

Steering molecular dipoles from centrosymmetric to a noncentrosymmetric and SHG active assembly using remote functionality and complexation†

S. Jayanty, P. Gangopadhyay and T. P. Radhakrishnan*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, India.

E-mail: tprsc@uohyd.ernet.in

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Utilization of flexible pendant groups bearing a remote functionality and complexation with an appropriate partner leading to the fabrication of a noncentrosymmetric molecular crystal lattice of interest in quadratic nonlinear optical applications is explored. 7,7-Diamino-8,8-dicyanoquinodimethane, which possesses a large molecular hyperpolarizability but shows an overriding tendency towards centrosymmetric crystal lattice formation, is chosen as a critical test case of a nonlinear optical chromophore. *N,N*-Dimethylethylene moieties attached to the amino groups of diaminodicyanoquinodimethane serve as the pendant groups and terephthalic acid as the complexing partner. Parallel investigation of the crystal structures of the pure chromophore and its complex demonstrates the crucial role of the pendant group and the complexing partner in the formation of the noncentrosymmetric lattice of the complex with concomitant induction of optical second harmonic generation capability. This study suggests the possibility of developing a simple chemical approach towards the fabrication of acentric crystals for quadratic nonlinear optical applications.

Introduction

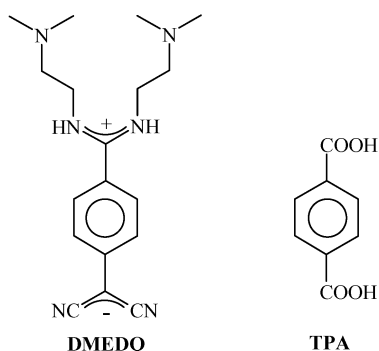
Design of functional molecules and their tailored assembly into materials with specific attributes is an area of continuing interest at the interface of synthetic chemistry and condensed matter science. Fabrication of molecular conductors, magnets and nonlinear optical (NLO) materials pose significant challenges at the level of molecular synthesis as well as materials fabrication. For instance, the development of efficient molecular NLO materials for quadratic effects such as optical second harmonic generation (SHG) comprises of the synthesis of molecular units possessing large hyperpolarizability (β) and their assembly into a noncentrosymmetric bulk structure with suitable orientation of the β tensor components.¹ A variety of dipolar and octupolar, organic and metal–organic molecules have been developed as candidates for the former.² However, the organization of these building blocks into optimal lattice structures with the desired molecular orientations is a difficult problem. The assembly can be achieved through physical methods such as electric field poling of molecules embedded in polymers³ and the Langmuir–Blodgett technique⁴ as well as a variety of chemical design approaches. Incorporation of H-bond functionalities,⁵ stereogenic centers⁶ and sterically bulky groups,⁷ host–guest complexation⁸ and helical superstructure formation⁹ are some of the chemical routes to the assembly of molecules into SHG active materials. We have developed a simple approach to the creation of noncentrosymmetric bulk lattices through the attachment of optimal length alkyl chains to dipolar NLO chromophores.^{10,11} This technique relies on a subtle interplay of dipolar energies and dispersion interactions, the latter influenced primarily by the alkyl chain length.¹¹ Cocrystallization and salt formation of NLO-phores with partner molecules and molecular ions have been reported to be efficient methods to generate quadratic

NLO materials.¹² Now we demonstrate the formation of a noncentrosymmetric crystal lattice, and the induction of SHG capability, through the involvement of flexible pendant groups, attached to the NLO chromophore and bearing remote functionalities which can enter into specific intermolecular interactions.

