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A charge density study of an intramolecular charge-transfer quinoid compound with strong NLO properties†

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An experimental charge density investigation of 7,7-di[(*S*)-(+)-2-(methoxymethyl)pyrrolidino]-8,8-dicyanoquinodimethane establishes the presence of a large charge separation as well as a high in-crystal dipole moment compared to the free molecule in frozen geometry, consistent with the high SHG activity of the compound.

Intramolecular charge transfer in aromatic push-pull molecules has been a subject of interest in several experimental charge density studies.[1–7] Thus, in *p*-nitroaniline[1] and *N*-(4-nitrophenyl)-L-prolinol,[2,3] the donor and the acceptor groups have been shown to carry comparable fractional charges of ~0.5 e, the phenyl ring itself carrying a relatively small charge. Charge separation between the donor and the acceptor groups is not always distinct in such molecules, intermolecular bonding effects often playing a crucial role. For instance, in the α-polymorph of *p*-nitrophenol,[4] the phenolic hydrogen participates in trifurcated hydrogen bonding with the nitro group and as a result, the donor and the acceptor groups do not have the expected formal charges. Similar observations have been made in the case of 2-methyl-4-nitroaniline[5] and *p*-amino-*p*′-nitrobiphenyl.[6] Since charge separation in these push-pull molecules is favored by the resonance dipolar or quinoid form, we considered it of interest to investigate an intramolecular charge transfer compound with the quinoid structure by the experimental charge density method. For this purpose, we have chosen 7,7-di[(*S*)-(+)-2-(methoxymethyl)pyrrolidino]-8,8-dicyanoquinodimethane (DMPDQ), which exhibits a large π-separation (~6 Å) between the donor (pyrrolidine ring) and the acceptor (cyano) groups. Besides investigating charge transfer in this molecule, we have examined the effect of the non-centric field on the group charges and also on the dipole moment of the molecule in the crystal, since DMPDQ is a good NLO material with SHG activity 55 times that of urea.[8]

In Fig. 1, we show the ORTEP diagram of DMPDQ with atom labeling. A Cambridge Crystallographic Database survey of molecules with the quinoid unit (141 compounds with $r < 10\%$) showed that the endocyclic and the exocyclic double bonds are generally shorter than the single bonds by *ca.* 0.09 and *ca.* 0.05 Å, respectively. In DMPDQ, the bond lengths associated with the quinoid ring are equal within 0.03 Å, indicating that the ring has some benzenoid character, an effect arising from the polarization of charge from the amino end to the cyano end. Accordingly, the exocylic double bonds are much longer: C(1)–C(7), 1.476 and C(4)–C(8), 1.444 Å.

The static deformation density of the molecule in the plane of the quinoid ring (Fig. 2) illustrates the quality of the multipole refinement using the program XD.[9] The bonds appear as concentric contours while the lone pairs on the cyano nitrogens appear as lobes. The contours associated with the pyrrolidine rings do not appear in this plane. In line with the equivalence of the bond lengths in the quinoid ring, the critical point densities in the formal double and single bonds are found to be similar. The C^{sp2}–N bonds [C(7)–N(1) and C(7)–N(2)] carry higher densities at the bond critical points (*ca.* 2.5

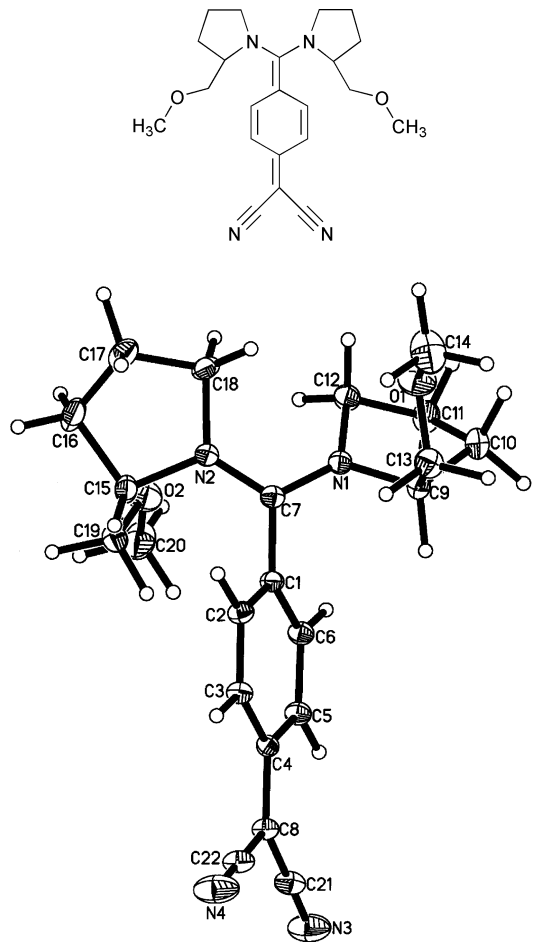

Fig. 1 ORTEP diagram of DMPDQ. Thermal ellipsoids shown at 50% probability level. The formula diagram of the molecule is shown at the top.

