 h and allowed to stand

Table 2 Important bond lengths (Å) and twist angles (°) in **2** and **4** from single crystal X-ray analysis[a]

2		4	
C(6)–N(1)	1.334(2)	C(5)–N(1)	1.327(3)
C(6)–N(2)	1.331(3)	C(5)–N(2)	1.335(3)
C(6)–C(7)	1.451(3)	C(5)–C(10)	1.482(3)
C(7)–C(8)	1.410(3)	C(10)–C(11)	1.390(3)
C(7)–C(12)	1.405(3)	C(10)–C(15)	1.391(3)
C(8)–C(9)	1.377(3)	C(11)–C(12)	1.374(3)
C(12)–C(11)	1.383(3)	C(15)–C(14)	1.368(3)
C(9)–C(10)	1.421(3)	C(12)–C(13)	1.406(3)
C(11)–C(10)	1.408(3)	C(14)–C(13)	1.415(3)
C(10)–C(13)	1.448(3)	C(13)–C(16)	1.437(3)
C(13)–C(14)	1.413(3)	C(16)–C(17)	1.418(3)
C(13)–C(15)	1.405(3)	C(16)–C(18)	1.416(3)
C(8)–C(7)–C(6)–N(2)	15.5(3)	C(15)–C(10)–C(5)–N(2)	62.3(2)

[a] The atom labeling is shown in Fig. 2 and 3.

at 25 °C overnight. The solution was cooled to about 10 °C, the precipitate filtered off and the filter cake washed with ether to give 0.1 g (75% yield) of a yellow crystalline compound, **4**. Recrystallisation from acetonitrile gave transparent pale yellow rectangular prism type crystals, which decompose at 300 °C. The IR spectrum of the compound (KBr wafer) shows absorptions at 2154, 2180 (conjugated nitrile) and 1215 cm^{-1} (C–F stretch). The UV-Vis absorption spectrum in acetonitrile solution shows a band at 368 nm. EI MS (m/z): 365 (M + H$^{+\cdot}$), 364 (M$^{+\cdot}$), 253. Elemental analysis, found (calculated): C, 59.51 (59.34); H, 4.23 (4.40); N, 15.45 (15.39)%.

Crystal structure determination

Single crystal structure determinations of **2** and **4** were carried out from data collected using graphite monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) on a Bruker SMART-CCD detector diffractometer equipped with a Cryostream N$_2$ flow cooling device.[11] A series of narrow ω-scans (0.3°) were performed at several ϕ-settings in such a way as to cover a hemisphere of data to a maximum resolution of 0.77 Å. Data collections were carried out at 150 K. Cell parameters were determined and refined using the SMART software[12] from the centroid values of 492 (**2**) and 192 (**4**) reflections with 2θ values between 27° and 53°. Raw frame data were integrated using the SAINT program.[13] The structures were solved using direct methods and refined by full-matrix least squares on F^2 using SHELXTL.[14] Crystal data and details for the structure determinations and refinements are given in Table 1. Selected bond distances and angles are given in Table 2.

CCDC reference number 440/127. See http://www.rsc.org/suppdata/nj/1999/841/ for crystallographic files in .cif format.

Results and discussion

Theoretical

All the computations presented in this paper were carried out using the MOPAC93 program.[15] Molecular structure optimisations were carried out using the AM1 method with the PRECISE keyword. The hyperpolarisabilities we present here are the average β (sometimes referred to as β_{vec} in the literature), defined as follows:

$$\beta = \left[\sum_{i=1}^{3} \beta_i^2\right]^{1/2}$$

where

$$\beta_i = \beta_{iii} + 1/3\sum_{j\neq i}(\beta_{ijj} + 2\beta_{jji})$$

and β_{iii}, β_{ijj} are the hyperpolarisability tensor components. As in other donor–acceptor substituted systems, β_{xxx} (by convention, x is chosen as the direction of the dipole axis) is the dominant component in these quinoid compounds, since the maximum polarisation occurs along the dipole direction as a result of the charge transfer interaction between the dicyanomethylene and diaminomethylene units.