7,7-Diamino-8,8-dicyanoquinodimethane (DADQ) is a versatile push–pull molecule amenable to a wide variety of substitutions at the amino end, providing chromophores possessing large¹³ and tunable hyperpolarizability.¹⁴ Ashwell and coworkers have investigated the NLO properties of related TCNQ derivatives as LB films.¹⁵ There has been considerable interest in the exploitation of similar systems as prototypes for molecular rectifiers.¹⁶ We have demonstrated in earlier work that the introduction of chiral substituents on DADQ leads to materials capable of moderate to strong optical SHG.¹⁷ Recently we have explored the introduction of a variety of conformationally rigid as well as flexible pendant groups with remote Lewis base functionality, which can be used to induce specific interactions between the molecule and its neighbors. We have shown that charge transfer complexation phenomena could be triggered by such ‘anchoring groups’.¹⁸ The pendant groups could also be used in salt formation and creation of a polar environment to model the impact of such an environment on the molecular structure.¹⁹ We present now the crystal structure of achiral 7,7-bis(*N,N*-dimethylethylenediamino)-8,8-dicyanoquinodimethane (DMEDQ) which forms, as this class of molecules often do,²⁰ a centrosymmetric crystal lattice. The interesting situation arising due to the disengagement of one of the pendant groups from intermolecular interactions through the formation of an intramolecular H-bond is highlighted. Experimentation with a variety of complexation partners led to the choice of terephthalic acid (TPA) using which we demonstrate a desirable engagement of the pendant groups bearing the remote base functionality in intermolecular H-bonds. These interactions facilitate a set of noncovalent interactions which drive the dipolar molecules into an unusual orthogonal orientation leading to a noncentrosymmetric lattice exhibiting

†Electronic supplementary information (ESI) available: powder SHG variation with particle size for DMEDQ-TPA. See <http://www.rsc.org/suppdata/jm/b2/b202804m/>

moderate solid state SHG. The role of the pendant groups and the complexation in inducing the noncentrosymmetry is particularly conspicuous in view of the generally dominant tendency of diaminodicyanoquinodimethanes to form centrosymmetric lattices.²⁰



Experimental

DMEDQ was synthesized following the protocols reported earlier.^{17,21} To a warm solution of 0.10 g (0.49 mmol) of tetracyanoquinodimethane in 30 ml of acetonitrile was added 0.108 g (1.22 mmol) of *N,N*-dimethylethylenediamine. The solution turned green immediately and a light yellow precipitate appeared. The reaction mixture was stirred at 65 °C for 2.5 h, cooled to 30 °C and filtered to produce 0.14 g (87% yield) of pale yellow DMEDQ. It was purified by recrystallization from acetonitrile. Crystals were grown from methanol-acetonitrile. DMEDQ was characterized as follows: mp = 246–248 °C (dec.); FT-IR (KBr): ν/cm^{-1} = 3234, 2179, 2137, 1601; UV-Vis (ethanol): $\lambda_{\text{max}}/\text{nm}$ = 374, $\lambda_{\text{cut-off}}/\text{nm}$ = 450; ¹H-NMR (CDCl₃): δ/ppm = 7.25 (d, 2H), 6.95 (d, 2H), 3.52 (m, 4H), 2.65 (t, 2H), 2.50 (t, 2H), 2.40 (s, 6H), 2.25 (s, 6H) (H-bonded protons on N not observed); ¹³C NMR (DMSO-d₆): δ/ppm = 165.1, 148.0, 129.7, 123.9, 117.4, 114.6, 58.2, 44.9, 32.3; elemental analysis (calculated for C₁₈H₂₆N₆): % C = 66.18 (66.26), % H = 8.10 (7.98), % N = 25.65 (25.76).

Ethanol solutions of equivalent amounts of DMEDQ and TPA were mixed at room temperature. On slow evaporation over 12 h pale yellow crystals of the 1 : 1 complex appeared. The complex was characterized as follows: mp = 238–242 °C (dec.); FT-IR (KBr): ν/cm^{-1} = 3238, 2166, 2129, 1637, 1597; UV-Vis (ethanol): $\lambda_{\text{max}}/\text{nm}$ = 374, 241, $\lambda_{\text{cut-off}}/\text{nm}$ = 450; ¹H-NMR (DMSO-d₆): δ/ppm = 8.01 (s, 4H), 7.28 (d, 2H), 6.83 (d, 2H), 3.43 (m, 4H), 2.62 (m, 2H), 2.48 (m, 2H), 2.31 (s, 6H), 2.15 (s, 6H) (H-bonded protons on N not observed); ¹³C NMR (DMSO-d₆): δ/ppm = 167.6, 165.0, 147.9, 135.6, 129.6, 129.3, 123.9, 117.4, 114.6, 57.2, 44.4, 32.3; elemental analysis (calculated for C₂₆H₃₂N₆O₄): % C = 63.76 (63.41), % H = 6.77 (6.50), % N = 17.13 (17.07).