† Electronic supplementary information (ESI) available: 3 supplementary tables giving the Hirshfeld rigid-bond test results, multipole populations and analysis of the bond critical points for DMPDQ. See http://www.rsc.org/suppdata/nj/b1/b103117c/
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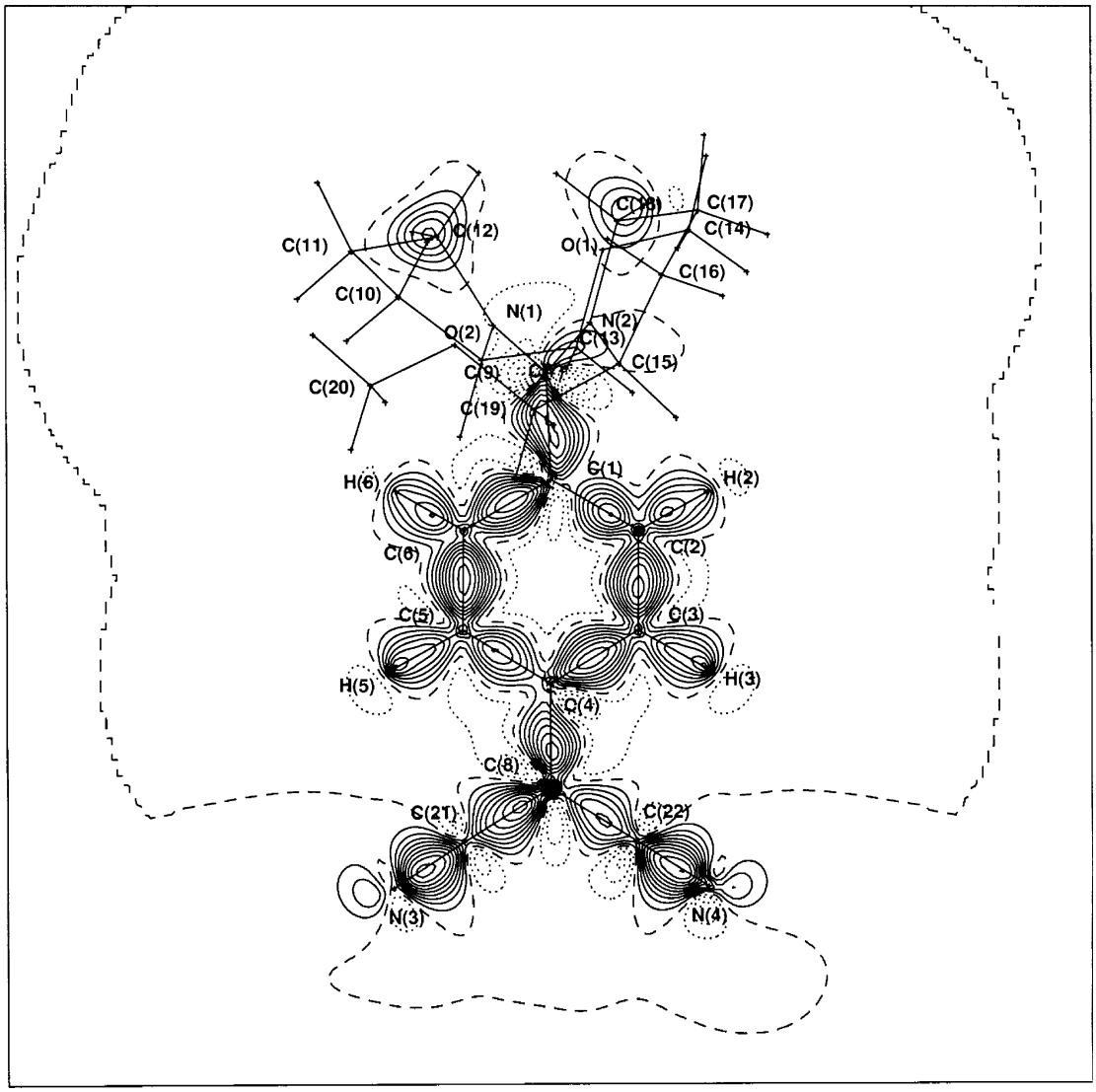

Fig. 2 Static deformation density of the molecule in the quinoid ring plane. Contours at 0.075 e Å^{-3}.

e Å^{-3}) as expected, compared to *ca.* 1.8 e Å^{-3} on the C^{sp3}–N bonds [C(12)–N(1), C(9)–N(1), C(15)–N(2) and C(18)–N(2)]. The deformation contours in the two cyano bond regions appear somewhat different although the densities are found to be the same, 3.20(9) e Å^{-3} (see Supplementary Table 3).