The computational results for the compounds **2** and **4** are reported in Table 3. The literature data[9] on compounds **1** and **3** are provided in the same table for comparison. The calculated ground state dipole moments and static hyperpolarisabilities (evaluated at excitation energy $h\omega = 0$ eV) are also presented in Table 3. These push–pull quinoid molecules have a characteristic twist between the diaminomethylene plane and the quinoid ring; we denote this twist angle as θ (defined with atom labelling in Table 2). This twist has been observed in all the previously determined crystallographic structures[8] as well as in the computed geometries. The θ values obtained from AM1 optimised geometries as well as from crystal structure (CS) geometries, where available, are provided in Table 3.

Table 3 The calculated ground state dipole moment (μ_g), static hyperpolarisabilities [$\beta(0)$] and twist angles (θ) from crystal structure (CS) and optimised AM1 geometries for compounds **1**–**4**

		Theoretical $\beta(0)/10^{-30}$ esu		Twist angle[a] $\theta/°$	
	μ_g/D	AM1	CS	AM1	CS
1[b]	14.8	3.2	—	0.0	—
2	12.5	1.5	41.3	3.5	15.5
3[b]	14.1	39.5	52.6	59.3	56
4	19.1	20.4	33.7	68.0	62.3

[a] Defined in Table 2. [b] Ref. 9.

The ground state dipole moments of these compounds were found to be large compared to known organic NLO systems. We measured the experimental dipole moments of **3** and **4** in dichloromethane and they were found to be 19.8 D and 17.7 D respectively (the agreement between theoretical and experimental dipole moments is good, within experimental error of 20%). These arise from the zwitterionic nature of the molecule which is due to intramolecular charge transfer from the diaminomethylene and to the dicyanomethylene. The static hyperpolarisabilities $\beta(0)$ of all the compounds are fairly large and negative. This negative sign arises from a decrease in dipole moment ($-\Delta\mu$) on excitation of these molecules, which we have verified experimentally by the observation of negative solvatochromism.[16] Comparisons could only be made between **1** and **2** or **3** and **4**, as these two pairs belong to different sub-classes in this class of quinoid compounds. The calculated twist angle, θ is quite small or zero in **1** and **2** but quite high in **3** and **4**. In the case of **1** and **2** the amino substituents derived from primary diamines, which form rigid type molecules, and the amino N-atoms possess secondary amino character. Consequently the steric repulsion, which occurs between the H-atoms on these N-atoms and the benzene ring *ortho* H-atoms, is weak. In the latter pair (**3** and **4**), the amino substituents are mainly derived from cyclic amines having tertiary amine character and thus the steric repulsion is stronger. As a result large twist angles for **3** and **4** were obtained from the calculations. As mentioned earlier, it is interesting to note that the $\beta(0)$ values have a strong correlation with the twist angles. The unusually large $\beta(0)$ value for **2**, calculated using the CS geometry, in comparison with the one obtained using the AM1 geometry, could be due to the considerable twist angle (16°) in the CS geometry.

It can be seen in Table 3, that the β(AM1) values are found to be smaller than the β(CS) values in **2**, **3** and **4**. This arises mainly due to the difference in the bond lengths (Table 2) within the quinoid framework in the CS geometries. This is confirmed by quantifying quinoid–benzenoid character (QBC), which is defined based on the magnitude of the deviations of the ring bond lengths from a standard value of 1.400 Å, assumed for benzene.[17] From QBC values, it is found that the CS geometries are more benzenoid than the AM1 equivalents, in agreement with an earlier report on this class of compounds.[17] Since the former are the optimal geometries for those molecules in a strongly polar crystal environment, they have larger QBC values than the AM1 geometries. It is also known that β values decrease monotonically with the QBC values[5a] and hence the low β values are expected for the AM1 structures, which have smaller QBC values.

Molecular and crystal structures

From Table 1, it can be seen that **2** belongs to a non-centrosymmetric space group ($P2_12_12_1$) whereas **4** belongs to a centrosymmetric space group ($P2_1/c$). We report for the first time the crystal structure of a rigid type molecule in the class

of quinoid materials, *i.e.* **2**. Efforts to grow single crystals of **1** and of the compounds where the H-atoms have been substituted by methyl groups failed as these compounds tend to form powders. **2** is a chiral molecule and could be considered as an improved version of **1**. **4** is the first tetrafluoro-TCNQ derivative in the class of quinoid compounds.