Second harmonic generation from microcrystalline powders was examined using the Kurtz–Perry²² method. Particle sizes were graded using standard sieves; sizes ranging from 100–300 μm were studied. Samples were loaded in glass capillaries having an inner diameter of 600 μm . The fundamental beam (1064 nm) of a Q-switched ns-pulsed (6 ns, 10 Hz) Nd:YAG laser (Spectra Physics Model INDI-40) was used. The second harmonic signal was collected using appropriate optics and detected using a monochromator, PMT and oscilloscope (Tektronix Model TDS 210, 60 MHz). Filters were used as needed, to bring the signals for all the samples in the same range. Microcrystalline urea with particle size >150 μm was used as the reference.

X-Ray diffraction data were collected on an Enraf-Nonius MACH3 diffractometer. Mo-K α radiation with a graphite crystal monochromator in the incident beam was used. Data was reduced using Xtal3.4;²³ Lorentz and polarization

Table 1 Crystallographic data for DMEDQ and DMEDQ-TPA

| | DMEDQ | DMEDQ-TPA |
|--|--|---|
| Molecular formula | C ₁₈ H ₂₆ N ₆ | C ₂₆ H ₃₂ N ₆ O ₄ |
| Formula weight | 326.45 | 492.58 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> (no. 14) | <i>Cc</i> (no. 9) |
| <i>a</i> /Å | 13.121(3) | 13.2413(11) |
| <i>b</i> /Å | 10.192(4) | 12.5696(8) |
| <i>c</i> /Å | 15.463(2) | 15.3847(11) |
| β /° | 111.94(2) | 95.004(6) |
| <i>Z</i> | 4 | 4 |
| $\rho_{\text{calc}}/\text{g cm}^{-3}$ | 1.130 | 1.283 |
| $\lambda/\text{Å}$ | 0.71703 | 0.71703 |
| μ/cm^{-1} | 0.71 | 0.89 |
| Number of unique reflections | 4384 | 3068 |
| Number of reflections with $I \geq \sigma_I$ | 1846 | 2914 |
| Number of parameters | 223 | 335 |
| GOF | 0.946 | 0.951 |
| <i>R</i> (for $I \geq 2\sigma_I$) | 0.0483 | 0.0502 |
| <i>wR</i> ² | 0.1298 | 0.1171 |

corrections were included. All non-hydrogen atoms were found using the direct method analysis in SHELX-97²⁴ and after several cycles of refinement the positions of the hydrogen atoms were calculated and added to the refinement process. Graphics were handled using ORTEP6a.²⁵ Data collection and structure refinement details are collected in Table 1.

CCDC reference numbers 181468 and 181469.

See <http://www.rsc.org/suppdata/jm/b2/b202804m/> for crystallographic data in CIF or other electronic format.