The group charges associated with the two pyrrolidine rings, the quinoid ring and the two cyano groups are 1.29(7), 0.02(8) and −1.31(8) e, respectively. As expected, the pyrrolidine rings form a donor group and the cyano groups act as an acceptor with the conjugated double bonds in-between acting like a molecular wire for intramolecular charge transfer to occur. The near-zero net charge on the π-link is noteworthy. These findings should be compared with those of *p*-nitroaniline[1] where the donor, acceptor and the π-link carry group charges of 0.37, −0.43 and −0.06 e, respectively. Charge separation is, however, not as clear in 2-methyl-4-nitroaniline (0.41, −0.99, 0.58 e),[5] *p*-amino-*p*-nitrobiphenyl (−0.09, −0.82, 0.91 e)[6] and the β-polymorph of *p*-nitrophenol (0.37, −0.83, 0.46 e).[4] The dipole moment vector in DMPDQ (Fig. 3, left) obtained from the experimental pseudo-atomic charges, lies close to the quinoid ring plane, nearly bisecting the pyrrolidine rings. Its magnitude is 44(6) D, a large value basically resulting from the distinct charge separation between the donor and the acceptor, which are held apart at a distance of *ca.* 6 Å.

In order to study the effect of the non-centric crystal field on the properties of DMPDQ, we have computed the atomic charges using the AM1 method of the MOPAC program[10] in the frozen molecular geometry. The net charges obtained in the frozen geometry for the two pyrrolidine rings, quinoid ring and the two cyano groups are 0.74, −0.17 and −0.58 e, respectively. These values are considerably lower than the in-crystal charges. Although the trend is similar, the π-link carries a small charge in the free state. The dipole moment (*ca.* 20 D) computed from the frozen geometry (Fig. 3, right) is much lower than that in the crystal (44 D), although its direction is similar. These observations demonstrate that the non-centric crystal field enhances the dipole moment of the molecule in the crystal. Compared to earlier observations made on 5-nitrouracil and 1,1-ethylenedicarbonitriles,[11] the present study illustrates the effect of the non-centric field more vividly. The enhancement in the dipole moment relative to the frozen molecule is more than 100% in DMPDQ as compared to *ca.* 60 and *ca.* 40% in 5-nitrouracil and 1,1-ethylenedicarbonitrile, respectively. This is attributed to the presence of a large, neutral π-system in the molecule, which neatly divides the donor and the acceptor groups. Such a large dipole moment is also expected based on the high SHG activity of this material.

In conclusion, our study of the experimental charge density in the quinoid intramolecular charge transfer compound, DMPDQ, demonstrates that there is a large charge separation not hitherto found in aromatic intramolecular charge transfer compounds such as *p*-nitroaniline. Furthermore, DMPDQ