SHG measurements on **2** using the Kurtz powder technique[18] showed an SHG intensity comparable to urea. The molecular structures and unit cell views of **2** and **4** are presented in Fig. 2 and 3, respectively. Selected bond lengths and twist angles are presented in Table 2 (the atom labelling is as shown in Fig. 2 and 3). Careful analysis of the unit cell packing in **2** revealed that although the molecule has a rod-like structure, the stereogenic centre on the donor end could have introduced crystallographic noncentrosymmetry. Molecular asymmetry created in the diaminomethylene end could have also helped in forming noncentrosymmetry in the crystal structure.

The H-bonding observed in the crystal structure of **2** along the *b*-axis (Fig. 4) is an interesting feature. A search for short intermolecular contacts revealed that the nitrogen on the diamino end acts as an H-bonding donor and the nitrogen of the cyano group of a neighbour molecule acts as an acceptor leading to an N(2)–H···N(3) bond. These H-bond links lead to a zigzag chain extending along the *b* direction. Recently it has been reported that H-bonding plays an important role in modifying the molecular structure by producing an enhanced twist in one of the quinoid systems.[8] It could be argued that in the case of **2**, H-bonding could have induced a change in the molecular structure by enhancing the molecular twist from $\theta = 3.5°$ (calculated from AM1 gas phase geometry) to $\theta = 15.5°$ (observed in the crystal structure geometry), which in turn has contributed positively to its molecular hyperpolarisability, calculated using the CS geometry.

Despite the fact that **4** is a derivative of TCNQF$_4$, which is a stronger electron acceptor than TCNQ, it is surprising to note that there is not much difference in **3** and **4** in terms of their experimental dipole moments and absorption energies. A similar comparison between the blue zwitterionic derivatives of TCNQ and TCNQF$_4$ reported earlier[19] showed a dramatic difference in the absorption energies of charge transfer bands, which is well understood in terms of their electron affinities and reduction potentials. The tetrafluoro version of **1**, prepared in our laboratory, also showed the absorption
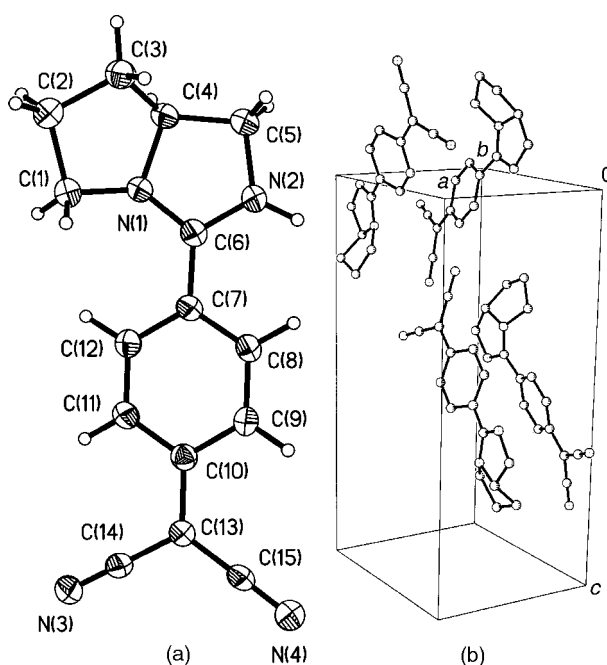