Results and discussion

Substituted diaminodicyanoquinodimethanes possess a large ground state dipole moment in solution²⁶ and an even larger dipole moment in the solid state²⁷ as a result of the strongly zwitterionic structure resulting from their push–pull nature. The zwitterionic character is clearly revealed by the benzenoid ring structure observed in their crystals.^{17,20} These molecules possess large hyperpolarizability,¹³ which is extremely sensitive to the molecular twist between the diaminomethylene moiety and the benzenoid ring plane.¹⁴ However, the crystals have a strong predilection towards centrosymmetric organization,²⁰ possibly promoted by the large ground state dipole moment. The chromophore part of DMEDQ shows a structure similar to those reported earlier. The crystallographic data are collected in Table 1 and the asymmetric unit is shown in Fig. 1a. The significant bond lengths and angles in the molecule are provided in Table 2. The molecular twist (average of the dihedral angles, N1–C13–C7–C8 and N2–C13–C7–C12) referred to above is 39.7°. The *N,N*-dimethylaminoethylene chain attached to one of the amino groups (N1) adopts multiple *gauche* conformations so as to fold back and enter into a strong intramolecular H-bond with the other amino group (N2); the appreciable positive charge of the zwitterionic motif residing on the amino groups makes them good proton donors. The H-bond parameters are collected in Table 3. This intramolecular H-bond effectively disengages the remote base functionality of one of the pendant groups from entering into any effective intermolecular interactions. The amino group (N1) however forms an intermolecular H-bond with the cyano nitrogen of a neighboring molecule (Table 3) leading to a chain structure along the *b* direction shown in Fig. 2a. The crystal lattice belongs to the *P*2₁/*c* space group and the adjacent chain oriented in the opposite direction is related by the center of inversion. Significantly, no strong or moderate H-bonding or other noncovalent interactions are observed between the chains. Semiempirical AM1/TDHF²⁸ computations on

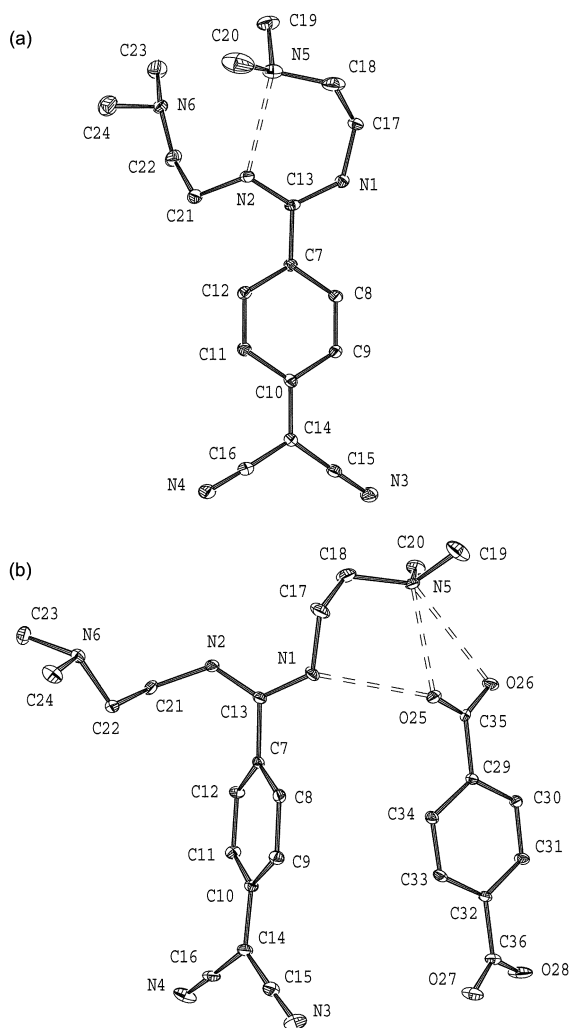


Fig. 1 Molecular structure of (a) DMEDQ and (b) DMEDQ-TPA from single crystal structure analysis. 10% probability thermal ellipsoids are indicated; the dashed line indicates H-bonding; H atoms are omitted for clarity.

DMEDQ, using the molecular structure from single crystal analysis with the H atom positions alone optimized, shows that it possesses a significant ground state dipole moment of 23.2 D and a large static β of -85.2×10^{-30} esu. However, the centrosymmetric structure adopted by this material, possibly supported by the large dipole moment as noted earlier, rules out all quadratic NLO properties.