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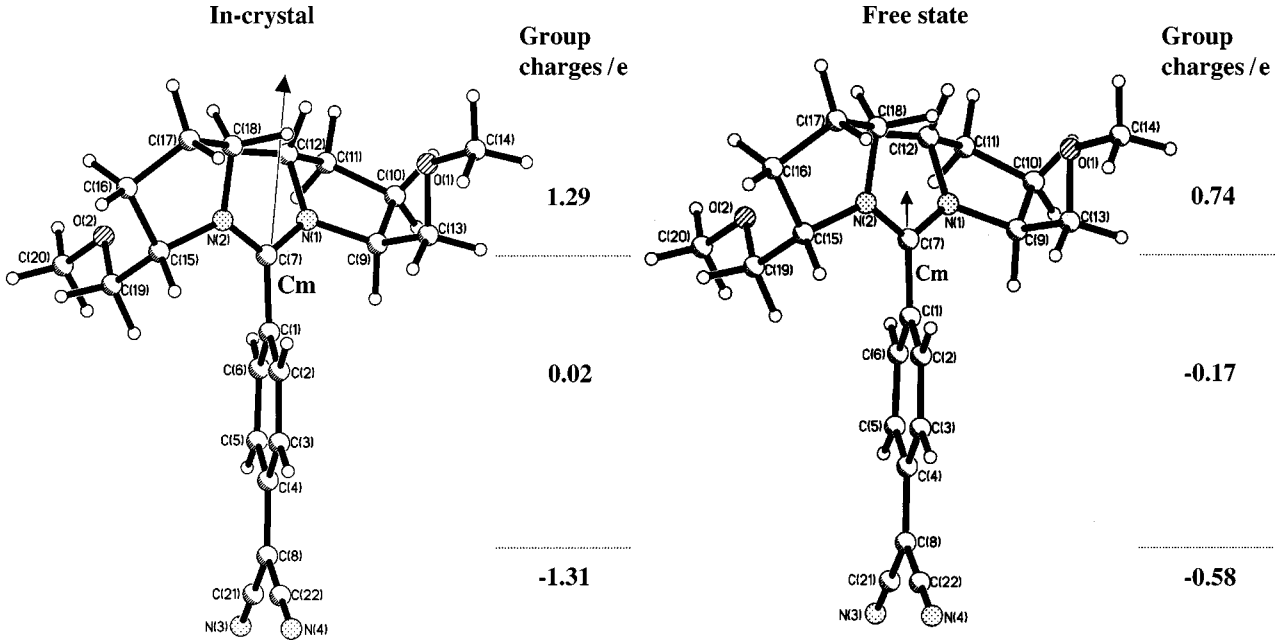

Fig. 3 Molecular dipole moments: (left) in-crystal from XD and (right) frozen geometry from AM1 calculations. The group charges are also shown in the two cases.

has an in-crystal dipole moment that is far larger than that normally found in aromatic push-pull compounds.

Experimental

The compound was prepared following literature procedure.[12] Recrystallization from acetonitrile gave pale yellow, transparent, prism-like crystals. X-Ray diffraction intensities at 130(1) K were measured by ω scans using a Bruker SMART 1K CCD diffractometer with monochromatized Mo-Kα radiation. Data, with sin θ/λ up to $\sim$1.1 Å^{-1}, was collected in full spheres of the reciprocal space using the SMART software with the 2θ settings of the detector at 28 and 75° ($\Delta\omega$, 0.3°; exposure, 30 s). The data reduction was performed using the SAINT program and the orientation matrix along with the detector and the cell parameters were refined every 40 frames on all the measured reflections. The crystal structures were solved by direct methods using the SHELXTL program.[13] All non-hydrogen atoms were refined anisotropically. The H atom positions were found using the difference Fourier method and were adjusted to average neutron values.[14] The solution obtained in this study agrees closely with the reported structure.[8] All bonds satisfied the Hirshfeld rigid bond test (Supplementary Table 1).

Crystal data for ($C_{22}H_{28}N_4O_2$) from this study: $M = 380.48$, monoclinic, $a = 9.2675(3)$, $b = 8.1573(3)$, $c = 13.8649(5)$ Å, $\beta = 102.9680(10)°$, $U = 1021.42(6)$ Å^3, $T = 130(1)$ K, space group $P2_1$ (no. 4), $Z = 2$, μ(Mo-Kα) = 0.081 mm^{-1}, 21 515 reflections, 16 454 unique reflections ($R_{int} = 0.046$), $R(F) = 0.138$ for 9001 reflections with $F_o > 4\sigma(F_o)$, $wR(F^2) = 0.217$ for all reflections. When the resolution was restricted to 0.9 Å, the structure solution improved [$R(F) = 0.036$ for 2760 reflections with $F_o > 4\sigma(F_o)$; $R(F^2)$ (for all data) = 0.039; $wR(F^2) = 0.098$]. The asymmetric unit is the whole molecule. The molecules in the lattice are held by two intermolecular C–H···N contacts (H···N: 2.41 and 2.47 Å, ∠C–H···N: 142.7 and 127.4°, respectively) and a C–H···O contact (2.74 Å and 117.5°).

CCDC reference number 157075. See http://www.rsc.org/suppdata/nj/b1/b103117c/ for crystallographic data in CIF or other electronic format.

Multipole refinement on the full data set was carried out using the XDLSM routine of the XD program package.[9] The XDPROP routine was used to calculate bond critical points and group charges. Final solution: R(F), 0.04; $R(F^2)$, 0.05; GOF, 1.05, 357 parameters. In compliance with the molecular geometry, a two-fold axis of symmetry was applied as a chemical constraint; the static deformation density map improved while critical point parameters showed no noticeable change. Multipole populations and critical point values are listed in Supplementary Tables 2 and 3, respectively.

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