Fig. 2 (a) Molecular structure and (b) unit cell view of **2**.
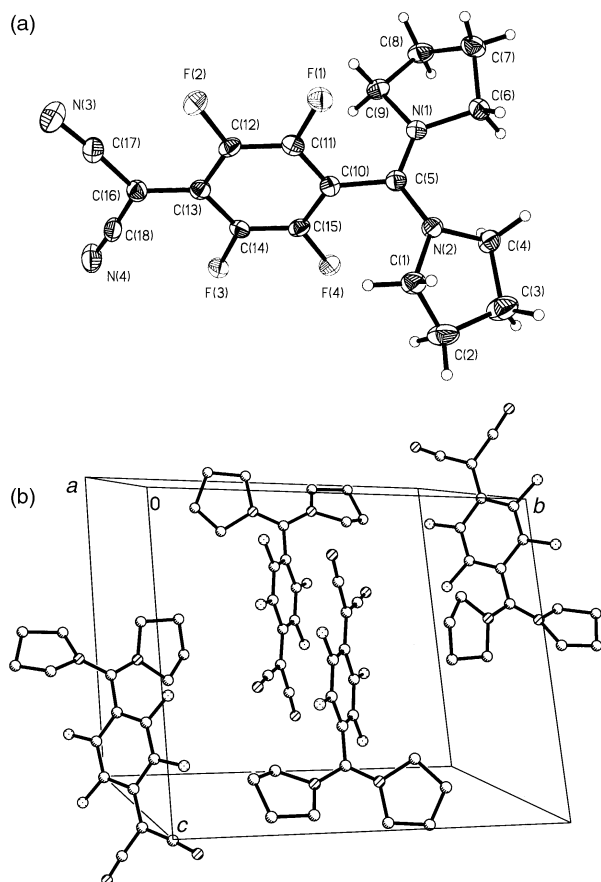
(a)

(b)

Fig. 3 (a) Molecular structure and (b) unit cell view of **4**.

maximum at 406 nm, which is present in **1**. From Fig. 3(b), it can be seen that the dipoles in **4** are arranged antiparallel to form a centric array roughly perpendicular to the *b*-axis. Thus **4** showed no powder SHG. Crystal structure analysis of **4**, revealed that its structural features are not much different from its TCNQ analogue **3**, except that the QBC calculated
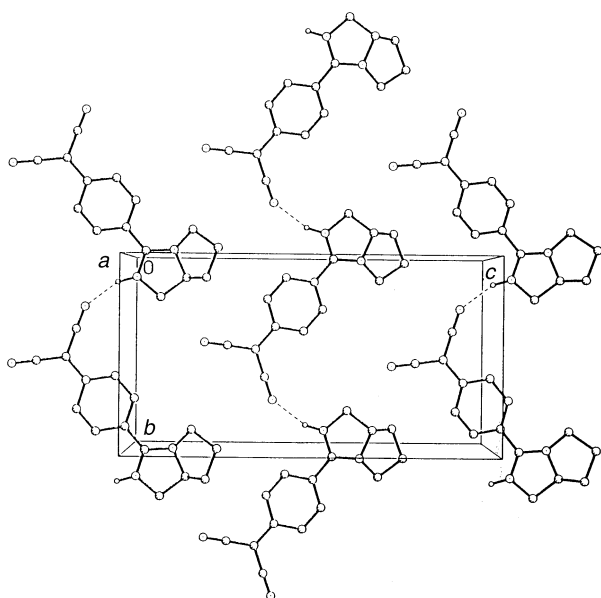

Fig. 4 H-bonding chains in **2** along the *b*-axis [N(2)–H···N(3); D–H = 0.92 Å, H···A = 1.96 Å; D···A = 2.842 Å; N–H···N = 159°]; the H-bonds are shown using dashed lines.

from CS geometry for **4** (0.7) is slightly smaller than for **3** (0.75). Nevertheless, the substitution of protons for fluorine atoms on the quinoid ring apparently enhances the molecular twist, which is an important factor in tuning the molecular hyperpolarisabilities.

Conclusion

Two new compounds in the class of diaminodicyano-quinodimethanes have been synthesised and their crystal structures have been determined. Compound **2** crystallised in a noncentrosymmetric space group and showed powder SHG comparable to urea. An intermolecular H-bond observed in **2** could be a positive factor in enhancing the molecular twist, which led to a large calculated hyperpolarisability in this molecule. **4** is the first tetrafluoro-TCNQ derivative in the class of quinoid compounds and crystallised in a centrosymmetric space group. From a comparison of **3** and **4**, it was found that the push–pull effect is similar in both, despite the fact that **4** is a derivative of a strong electron acceptor, *i.e.* TCNQF$_4$. We are currently investigating these aspects in more detail. The synthesis of polymers incorporating these highly dipolar molecules is also underway in our laboratory.

Acknowledgements

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Paper 9/03793D