Crystals of DMEDQ-TPA belong to the noncentrosymmetric space group, *Cc*. The crystallographic data are collected in Table 1 and the asymmetric unit is shown in Fig. 1b. The significant bond lengths and angles are collected in Table 4. The molecular structure of the DMEDQ moiety in the complex shows important differences from that in the crystal of pure DMEDQ. In the NLO chromophore unit, namely the

Table 2 Significant bond lengths (Å) and angles (°) in DMEDQ

| | | | |
|------------------|----------|-------------------|----------|
| N(1)–C(13) | 1.311(4) | N(6)–C(23) | 1.464(4) |
| N(1)–C(17) | 1.458(4) | C(7)–C(8) | 1.391(4) |
| N(2)–C(13) | 1.314(4) | C(7)–C(12) | 1.390(4) |
| N(2)–C(21) | 1.464(4) | C(7)–C(13) | 1.474(4) |
| N(3)–C(15) | 1.148(4) | C(8)–C(9) | 1.371(4) |
| N(4)–C(16) | 1.146(5) | C(9)–C(10) | 1.395(4) |
| N(5)–C(18) | 1.441(5) | C(10)–C(11) | 1.404(4) |
| N(5)–C(19) | 1.447(5) | C(10)–C(14) | 1.431(4) |
| N(5)–C(20) | 1.455(6) | C(11)–C(12) | 1.369(4) |
| N(6)–C(22) | 1.446(4) | C(14)–C(16) | 1.394(5) |
| N(6)–C(24) | 1.451(5) | C(14)–C(15) | 1.401(5) |
| C(13)–N(1)–C(17) | 126.5(3) | C(8)–C(9)–C(10) | 121.9(3) |
| C(13)–N(2)–C(21) | 126.9(3) | C(9)–C(10)–C(11) | 116.3(3) |
| C(18)–N(5)–C(19) | 110.8(4) | C(9)–C(10)–C(14) | 122.3(3) |
| C(18)–N(5)–C(20) | 112.5(4) | C(11)–C(10)–C(14) | 121.4(3) |
| C(19)–N(5)–C(20) | 110.1(4) | C(12)–C(11)–C(10) | 121.6(3) |
| C(22)–N(6)–C(24) | 112.5(4) | C(11)–C(12)–C(7) | 121.6(3) |
| C(22)–N(6)–C(23) | 109.3(3) | N(1)–C(13)–N(2) | 120.7(3) |
| C(24)–N(6)–C(23) | 110.3(4) | N(1)–C(13)–C(7) | 117.2(3) |
| C(8)–C(7)–C(12) | 117.1(3) | N(2)–C(13)–C(7) | 122.0(3) |
| C(8)–C(7)–C(13) | 121.0(3) | C(16)–C(14)–C(15) | 117.7(3) |
| C(12)–C(7)–C(13) | 121.7(3) | C(16)–C(14)–C(10) | 120.2(3) |
| C(9)–C(8)–C(7) | 121.4(3) | C(15)–C(14)–C(10) | 122.1(3) |

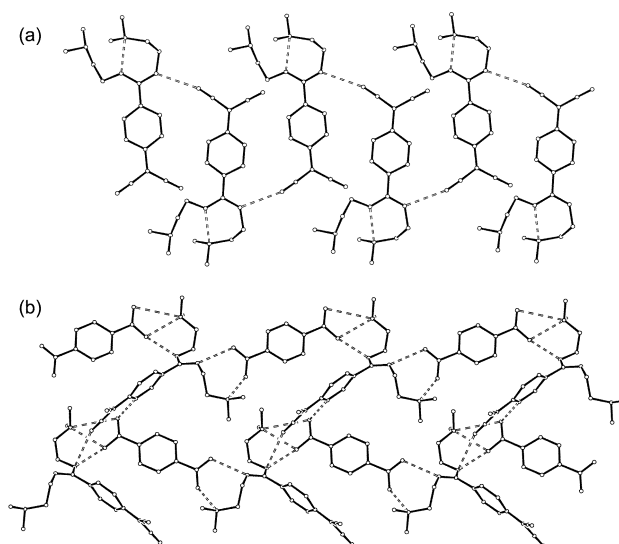


Fig. 2 Molecular chains propagating along the *b* direction in (a) DMEDQ and (b) DMEDQ-TPA. The dashed lines indicate H-bonds and close electrostatic interactions; the short contact C13...N3' in DMEDQ-TPA is not indicated and all H atoms are omitted for clarity.

diaminodicyanoquinodimethane part, the main deviation is in terms of the twist angle. The angle is now enhanced to 48.4° (mean of the dihedral angles as noted earlier), possibly a consequence of the large number of intermolecular H-bonds that arise in this crystal as shown below. The more significant structural variation in DMEDQ occurs in the pendant chains. Both *N,N*-dimethylaminoethylene groups are now spread

Table 3 Significant intramolecular (symmetry: *x*, *y*, *z*) and intermolecular H-bonds in DMEDQ and DMEDQ-TPA complex. D and A are the H-bond donor and acceptor atoms respectively in the D–H...A bond; *r* and θ are the relevant distance and angle

| Crystal | D–H | A [Symmetry] | $r_{D...A}/\text{Å}$ | $\theta_{D-H...A}/^\circ$ |
|-----------|-------|--|----------------------|---------------------------|
| DMEDQ | N2–H2 | N5 [<i>x</i> , <i>y</i> , <i>z</i>] | 2.839 | 155.4 |
| | N1–H1 | N4 [$-x+1$, $y-0.5$, $-z+0.5$] | 2.879 | 156.4 |
| DMEDQ-TPA | N1–H1 | O25 [<i>x</i> , <i>y</i> , <i>z</i>] | 2.722 | 140.2 |
| | N5–H5 | O25 [<i>x</i> , <i>y</i> , <i>z</i>] | 2.669 | 166.5 |
| | N5–H5 | O26 [<i>x</i> , <i>y</i> , <i>z</i>] | 3.190 | 132.5 |
| | N2–H2 | O28 [<i>x</i> , $y+1.0$, <i>z</i>] | 2.746 | 157.4 |
| | N6–H6 | O27 [<i>x</i> , $y+1.0$, <i>z</i>] | 2.606 | 159.4 |
| | C9–H9 | O26 [<i>x</i> , $-y$, $z+0.5$] | 3.497 | 150.5 |

Table 4 Significant bond lengths (Å) and angles (°) in DMEDQ-TPA

| | | | |
|-------------------|----------|-------------------|-----------|
| N(1)–C(13) | 1.331(7) | C(7)–C(8) | 1.395(8) |
| N(1)–C(17) | 1.449(8) | C(7)–C(13) | 1.477(8) |
| N(2)–C(13) | 1.304(7) | C(8)–C(9) | 1.372(8) |
| N(2)–C(21) | 1.463(7) | C(9)–C(10) | 1.400(8) |
| N(3)–C(15) | 1.161(9) | C(10)–C(11) | 1.381(8) |
| N(4)–C(16) | 1.134(9) | C(10)–C(14) | 1.468(8) |
| N(5)–C(19) | 1.464(9) | C(11)–C(12) | 1.394(8) |
| N(5)–C(20) | 1.486(9) | C(14)–C(15) | 1.398(10) |
| N(5)–C(18) | 1.493(9) | C(14)–C(16) | 1.413(11) |
| N(6)–C(22) | 1.468(8) | C(29)–C(30) | 1.384(8) |
| N(6)–C(24) | 1.474(7) | C(29)–C(34) | 1.402(8) |
| N(6)–C(23) | 1.496(8) | C(29)–C(35) | 1.509(8) |
| O(25)–C(35) | 1.274(7) | C(30)–C(31) | 1.381(8) |
| O(26)–C(35) | 1.227(6) | C(31)–C(32) | 1.382(7) |
| O(27)–C(36) | 1.257(7) | C(32)–C(33) | 1.378(8) |
| O(28)–C(36) | 1.210(7) | C(32)–C(36) | 1.510(8) |
| C(7)–C(12) | 1.388(8) | C(33)–C(34) | 1.372(8) |
| | | | |
| C(13)–N(1)–C(17) | 124.5(6) | N(2)–C(13)–C(7) | 122.7(5) |
| C(13)–N(2)–C(21) | 126.1(5) | N(1)–C(13)–C(7) | 115.8(6) |
| C(19)–N(5)–C(20) | 111.7(6) | C(15)–C(14)–C(16) | 116.9(6) |
| C(19)–N(5)–C(18) | 115.6(7) | C(15)–C(14)–C(10) | 121.6(6) |
| C(20)–N(5)–C(18) | 106.9(7) | C(16)–C(14)–C(10) | 121.4(6) |
| C(22)–N(6)–C(24) | 109.9(5) | C(30)–C(29)–C(34) | 117.8(5) |
| C(22)–N(6)–C(23) | 111.5(5) | C(30)–C(29)–C(35) | 121.1(5) |
| C(24)–N(6)–C(23) | 109.7(5) | C(29)–C(30)–C(31) | 121.7(5) |
| C(12)–C(7)–C(8) | 117.6(5) | C(30)–C(31)–C(32) | 119.9(6) |
| C(12)–C(7)–C(13) | 123.7(6) | C(33)–C(32)–C(31) | 119.0(5) |
| C(8)–C(7)–C(13) | 118.6(5) | C(31)–C(32)–C(36) | 119.2(6) |
| C(9)–C(8)–C(7) | 122.6(6) | C(34)–C(33)–C(32) | 121.4(5) |
| C(8)–C(9)–C(10) | 119.5(6) | C(33)–C(34)–C(29) | 120.1(6) |
| C(11)–C(10)–C(9) | 118.5(5) | O(26)–C(35)–O(25) | 124.3(6) |
| C(11)–C(10)–C(14) | 121.0(6) | O(26)–C(35)–C(29) | 119.8(6) |
| C(9)–C(10)–C(14) | 120.5(5) | O(25)–C(35)–C(29) | 115.8(5) |
| C(10)–C(11)–C(12) | 121.5(6) | O(28)–C(36)–O(27) | 125.5(6) |
| C(7)–C(12)–C(11) | 120.1(6) | O(28)–C(36)–C(32) | 119.0(5) |
| N(2)–C(13)–N(1) | 121.4(5) | O(27)–C(36)–C(32) | 115.4(6) |

outwards so that they are able to enter into intermolecular interactions. One of these groups is connected to the TPA partner through multiple and bifurcated H-bonds. The other group engages the TPA from a neighboring complex unit so that an extended chain structure propagating along the *b* direction emerges (Fig. 2b). It should be noted that the C–O bond lengths of TPA (Table 4) clearly indicate deprotonated carboxylic acid groups; hence the protons were added to the tertiary amine nitrogen atoms during the structure refinement. The significant H-bond parameters in DMEDQ-TPA are collected in Table 3. The static β computed as earlier, for the DMEDQ unit without including the protonation at the tertiary amine ends of the pendant groups is -96.5×10^{-30} esu. The enhancement of β is a consequence of the increased twist angle.¹⁴ Interestingly the diprotonated (on the tertiary amine nitrogen) DMEDQ shows a calculated static β of -70.7×10^{-30} esu. The reduction is a consequence of the destabilization of the zwitterionic structure as a result of the positive charge accumulation on protonation.

Unlike the chains in pure DMEDQ, the H-bonded chain in DMEDQ-TPA composed of alternating DMEDQ and TPA, enters into several noncovalent interactions with the adjacent chain which is related by the glide reflection operation. The significant noncovalent interactions between these chains are (i) the electrostatic interactions between the amino and cyano ends carrying partial positive and negative charges respectively, resulting in the short contacts N1...N3' (3.475 Å) and C13...N3' (3.404 Å) and (ii) the weak H-bond, C9–H9...O26' (Table 3) (see Fig. 2b). As a result of these interactions the DMEDQ molecules of adjacent chains adopt an interesting orientation wherein the molecular dipole vectors are oriented nearly orthogonal to each other; the angle between the C13–C14 vectors is 99.0°. Further the mean planes of the benzenoid rings of these DMEDQs are also nearly orthogonal to each

other, the angle being 80.6°. A view of the electrostatically bound DMEDQs with orthogonal dipole vectors and ring planes propagating along the *c* direction is shown in Fig. 3.

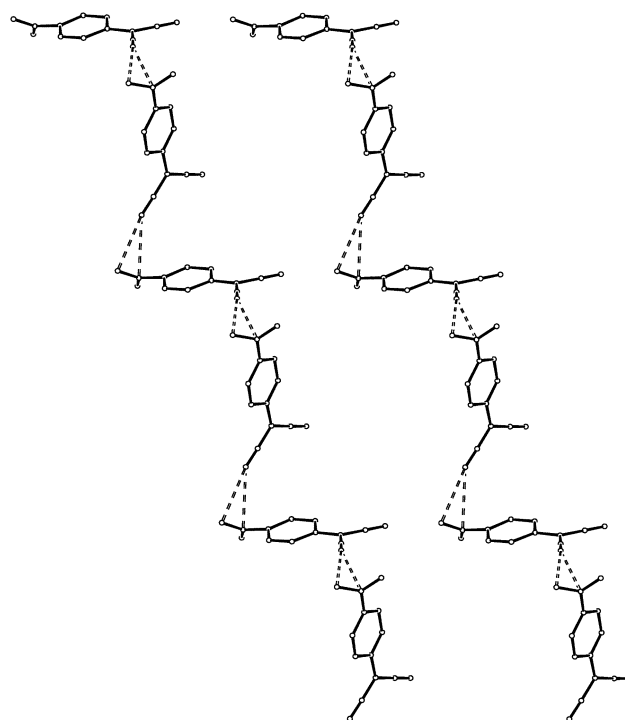


Fig. 3 Molecular chains formed through electrostatic interactions, propagating along the *c* direction in DMEDQ-TPA. Dashed lines indicate the close electrostatic interactions; the *N,N*-dimethylaminoethylene chains and all H-atoms are omitted for clarity.

A comparison of the unit cell dimensions of DMEDQ and DMEDQ-TPA (Table 1) is instructive. The cell dimension *a* shows a very small increase on complexation whereas *c* shows a small decrease. The presence of the TPA counterions in the H-bonded chains propagating along *b*, causes this dimension to increase by $\sim 2.4 \text{ \AA}$. The calculated density shows a clear and significant increase ($\sim 13.5\%$) from DMEDQ to DMEDQ-TPA. This implies that the large number of intrachain H-bonds (along *b*) and interchain noncovalent interactions in DMEDQ-TPA leads to a tighter packing of the crystal lattice. The values of the unit cell dimensions suggest that there is a gross similarity in the lattice structures of DMEDQ and DMEDQ-TPA; the emergence of new noncovalent intermolecular interactions influence the breaking of the center of inversion symmetry and formation of the orthogonal orientation of the DMEDQ moieties in the latter.

AM1/TDHF computation shows that DMEDQ follows the one-dimensional model with the major β tensor component coincident with the dipole axis along C13–C14. The nearly orthogonal orientation of the DMEDQ molecules in the monoclinic crystal lattice of DMEDQ-TPA leads to an angle of 40.5° and 139.5° respectively between the crystallographic *b* axis and the molecular dipole axes of the two molecules related by the glide plane. In the context of the oriented gas model,²⁹ these considerations suggest a moderate SHG in the complex. In agreement with this, we observe an SHG of $\sim 9 \text{ U}$ in the microcrystalline powders of this material. The variation of the SHG with particle size indicates phase-matchable behavior. The material has good thermal stability ($m_p = 240 \text{ }^\circ\text{C}$) and is stable to extended laser irradiation (at a power of $\sim 1 \text{ GW cm}^{-2}$). In view of these factors and the ease of crystallization, DMEDQ-TPA is a promising material for further elaboration on the theme of using flexible pendant groups and complexation partners to modify the orientation of NLO chromophores in crystal lattices.

Conclusion

We have presented the structural characterization and solid state SHG of the complex of a substituted push–pull diaminodicyanoquinodimethane molecule with terephthalic acid. The critical use of (i) the flexible pendant groups with sticky ends and (ii) the complexation partner, in directing the assembly of the NLO chromophore is brought out by the parallel solid state structural investigations of the diaminodicyanoquinodimethane molecule and its complex. This exercise demonstrates a simple chemical synthetic approach to the modification of crystal architecture using remote functionalities. Our current efforts are focussed on the use of these remote functionalities to attach the NLO chromophore to a variety of template structures to design desired chromophore orientations and assemblies.

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